Monday Morning, November 2, 1998

Applied Surface Science Division
Room 307 - Session AS-MoM

Materials Analysis (including Small Dimensions and Synchrotron)

Moderator: F.A. Stevie, Lucent Technologies

8:20am **AS-MoM1 Synchrotron Based Low Z Materials Analysis*, D.A. Fischer,*** National Institute of Standards and Technology **INVITED**

A new soft-x-ray (C,N,O,F) materials science end station to study the structure and chemical nature of diverse materials at the National Synchrotron Light Source has been designed, built and commissioned. Practical industrial problems, are currently being investigated, such as model catalyst systems, polymer surfaces and their interfaces, hard disk lubricant chemistry, self assembled monolayers and high Tc super conducting tapes. This presentation will describe the Dow / NIST soft x-ray materials characterization facility and review the on going NEXAFS research from a scientific and practical perspective. The experimental station, which delivers state-of-the-art intensity, resolution, and detection sensitivity is the result of a collaboration between NIST, The Dow Chemical Co., Brookhaven National Laboratory, and NIST Small Business Innovation Research (SBIR) awardees, International Radiation Detectors and Osmic Inc. Polarized ultra soft x-rays from the newly configured and upgraded NSLS U7A beamline are utilized as a search light for chemical bond identification, quantification, and orientation via the NEXAFS technique. Utilizing electron and fluorescence detection methods the surface (5nm) and bulk (200nm) structure and chemistry can be compared and contrasted simultaneously.

9:00am **AS-MoM3 Contribution of a Fano Resonance and Pt-H EXAFS in the Pt L@sub 23@ XANES of Supported Pt Particles: Application to Materials Characterization*, D.E. Ramaker,*** George Washington University*; B.L. Mojet,* Utrecht University, The Netherlands, Netherlands*; J.T. Miller,* Amoco*; D.C. Koningsberger,* Utrecht University, The Netherlands, Netherlands

The electronic and geometric effects induced by hydrogen chemisorption on small platinum particles supported on high surface area @gamma@-Al@sub 2@O@sub 3@ and zeolite LTL, were studied by XANES. A new subtraction procedure was developed to separate the electronic from the geometric effects. The Pt-H anti-bonding state (electronic effect) was isolated and was found to have a Fano-resonance line shape. In addition, a significant Pt-H EXAFS scattering (geometric effect) was found for energy values between 0 and 20 eV. The resonance energy, width, and background phase parameter were obtain by least squares fit of the Fano lineshape function to the isolated experimental lineshape. For the Pt/LTL samples the shape and energy of the Fano resonance was found to strongly depend on the acidity/alkalinity of the support material, implying a direct influence of the support on the electronic properties of the Pt particles. The identification of the resonance and Pt-H EXAFS features on these Pt catalysts demonstrates the potential of this new analysis technique for the study of hydrogen chemisorption, metal-promoter, and metal-support effects in catalysis, electrochemistry, and nanoscale technology.

9:20am **AS-MoM4 An Investigation of the Surface Chemistry of Lubricant Additives on Steel by NEXAFS Spectroscopy*, T.S. Rufael,*** *J.K. Mowlem,* Texaco Inc.*; D.A. Fischer,* National Institute of Standards and Technology

Molecular level investigations of highly complex adsorption systems, such as the lubrication process in automotive parts, provide a challenge for mechanistic understanding and spectroscopic identification of surface intermediates. In this study, Near-Edge X-ray Absorption Fine Structure Spectroscopy is used to probe the surface reactions of a well-known anti-wear additive, zinc dialkyl dithiophosphate (ZDDP), and a novel friction modifier, molybdenum dithiocarbamate (MoDTC) on a polished steel alloy surface. Thin films from representative concentrations of ZDDP and MoDTC in base oil have been studied individually as well as in combination with each other following thermal processing at temperatures conducive for ZDDP decomposition. Soft X-ray absorption at the oxygen K-, carbon K-, iron-L, zinc L-, and molybdenum M-edges has been used to examine the structural and chemical changes taking place at the interface. In addition, we have investigated the effect of a model pro-oxidant, cumene hydroperoxide (CHP), on the above systems. We discuss the suitability of NEXAFS spectroscopy to study such complex adsorption systems by presenting results from these model lubricant systems.

9:40am **AS-MoM5 Small Area Analysis: The Synergism of FIB/TEM Instrumentation*, L.A. Giannuzzi,*** *B.I. Prenitzer, J.L. Drown,* University of Central Florida*; S.R. Brown,* Cirent Semiconductor*; T.L. Shofner,* Bartech Group*; R.B. Irwin, F.A. Stevie,* Cirent Semiconductor **INVITED**

The use of transmission electron microscopy (TEM) as a routine characterization tool has increased over the years, particularly in the microelectronics industry, as a result of the decreasing dimensions of the design rules used in integrated circuits. The need to detect compositional analysis from site specific regions is also a primary concern. TEM is often the only technique that may resolve microstructural and compositional features that are present in complex material components. Until recently, the production of a suitable TEM specimen has often been the limiting factor in TEM analysis. However, the use of focused ion beam (FIB) instrumentation for the production of site-specific TEM specimens has greatly increased the TEM productivity. The versatility of the novel FIB lift-out technique has also allowed for little or no prior sample preparation. In addition, since the bulk sample can be preserved, several TEM specimens may be acquired from the same sample between processing steps. This technique has been expanded to the TEM specimen preparation of microelectronic materials, metals, ceramics, composites, multi-layers, biological materials, fibers, and powders in both cross-section and plan view section.

10:20am **AS-MoM7 Small Area X-ray Photoelectron Spectroscopy using a Spherical Mirror Analyzer*, B.J. Tielsch,*** *S.P. Page,* Kratos Analytical Ltd, United Kingdom*; D.J. Surman,* Kratos Analytical, Inc.*; S. Scierka,* Millenium Inorganic Chemicals*; E.A. Thomas, J.E. Fulghum,* Kent State University

The analysis of heterogeneous or patterned samples by XPS frequently requires both imaging and small area spectroscopy. As the spatial resolution in photoelectron images decreases, the need for improvements in high energy resolution, small area spectroscopy increases. In most cases, the current limit on small area spectra is ~ 10 microns using either a virtual probe or a focussed x-ray spot. The Kratos AXIS Ultra uses a spherical mirror analyzer for real-time, parallel image acquisition, enabling images with a spatial resolution of 2-4 microns to be acquired in minutes. Spectra are routinely acquired using the hemispherical analyzer, however, the spherical mirror analyzer can be utilized by acquiring a series of images at different binding energies. Spectra can then be calculated from any point within the image by plotting the intensity of the selected pixels as a function of binding energy. We will show spectra determined from images for a variety of samples. The energy resolution obtained with the spherical mirror analyzer will be shown to be comparable to the hemispherical analyzer. The speed of image acquisition means the analysis time is similar to the time required for acquisition of small area spectra in some cases, although better spatial resolution is possible. Using this "images-to-spectra" mode, spectra can be obtained from areas of approximately 5 microns. The spatial resolution will be demonstrated using test samples containing features of known size, and the utility of the "images-to-spectra" mode will be evaluated using composites and polymer blends. This research has been partially supported by NSF (CHE-9631702, CHE-9613880, DMR89-20147) and 3M.

10:40am **AS-MoM8 Analysis of Heterogeneous Polymer Samples using XPS*, J.E. Fulghum,*** *E.A. Thomas, A.C. Ferryman,* Kent State University*; B.J. Tielsch,* Kratos Analytical, United Kingdom

The surface of samples prepared from polymer blends may have a composition different from that of the bulk material. If the polymers are not completely miscible, lateral heterogeneities on the surface may exist as well. Surfaces which are heterogeneous on the scale of microns can be characterized by XPS through small area spectroscopy and imaging. Determining the existence of concentration gradients within the XPS sampling depth is difficult for such samples, however. Several polymer blend systems will be used to demonstrate the near-surface and bulk gradient information which can be obtained from polymer blends if a combination of XPS experiments is utilized. Significant information can be obtained from quantitative analysis of the valence band, and this will be compared to results utilizing core level spectra. Polymer systems to be discussed include blends of modified polyimides used in liquid crystal displays, poly(vinyl chloride) and poly(methyl methacrylate) (PVC and PMMA) blends which have been previously studied using using XPS, TOF-SIMS and FTIR, and polyacrylates. This work has been partially supported by NSF (CHE-9631702, CHE-9613880, DMR89-20147) and 3M.

11:00am **AS-MoM9 TOF-SIMS analysis of Atmospheric Aerosol**, ***R.E. Peterson***, *B.J. Tyler,* Montana State University

We are evaluating the potential for using TOF-SIMS to study single particles from atmospheric aerosol. X-ray analysis has commonly been used to analyze the composition of single particles but there are several limitations to X-ray analysis. Principally, x-ray analysis cannot be used to study organic compounds in the aerosol, it offers low sensitivity for light elements common in crustal material and it cannot distinguish isotopes. TOF-SIMS has the potential to provide superior performance in these areas. Samples of naturally occurring and anthropogenic atmospheric aerosol were collected on Millipore fluoropore (PTFE) filters in southwest montana. Sections of the filters were imaged using a PHI TRIFT I instrument with a Ga primary ion source. Both positive and negative ion images were studied. A large number of particles could be distinguished on the filter surfaces, which were absent on control samples. Particle diameters varied from 2 to 10 µm. Hydrocarbons, silicon, aluminum, potassium, calcium, and sulfates were associated with the particles found in the images. These correspond to common sources of aerosol in the region including crustal dust, partially neutralized sulfuric acid droplets, and carbonaceous compounds associated with forest fires. The aerosol found indicate a combination of particles originating from gas to particle conversion and surface sources

11:20am **AS-MoM10 Evaluation of Ge Based Detectors for Small Area Analysis**, ***X. Lu***, *J.R. Kingsley,* Charles Evans & Associates

The development and comercial availability of Energy Dispersive X-ray Spectroscopy (EDS) detectors employing Ge rather than Si detectors, combined with thermally assisted Field Emission Scanning Electron Microscopy (FE-SEM) has allowed EDS to be re-evaluated as a small area analytical tool. The higher spectral resolution of the Ge EDS detector allows lower accelerating voltage to be effectively used for elemental identification, while the thermally assisted FE-SEM has the ability to maintain a usable amount of current, at low voltage, in a spot smaller than the inherent interaction volume. In this paper we will characterize the performance of just such a system when used for particle and IC cross section analysis.

11:40am **AS-MoM11 Detection and Passivation of Surface States in InP by Thermally Stimulated Exo-electron Emission Spectroscopy**, ***S.S. Hullavarad***[1], *S.V. Bhoraskar,* University of Pune, India

InP based devices are rapidly becoming dominant in high mobility and optoelectronic device technologies. InP has an electron mobility that is three times that of conventional Si. In principle, devices built with InP should be faster by this factor than the comparable Si devices. However, the surface properties of InP have prevented its use in MIS devices. Devices based on InP suffer from defects that occur in the material which act as charge traps, changing the bias of the device and so impeding its performance. We have attempted to tailor the surface of InP so as to reduce the surface state density by tying up the dangling bonds with proper passivant. The energy distribution and relative densities of such electronically active surface states in InP have been studied using thermally stimulated exo-electron emission spectroscopy (TSEE). This novel and relatively simple technique has high sensitivity for detecting the surface states which is difficult to be assessed by other techniques. Here this technique is successfully used for the first time for detecting the pinned Fermi positions of the Fermi level in n-(100) InP. The TSEE measurements were performed in the high vacuum conditions using channel electron multiplier, in the clean environment. The surface states in InP in the presence of its native oxide were detected when the sample was heated from 175 K to 450 K. TS EE peaks were identified at 207.5 K and 350 K. The energies of these defects were calculated to be 0.43 eV and 0.74 eV respectively. The surface state passivation of pinned Fermi level is achieved by ECR coupled thiophene plasma polymerization. The constituents of the polymerized InP surface were identified using energy dispersive X-ray analysis (EDXAS). Microwave assisted electron cyclotron resonance (ECR) plasma was used to deposit thin films of passivating overlayers. Polythiophene (CH3CH2S) was deposited by injecting the monomer thiophene into the reaction chamber preevacuated to a base pressure of ~ 10-5 Torr. The TSEE spectrum recorded after the deposition of polymer differed from the one which was recorded earlier. The peak in the TSEE appearing at 207.5 K has disappearede. The very fact that this corresponded to the pinned Fermi level in InP show s that the plasma polymer has been effective in chemically passivating the surface.

Biomaterial Interfaces Group
Room 326 - Session BI-MoM

Protein Solid-Surface Interactions

Moderator: J.J. Hickman, The George Washington University

8:20am **BI-MoM1 Effect of Surface Rheology on Anti-Adhesive Properties of Water-Soluble Thin Films**, ***J.W. Schneider***, *W.R. Barger, J.-B.D. Green, R.F. Brady, Jr., G.U. Lee,* Naval Research Laboratory

Thin films of water-soluble polymers, including poly (ethylene oxide), have been used to improve the biofouling resistance and biocompatibility of surfaces. Their effectiveness has been traced to strong associations with water, leading to short-ranged, repulsive hydration forces, and to steric stabilization forces, which are related to the restriction of surface mobility as potential adherends approach them. With the rational molecular design of anti-bioadhesive coatings in mind, we work to decouple each of these effects by making sensitive nano-scale force measurements on organized monolayers hosting oligomers of controlled molecular weight and surface density. In this work, we employ the atomic force microscope (AFM) in two modes to obtain these two surface characteristics. Surface rheological properties, which are a measure of the propensity for steric stabilization, are obtained by driving the AFM tip across a frequency spectrum and measuring the phase and amplitude of the cantilever response as a function of probe/surface separation distance. Short-range forces are measured by operating the AFM in conventional static force modulation mode. AFM tips are functionalized to reflect pertinent biological chemistry using thiol SAM's terminated by carboxylic acids, amine groups, and the monosaccharide sialic acid.

8:40am **BI-MoM2 Probing the Local Interaction Forces with the AFM between Tertraglyme and Fluorinated Polymers and Biomolecules**, ***R. Luginbühl***, *Y.V. Pan, B.D. Ratner,* University of Washington

The interactions between biomolecules and surfaces play a major role in biological process. In biomaterial science, a key to success lays in understanding and controlling the local characteristics of the material surfaces. Engineering of recognition surfaces with well-defined chemical and physical properties is of highest interest for fabrication of biocompatible surfaces, biosensor technology, medical devices and/or molecular electronics. Polymer films, deposited in a radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) process, are of increasing interest as biomaterial coatings. Plasma polymerization of tetraglyme (CH3-(O-CH2-CH2)4-O-CH3) was reported by Lopez and Ratner in 1992. The resulting thin films show resistance to protein adhesion, cell and bacteria attachment, similar to poly-(ethylene glycol) (PEG). In contrary to tetraglyme coatings, fluorine-containing films polymerized from perfluorinated monomers are very hydrophobic and exhibit a high interaction to biomolecules and cells. The interactions between biomolecules and a material surface can be probe with the atomic force microscope (AFM) at the molecular level. AFM cantilever tips were modified with a thin film of either one of the above mentioned plasma polymers and/or with biomolecules. The adhesion force was quantified by the mean of force versus displacement curves. In addition, recognition images of polymer patterned surfaces with biomolecule modified AFM tips were obtained applying a new modulation technique.

9:00am **BI-MoM3 Proteins at the Solid-Solution Interface: Significance, Behavior and Manipulation**, ***J.L. Brash***, McMaster University, Canada **INVITED**

Proteins are large, amphiphilic molecules and as such are highly surface-active: they seek out the interfacial environment. Proteins will thus tend to accumulate at any gas-liquid or solid-liquid interface, and in doing so their biological activity is often altered. Such behavior has consequences for many areas of science and technology where protein-containing fluids are present. Examples are protein separation and purification, the "biofouling" of surfaces in bioprocess equipment and biosensors, and the biocompatibility of medical devices such as vascular prostheses and contact lenses. In the case of biocompatibility, the adsorbed proteins determine subsequent cell interactions. A theme which emerges from these considerations is the need to be able to "control" or "direct" protein adsorption. In this presentation the interfacial behavior of proteins will first be discussed. Approaches to the control of protein adsorption will then be suggested. Such control has a number of aspects, including selecting a given protein from a multiprotein fluid (eg blood), controlling the conformation (and thus the function) of adsorbed proteins, and preventing adsorption altogether. Examples from the author's research in the blood compatibility area will be presented. These will include fibrinolytic (clot-

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[1] **Best ASSD Student Paper Competitors**

dissolving) surfaces based on the preferential adsorption of plasminogen, anticoagulant surfaces based on thrombin scavenging, and protein repellent surfaces based on polyethylene oxide grafting.

9:40am **BI-MoM5 Molecular Recognition Between Genetically-Engineered Streptavidin and Surface-Bound Biotin*, V.H. Perez-Luna*,** *K.A. Opperman, P.D. Hampton, M.J. O'Brien,* University of New Mexico*; L. Klumb, P. Stayton,* University of Washington*; G.P. Lopez,* University of New Mexico

There are fundamental differences between molecular recognition at the solid-liquid interface and in solution. In solution, ligands and receptors are randomly distributed in space, have high mobility, random orientation and, after binding, the ligand receptor pair can freely move in the solution. At the solid-liquid interface, the immobilized species is concentrated at the solid surface, has low mobility, preferential orientation for the ligand and, upon binding, the ligand-receptor pair becomes constrained to the surface region. Interactions between the immobilized biomolecules and the surface may occur or, at high densities of the immobilized receptors, attractive interactions among adjacent adsorbed ligands can give rise to cooperative effects. In this work, we study such differences with the streptavidin-biotin molecular recognition system. Binding of streptavidin to biotin-terminated self assembled monolayers (SAMs) on gold is reported. Three streptavidin mutants were used in this work: wild type, Y43A and W120A. Desorption of the bound protein molecules was obtained by incubation of the SAMs in 1 mM biotin. Desorption from disordered monolayers was incomplete, which suggests that non-specific interactions occurred either with the gold substrate or hydrophobic moieties of the thiolate after binding. Non-specific interactions did not occur on well organized monolayers and complete dissociation was achieved. Desorption of the surface bound molecules was modeled considering that the bound proteins could come off the surface either by sequential dissociation of biotin-streptavidin bonds or by simultaneous dissociation of two biotin-streptavidin bonds. The calculated dissociation constants differed by several orders of magnitude for the three mutants and they depended on the degree of coverage of surface bound biotin. The later indicating the presence of attractive interactions among adsorbed molecules at high surface coverage.

10:00am **BI-MoM6 Interfacial Influences on the Apparent Activity of Immobilized Electron Transfer Proteins*, D.E. Leckband*,** *C. Yeung, N. Lavrik, A. Kloss,* University of Illinois, Urbana-Champaign

We determined the influence of the interfacial microenvironment on the apparent activity of immobilized proteins. In particular, we investigated the effect of the electrostatic potential of the underlying support on the interaction of soluble cytochrome b5 with immobilized cytochrome c. By varying solution pH, we controlled the magnitude of the negative charge on the supporting matrix. Because cyt b5 is also negatively charged at neutral pH, the substrate repels the soluble cyt b5 and thus opposes the cyt c/cyt b5 attraction. We show, using surface plasmon resonance, that the apparent pH-dependence of the interprotein affinity is determined largely by the pH-dependence of the substrate, and not by the intrinsic interactions between the two proteins. On the matrix used in this work, we showed that the pH-optimum for the cyt c/cyt b5 recognition shifts by 1.2 pH units relative to that of the soluble proteins. Our results demonstrate that the apparent biological activity of immobilized species must be considered within the context of the microenvironment in which they function.

10:20am **BI-MoM7 Interfacial Supra-Biomolecular Assemblies on Solid Supports*, W. Knoll,*** The Institute of Physical and Chemical Research (RIKEN), Japan, Germany*; A. Offenhaeusser,* Max-Planck-Institut für Polymerforschung, Germany **INVITED**

This contribution summarizes some of our efforts in designing, preparing, and characterizing supramolecular interfacial assemblies integrating biomolecular functional units. Among the presented bio-interfaces are oligonucleotide matrices fabricated by self-assembly strategies based on thiol coupling to Au-substrates or on biotin-streptavidin interactions. A multispot parallel read-out of hybridization reactions between various surface-bound capture probes and complement strands from solution is presented. The concept is based on surface plasmon microscopy and image analysis computer routines. It is shown how the interfacial architecture can be optimized for maximum binding efficiency by using monomolecular layers assembled from binary thiol solutions composed of the catcher probes and diluent molecules that control the lateral separation of the individual binding sites. First results on the influence of the ionic strength, the degree of mismatch, and the temperature are presented. In addition the extension of this concept to PNA catcher probes in discussed. The second class of surface architectures concerns tethered membranes. Various concepts for the coupling of lipid bilayers to solid supports of different materials (Au, SiOx) based on polymers or peptides are briefly discussed. Particular emphasis is put on the structural analysis of the complex multilayer assembly and on the functional characterization by electrochemical techniques. The reconstitution of membrane-integral ion translocating proteins into the supported bilayers bears great potential for biosensor formats.

11:00am **BI-MoM9 Qualitative and Quantitative Mass Spectrometric Methods for Probing Surface-Protein Binding Affinity*, G.R. Kinsel,*** *A.K. Walker, L. Chen, K.D. Nelson, Y. Wu,* University of Texas, Arlington*; R.B. Timmons,* University of Texas, Arlington, U. S. A.

We have recently shown that Matrix Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry (MS) can be used as an efficient tool for characterizing surface protein interactions. When using a standard sample preparation methodology there is a direct inverse correlation between the surface-protein binding affinity and the magnitude of the protein MALDI MS ion signal. The MALDI MS method offers numerous advantages over conventional bioanalytical methods for assaying surface-protein binding including: 1) surface binding of a broad spectrum of proteins and biomolecules can be assayed, 2) no modification (e.g. radiolabeling, fluorescent labeling) of the protein is required, 3) analysis is straightforward and can be completed in under 30 minutes 4) sensitivities are comparable to radiolabeled protein binding studies. Our present research is focused on assessment of the conditions under which the MALDI ion signal can be quantitatively correlated to the surface-protein binding affinity. Specifically we have examined the impact of changes in a variety of surface (morphology, chemical functionality, etc) and protein solution (protein choice, solution pH, etc.) characteristics on the general quantitative MALDI ion signal / binding affinity correlation. These studies reveal both the range of conditions across which the MALDI MS methodology can be applied to quantitate surface-protein binding as well as insights into the relative impact of various surface / solution parameters on the adsorption process.

11:20am **BI-MoM10 Biosensing Using Colloidal Au Arrays as Biocompatible Substrates and Au:Protein Conjugates as Signal Enhancing Agents*, M.D. Musick*,** *L.A. Lyon, G.P. Goodrich, M.J. Natan,* Pennsylvania State University

Sensing strategies are discussed using arrays of colloidal Au as a sensor substrate and solutions of protein:Au colloid conjugates as signal amplification reagents. Colloidal Au shares similar properties with bulk Au, a common transducer substrate due to its reflectivity, conductivity, and ease of chemical modification. However, colloidal Au offers increased biocompatibility and flexibility. Particles can be assembled directly from solution onto a wide range of supports. Furthermore, particle size and spacing are easily controlled. 2-D and 3-D arrays have been fabricated from combinations of biomolecules, ligands, organic crosslinkers, and colloidal Au. Assemblies have been characterized by AFM, FE-SEM, uv-vis/NIR, electrical resistance, and electrochemical analysis. The stability and immobilization of protein:Au colloid complexes have been examined. An amplified surface plasmon resonance (SPR) sandwich assay is presented. In this assay, a protein layer immobilized on an evaporated Au film is exposed to analyte solution and incubated with a protein:Au conjugate. The result is a enhanced shift in the SPR curve as compared to conventional SPR. The use of colloidal Au amplified surface plasmon resonance should offer increased molecular weight sensitivity and lower detection limits. Imaging and arraying methods that allow for simultaneous analysis of many samples, and sensors based on changes in electrical and electrochemical signals will also be described.

11:40am **BI-MoM11 Electron Transfer of Cytochrome c on Lipid-Coated Graphite Electrode*, S. Boussaad*,** *R. Arechabaleta, N.J. Tao,* Florida International University

The structural and electron transfer properties of Cytochrome c (Cyt c) Langmuir-Blodgett (LB) films, and Cyt c on Cardiolipin (CL) and Phosphatidylcholine (PC) monolayers have been studied on graphite electrode with tapping mode atomic force microscopy (AFM) and cyclic voltammetry. The protein in the LB film forms an ordered structure and exhibits a reversible electron transfer reaction in phosphate buffer. The analysis of the AFM images reveals a quasi-hexagonal structure with a=4.4 ± 0.2 nm, b=5.3 ± 0.2 nm and @gamma@=71 ± 3°. These dimensions are in good agreement with the X-ray data. The redox peaks of the Cyt c monolayer are about 80 mV more positive than those of the spontaneously adsorbed protein, and the electron transfer rate (20-30 s@super -1@) is smaller than 60-80 s@super -1@, the value for the adsorbed Cyt c. Furthermore, both monolayers of CL and PC are ordered on graphite, but their interactions with Cyt c are quite different. On CL monolayer, Cyt c adsorbs spontaneously and the adsorbed protein preserves the electron transfer reaction. In addition, the protein disrupts seriously the ordered structure of the lipid monolayer. However, on PC monolayer, Cyt c does not adsorb. This difference is consistent with the fact the CL plays an important role in the activity of Cyt c oxidase than PC.

Electronic Materials and Processing Division
Room 316 - Session EM-MoM

Processing for Advanced Technology

Moderator: D. Temple, Microelectronics Center of North Carolina

8:20am **EM-MoM1 SCALPEL: Projection Electron Beam Lithography*, L.R. Harriott,*** Bell Laboratories, Lucent Technologies **INVITED**

SCALPEL (SCattering with Angular Limitation Projection Electron beam Lithography) combines the high resolution and wide process latitude inherent in electron beam lithography with the throughput of a projection system. This approach has the potential to satisfy the lithographic requirements for many IC generations, down to the minimum feature sizes contemplated in the SIA roadmap. We believe that with solid industry support and resources, SCALPEL can be introduced in the 130 nm generation as a replacement for 193 nm lithography for critical levels with reduced cost. SCALPEL masks are expected to be considerably lower cost than optical masks which will require OPC and phase shift for the 130 nm generation. We see the evolution of lithography technology directly from 193 nm to SCALPEL. Throughput is usually thought of as the determining factor in determining the cost of ownership for a lithographic technology. As the limits of optical lithography are pushed toward and beyond sub-wavelength printing, strategies such as phase shifting and optical proximity effect correction (OPC) are required. These technologies add significantly to the cost of the masks and thus, contribute to the cost of wafer printing. The size of the mask factor depends strongly on the mask usage. The number of wafers printed for each mask varies according to the nature of an individual IC business with averages for ASIC at 1000 wafers or less printed per mask. The averages for logic and DRAM are roughly 2000 and 3000 respectively. The total cost of printing a wafer level can, particularly in cases of low mask usage, then be dominated by mask costs and less effected by throughput than has been the case in the past. For SCALPEL, technologies such as phase-shifting and OPC are not required and the resulting mask costs at a given design rule (such as 130 nm) can be significantly less than the corresponding photomask costs. Thus, even though SCALPEL throughput will be less than that for 193 nm optical lithography, the overall cost per level of lithography will be lower due to significantly lower mask costs. We believe that this factor will be a major driving force in determining the timing of the shift away from optical lithography to SCALPEL. We have recently completed our proof-of-lithography system which implements the step-and-scan writing strategy. Our recent data shows that we can write stripes over a 1 X 1 cm field and stitch them together with a raw accuracy of better than 50 nm three-sigma. These measurements were made using box-in-box type patterns at the joining of adjacent stripes across the field. Other errors such as those of the mask beam-writer have not been accounted for in this preliminary experiment. We expect that with further calibration and removal of mask errors that we can achieve stitching to the 10 nm level or less as we have seen in the static stitching data. In order to bring SCALPEL technology to the nest step in its evolution, we are beginning a three-year development program aimed at the full-field high throughput system. The program will focus on larger format mask technology, a high throughput exposure tool, and resist and process development. In this talk, we will outline the status of SCALPEL technology as well as the plans for its continued development. This work has been supported in part by DARPA and SEMATECH

9:00am **EM-MoM3 Fundamental Issues in Wafer Bonding and SOI*, U.M. Goesele,*** Max Planck Institute of Microstructure Physics, Germany **INVITED**

During the last decade, wafer bonding has developed from an approach with a "black magic" image to a versatile technology which is partly already used industrially and which allows to avoid the restrictions usually imposed by epitaxy. The science and technology of wafer bonding has been advanced almost independently in three major areas: i) fabrication of SOI (Silicon-On-Insulator) substrates; ii) silicon based micromechanics (where wafer bonding is known as fusion bonding), and iii) bonding of III-V compounds for light-emitting devices and compliant substrates. Present day research aims at understanding and controlling the processes happening at the bonding interface especially for general material combinations and at developing low temperature bond strenghtening approaches for already processed wafers and/or dissimilar materials with different thermal expansion coefficients. Versatile thinning methods for many different technologically relevant materials such as the smart-cut or related methods are also of special interest. The processes involved in atmospheric, low vacuum, or ultra high vacuum wafer bonding at room temperature will be outlined. Hydrogen implantation-induced delamination and layer transfer (smart-cut and smarter cut procedures) will also be discussed for a number of materials including silicon, germanium, diamond, SiC, GaAs and sapphire.

9:40am **EM-MoM5 The Fundamental Mechanisms of Silicon Wafer Bonding and Layer Exfoliation*, M.K. Weldon,*** Bell Laboratories, Lucent Technologies **INVITED**

The fabrication of Silicon-On-Insulator (SOI) materials has progressed to such an extent over the past decade that the material specifications are approaching those of bulk silicon and many viable manufacturable processes are now in operation. Silicon wafer bonding is one such commercially-employed approach to SOI synthesis in which two (oxide-terminated) Si wafers are directly bonded under ambient conditions and then annealed to elevated temperatures (1100 C) to form a permanent chemical bond. In the conventional process, the device wafer is subsequently thinned to the required dimensions by extensive grinding/polishing. The limitations imposed by this latter step have recently been removed with the advent of a remarkable new process wherein H+ is pre-implanted into the device wafer at a critical concentration and depth, prior to bonding. Upon subsequent joining to the companion 'handle' wafer and annealing to ~400 C, complete lift-off (exfoliation) of the overlying Si occurs, so that the final SOI structure can now be formed in one elegant annealing step, with thickness uniformities of ~50 Å over the entire wafer. Research has played an important role in the advancement of this field, despite the inherent difficulties in obtaining spectroscopic information about the physics and chemistry of interfaces that typically lie ~500 microns below the surface. In this talk, I will describe how we have obtained@footnote 1@ unprecedented insight into the thermal evolution of the buried interfaces that comprise both the bonded and the exfoliation interfaces, using a wide variety of different experimental probes in combination. In particular, I will highlight the pivotal role of infrared spectroscopy in delineating the microscopic mechanisms that permit the intimate chemical bonding of two wafers and the transformation of isolated hydrogenated defects into extended internal cracks that ultimately lead to exfoliation of macroscopically large areas of Si. @FootnoteText@ @footnote 1@M.K. Weldon, V.E. Marsico, Y.J. Chabal, A. Agarwal, D.J. Eaglesham, J. Sapjeta, W.L. Brown, D.C. Jacobson, Y. Caudano, S.B. Christman and E.E. Chaban, J. Vac. Sci. Technol. B 15, 1065 (1997).

10:20am **EM-MoM7 DARPA High Definition Systems Program*, B.E. Gnade,*** Defense Advanced Research Projects Agency **INVITED**

The DARPA High Definition Systems (HDS) Program has the overall goal to meet the diverse, but specific, needs for information display for the Department of Defense. The goals of the HDS program include increasing power efficiency, reducing weight, and improving the overall ruggedness of display systems. The HDS program is also actively working to transition DARPA-funded display technologies into specific military applications. A brief review will be presented which shows how new display technologies are being used in the military, as well as examples of new technologies which are being supported under the DARPA HDS program.

11:00am **EM-MoM9 Field Emission Energy Distributions from Silicon Field Emitter Arrays*, J.L. Shaw,*** *H.F. Gray, K. Hobart,* Naval Research Laboratory

A great deal of work on field emitter array (FEA) surface coatings, treatments, and "conditioning" effects has been has been reported in hopes of improving the maximum current, robustness, and transconductance. However, the typical current-voltage diagnostic technique has limited utility in understanding the effects of such treatments. Field enhancement and work function effects are difficult to separate using I-V measurements and assuming the classical Fowler-Nordheim theory. Furthermore, the I-V characteristics typically vary with time and emission even in UHV. To better understand the emission process, we have measured FEA emission energy spectra. Our equipment includes a hemispherical analyzer and allows in-situ wafer probing and simultaneous I-V characterization. The spectra we obtain include structure at lower energies than reported from single, macroscopic, clean silicon tips. Since the emission energy relative to the bulk Fermi level represents a loss, such spectra are of considerable interest. The spectra change as a function of emission current, conditioning, and processing. In some cases we find energy losses in excess of 10 volts. Such losses may explain why failures can occur at emission levels below 1uA, even though calculations (that assume straightforward Joule and Nottingham heating) predict no temperature increase at emission currents below 100uA. Our measurements suggest that both the emission current and dissipated energy can be strongly influenced by the presence of surface states. Thus detecting such effects is likely to prove useful in improving FEA emission uniformity and total current density.

11:20am **EM-MoM10 Effects of Oxygen on Silicon and Platinum-coated Silicon Field Emitter Arrays***, **W.D. Palmer**, D. Temple, D.G. Vellenga, L.N. Yadon, G.E. McGuire,* Microelectronics Center of North Carolina

Field emission depends strongly on the work function of the emitter surface. At any vacuum level, molecules will adsorb on the emitter surface and change the work function by forming a chemical bond with the emitter material. . This study addresses this problem and one possible solution by testing silicon and platinum-coated silicon field emitter arrays in oxygen over a wide pressure range similar to that expected in commercial field emission flat panel displays. Platinum is less likely than silicon to form these bonds, and so should exhibit less sensitivity to the ambient gases in the display panels. The experiments were undertaken using silicon and platinum-coated silicon gated field emitter arrays fabricated at MCNC. The arrays were initially operated at base pressure (5x10@super -9@ Torr) using an automated system to guarantee that all tests were performed consistently. After collecting current versus voltage (I-V) curves for each device at base pressure, a leak valve was used to introduce oxygen at the target pressure. The arrays were then operated with a constant voltage on the gate electrode until the emission current stabilized. In this study, the data is shown as a function of exposure, the product of pressure and time, to normalize the results. I-V curves were collected at the target pressure after stabilization, then the leak valve was closed and the chamber was pumped back to base pressure. Finally, I-V curves were again collected at base pressure to verify that the array had recovered to its initial level of performance. The data collected on silicon and platinum-coated silicon field emitter arrays will be shown and compared. This work was performed under the DARPA/ETO High Definition Systems program, contract number N00014-96-C-0283.

11:40am **EM-MoM11 Improved Performance in Thin Film Electroluminescent Phosphors by Fluxing***, **J.S. Lewis**, K.E. Waldrip, M.R. Davidson, D. Moorehead,* University of Florida, Gainesville, U.S.*; S.S. Sun,* Planar Systems, Inc.*; P.H. Holloway,* University of Florida, Gainesville

The brightness and efficiency of AC thin film electroluminescent devices (ACTFELD's) which use ZnS:Mn as the thin film phosphor have been improved by the incorporation of various fluxes. The brightness of fluxed, sputter deposited films were doubled and the efficiencies are nearly tripled compared to unfluxed, sputter-deposited films. In addition, the improved brightness and efficiency values surpass those achieved by the standard evaporated or ALE (atomic-layer epitaxy) grown devices. The fluxes have been incorporated both during and after sputter deposition of the phosphor, and a post-deposition anneal is required. Data will be presented which demonstrate improved brightness and efficiency. The flux treatment gave significant improvement in the degradation of luminescence after accelerated device operation. Microstructural changes that result from fluxing as detected by X-ray diffraction, transmission electron microscopy, and scanning electron microscopy will be presented.

The Science of Micro-Electro-Mechanical Systems Topical Conference

Room 324/325 - Session MM+PS-MoM

MEMS Processing and Deep Si Etch Technology

Moderator: L.M. Miller, Jet Propulsion Laboratory

8:20am **MM+PS-MoM1 Overcoming Barriers to MEMS Prototyping and Production***, **D.A. Koester**, K.W. Markus,* MCNC **INVITED**

As MEMS continues to grow and expand into new markets, there continues to be a need for low cost proof-of-concept and prototype fabrication. For the past 6 years, MCNC has provided a number of services designed to provide the domestic MEMS community with an array of fabrication and design services intended to help overcome the cost and accessibility barriers to MEMS product development. The cornerstone of this DARPA-supported program, called the MEMS Technology Network (TechNet), is the Multi-User MEMS Processes (MUMPs). MUMPs is a three-polysilicon surface micromachining process offered in a multi-user environment to offset the high cost of fabrication. Since its inception in January '92, MUMPs has fabricated over 1000 designs for more than 140 different R&D groups and has been available to the world-wide community since July of '98. The SmartMUMPS program enables electronics integration of MUMPs by way of flip chip of a standard ASIC designed with a variety of sensing blocks. LIGA technology is also made available through the program. The MEMS Technology Network also provides a spectrum of custom services to the community including deep silicon RIE, backside patterning, stock substrates and access to a Microcosm MEMCAD 4.0 seat.

9:00am **MM+PS-MoM3 Materials, Process, and Integration Issues in SiC MEMS***, **M. Mehregany**,* Case Western Reserve University **INVITED**

SiC MEMS technology holds great promise for applications which are characterized by presence of harsh environments (e.g., high temperatures, large number of vibrational cycles, erosive flows, and corrosive media). Historically, SiC research has focused on the materials and processes needed for high-temperature and high-power microelectronics. These devices require high-quality single crystal films and substrates, which lead most researchers to use 6H-SiC, since nearly defect-free wafers and epitaxial films are available. Unfortunately, high quality comes at a high price; 6H-SiC wafers are very expensive and are available only in small wafer diameters. Thus, applications for 6H-SiC devices are limited to areas which can absorb such high costs, such as (military) aircraft and spacecraft. Our work has been motivated by the necessity to develop a low-cost SiC MEMS technology to penetrate a much more diverse set of markets, including for example automotive. Additionally, we have been motivated to leverage off of the latest fabrication process technologies available from Si to push the SiC MEMS technology further, faster. As a result, we have pursued large-area substrates, i.e., 3C-SiC on Si. Unlike 6H-SiC, 3C-SiC is the only SiC polytype which can be heteroepitaxially grown on Si substrates. Heteroepitaxy on Si gives 3C-SiC a distinct advantage over 6H-SiC in terms of batch fabrication, since high quality, large-area Si substrates are readily available and comparatively very inexpensive. We have pursued the development of bulk and surface micromachining processes using 3C-SiC and poly-SiC, respectively. Heteroepitaxy of 3C-SiC on Si is attractive to MEMS not only for batch fabrication, but also for bulk micromachining. In fact, SiC is undoubtedly an excellent etch stop material for Si bulk micromachining, since Si anisotropic etchants such as KOH and EDP are impervious to SiC. We have used Si bulk micromachining techniques to fabricate a multitude of 3C-SiC structures, ranging from diaphragms for mechanical properties studies, pressure sensors, and optical transmission windows, to cantilever beams and torsional micromechanical structures. Bulk micromachining of 6H-SiC has been demonstrated by others, however the process is much more complicated and the dimensional control and etch stop capabilities are limited at this time. Unlike electronics applications which require high-quality single crystal films, MEMS is much more flexible in that structures can be fabricated from polycrystalline films. SiC MEMS is no exception. We have developed poly-SiC as a basic structural material for SiC MEMS. We have deposited APCVD poly-SiC films atop polysilicon and silicon dioxide sacrificial films on 4 inch diameter Si wafers. We have demonstrated SiC surface micromachining processes, and these have been used to fabricate the first SiC lateral resonant structures. These devices tested at temperatures up to 900C outperformed polysilicon resonators of like geometry with respect to high temperature capability. Of course, the surface micromachining technology using poly-SiC would be extendable to 6H- and 4H-SiC substrate technology, as well as integration with SiC electronics on these substrates. An overview of materials, process, and integration issues in SiC MEMS will be presented, including current device examples.

9:40am **MM+PS-MoM5 Thermally-Actuated Micro-Beam for Large In-Plane Mechanical Deflections***, **E.S. Kolesar**, P.B. Allen, J.T. Howard, J.W. Wilken,* Texas Christian University

Numerous electrically-driven microactuators have been investigated for positioning individual elements in microelectromechanical systems (MEMS). The most common modes of actuation are electrostatic, magnetostatic, piezoelectric and thermal expansion. Unfortunately, the forces produced by electrostatic and magnetostatic actuators tend to be small, and to achieve large displacements, it is necessary to either apply a large voltage or operate the devices in a resonant mode. On the other hand, piezoelectric and thermal expansion actuators can be configured to produce large forces and large displacements. Unfortunately, piezoelectric materials are not routinely supported in the fabrication processes offered by commercial MEMS foundries. Consequently, these limitations have focused attention on thermally-actuated devices for generating the large forces and displacements frequently required to position and assemble complex MEMS. This research focuses on the design, finite element analysis and experimental performance evaluation of a MEMS thermally-actuated beam. The motivation is to present a unified description of the behavior of the thermal beam so that it can be adapted to a variety of applications in the microsensor and microactuator arenas. A MEMS polysilicon thermally-actuated beam uses resistive (Joule) heating to generate thermal expansion and movement. When current is passed through the actuator from anchor-to-anchor, the larger current density in the released "hot" arm causes it to heat and expand more than the "cold" arm. Since both arms are joined at their free (released) ends, the actuator tip is forced to move in an arc-like pattern. Removing the current from the device allows it to return to its equilibrium state. To be a useful MEMS device, a thermally-actuated beam will need to produce incremental in-plane mechanical beam tip deflections that span 0-10 microns while generating force magnitudes greater than 10 micro-newtons. The thermally-actuated beam design was accomplished with the L-Edit software program, and the devices were fabricated using the Multi-User Microelectromechanical Systems (MEMS) Process (MUMPs) foundry at the Microelectronics Center of North Carolina (MCNC). A finite element modeling analysis was accomplished with the IntelliCAD computer program. This CAD software incorporates an MCNC fabrication process description file that generates a 3-D solid model of the thermal beam. Additionally, the thermal and electromechanical finite element analyses predicted beam tip deflections and forces consistent with experimental observations. When the "hot" arm's temperature is 600@degree@C (Joule heating), the resulting beam tip deflection is 4.55 microns. For a beam tip force of 14 micro-newtons, the displacement was calculated to be 12.9 microns. The resonant frequency, without damping, was calculated to be 74.7 kHz. The MEMS thermally-actuated beam performance was also experimentally characterized. When the drive voltage was varied between 0 and 8 VDC, tip deflections spanning 0-7 microns were observed. The corresponding tip forces spanned 0-12 micro-newtons. The resonant frequency in ambient air was 68.7 kHz. A measure of the reliability of the thermal beam was established to be greater than 2 million cycles, when continuously operated with a 60 Hz, 4-volt amplitude square wave.

10:00am **MM+PS-MoM6 Development of a Micro EHD Pump Using Laser Micro-machining**, ***C.C. Wong***, *D. Chu, D.R. Adkins,* Sandia National Laboratories

At Sandia, we are developing an active cooling MEMS device for microelectronics applications. This integrated device will incorporate a micro-pump, temperature sensors, micro-channels, and heat exchanger components into a single unit. The first step of this development is to rapidly prototype a micro-pump based on electro-hydrodynamic (EHD) injection principle using laser micro-machining technology. Two initial micro-pumps designs have examined for full fabrication. The first design has two silicon parts stacked vertically on top of each other. Gold is deposited on one side of each stacked plate to serve as electrodes for the electro-hydrodynamic pumping. A Nd:YAG laser is used to drill an array of circular holes in the "well" region of both silicon parts, leaving an open pathway for fluid movement. The Nd:YAG laser is preferred for our fabrication process than excimer laser because of a smaller up-front cost and a less potential environment, safety, and health concern with toxic gases when using excimer laser. Moreover the Nd:YAG laser will allow the operational wavelength to be converted to several frequencies from the near infrared portion of the spectra (1064 nm @lambda@) to the ultraviolet portion of the spectra (266 nm @lambda@). After the holes are drilled, the silicon parts are aligned and bonded together with polyimide, thus becoming a EHD pump. Fluid flow has been observed when an electric voltage is applied across the electrodes. The newest design has the silicon parts which contain the flow grid oriented "back-to-back" and bonded together. This "back-to-back" design has a shorter grid distance between the anode and cathode plates so that a smaller voltage is required for pumping. A thinned Si spacer was used to maintain consistent grid distance between plates. Experimental results have demonstrated that this EHD micro-pump can generate a pressure head of about 287 Pa with an applied voltage of 120 V. @FootnoteText@ This work was supported by the US DOE under Contract DE-AC04-94AL85000.

10:20am **MM+PS-MoM7 Laminated Plastic Microfluidic Components for Biological and Chemical Systems**, ***P.M. Martin***, *D.W. Matson, W.D. Bennett, D.J. Hammerstrom,* Battelle Pacific Northwest National Laboratory

Laminated plastic microfluidic components are being developed for biological testing systems and chemical sensors. Applications include a DNA thermal cycler, DNA analytical systems, electrophoretic flow systems, dialysis systems, blood sampling, and metal sensors for ground water. This paper describes fabrication processes developed for these plastic microscale components. Most of the components have a stacked architecture, the fluid flows, or is pumped through as many as nine laminated functional levels. Functions include mixing, reaction, and detector channels, reservoirs, and detector electronics. Polyimide, PMMA, and polycarbonate materials with thicknesses between 25 and 100 µm are used to construct the components. This makes the components low cost, inert to many biological fluids and chemicals, and disposable. The components are fabricated by excimer laser micromachining the microchannel patterns and microstructures in the various laminates. In some cases, micropumps are integrated into these components to move the fluids. Vias and interconnects are also cut by the laser, and integrated with micropumps. The laminates are sealed and bonded by adhesive and thermal processes, and are leak tight. The parts withstand pressures as high as 790 kPa. Typical channel widths were 50 µm to 100 µm, with aspect ratios near 5. Performance data will be presented for the DNA thermal cycler and a voltammic chromium metal sensor.

10:40am **MM+PS-MoM8 Deep Anisotropic Etching of Silicon**, ***S. Aachboun***, *P. Ranson,* University of Orleans, CNRS, France

Dry etching of silicon has been largely studied in HDP reactors for many applications such as in Microelectronics. Moreover, deep etching is a relatively new approach that can be widely used in MEMS in the near future. However, as required depths increase, the etch rate and the anisotropy decrease radically with the Aspect Ratio (width/depth). We are interested in etching very deep anisotropic trenches (~100µm) with high Aspect Ratios (~50) and high etch rates (~5µm/mn). A HDP Helicon reactor using a SF6/O2 chemistry and a cryogenic chuck has been used for etching very narrow trenches and holes from 1,2µm to 10µm of width on n-type Si wafers with a SiO2 mask. The first results of this investigation show significant features that demonstrate the feasabilty of this method. Two microns width trenches have been etched over a depth of 50µm at 3µm/mn . The resulting profiles are highly anisotropic and the selectivity Si/SiO2 is over 500. A DOE has been set in order to evaluate the effects of the different parameters and, in order to monitor the plasma and improve the features, Langmuir probe, optical spectrometer and mass spectrometer investigations are planned.

11:00am **MM+PS-MoM9 Application of the Footing Effect in the Microfabrication of Self-Aligned, Free-Standing Structures**, ***A.A. Ayon***, *K. Ishihara, R. Braff, H. Sawin, M.A. Schmidt,* Massachusetts Institute of Technology

The footing or notching effect is observed when dry etching silicon or polysilicon layers on buried dielectric films.@footnote 1@ This effect is usually considered an undesirable feature for most applications, although it is frequently small in conventional reactive ion etching (RIE) tools due to the low density of the plasmas utilized. However, with the new generation of inductively coupled plasma etching tools the notching effect can extend laterally several microns depending not only on operating conditions but also on the aspect ratio@footnote 2@ and extent of overetching time. The suppression of this effect depends in a critical manner on achieving a balance between etching and deposition of passivating films.@footnote 3@ Deviations from such balance promote the appearance of grass or even excessive deposition of passivating films. We review the dependence of footing effect on etching conditions in a time multiplexed deep etcher (TMDE) and suggest specific operating conditions to preclude the appearance of notching even when overetching for as much as 85%. Additionally, we introduce the application of the footing effect in the microfabrication of free-standing structures, by demonstrating the micromachining of self-aligned, wafer-free electrostatic actuators for which etching, releasing, ashing and passivating (dielectric isolation) were done in the same piece of equipment. All processes needed to produce cantilevered structures are done in situ using VLSI compatible plasma chemistries only. The measured pull-in voltage for a 1000 µm cantilevered beam, of the order of 85 V, agrees with predicted values. The novel low-temperature, soft-mask scheme presented here, is compatible with other VLSI processes and can be easily integrated in the microfabrication of intelligent sensors and actuators. This robust new concept allows unparalleled fabrication simplicity while permitting the fabrication of sctructures and devices in an efficient and timely fashion. Electrostatic actuators with or without interdigitated fingers, valves, pumps and relays, to name but a few, are applications that immediately benefit with this technique. @FootnoteText@ @footnote 1@G. S. Hwang and K. P. Giapis, J. Vac. Sci. Technol., B 15 (70) 1997. @footnote 2@T. Nozawa, T. Kinoshita, T.

Nishizuka, A. Naral, T. Inoue and A. Nakaue, Jpn. J. Appl. Phys., 34 (2107) 1995. @footnote 3@J. P. Chang, Ph. D. Thesis, Massachusetts Institute of Technology, 1997.

11:20am **MM+PS-MoM10 Test Structure Experiments and Modeling of Very Deep Dry Etching Processes for MEMS Applications***, **S. Abdollahi-Alibeik**, J.P. McVittie, K.C. Saraswat,* Stanford University

One successful approach for getting the desired high (~ 4µmm/min) etch rates for MEMS device fabrication is separating the etch and passivation steps in order to eliminate the interference in chemistry. The focus of this work is on the understanding and modeling of the very deep (>100µmm) trench etch process based on this approach. Experiments were done to investigate different aspects of both deposition and etch phases. C@sub 4@F@sub 8@ gas was used for the deposition phase. The deposited material is a CF@sub x@ polymer. It was observed that the deposition rate is highly dependent on the ion flux and ion energy received by the surface. This can be modeled as an increase in the effective sticking probability of the deposition species. While polymer deposition in an overhang test structure is not that conformal, the rate of passivation does not change when the trenches become very deep. The above model and the fact that the trench sidewalls receive little ion flux can explain this discrepancy. In addition, ion reflection also appears to be important since sidewall deposition shows a dependence on the opposite sidewall. For the etch phase SF@sub 6@ gas was used. Lag experiments show that the transport of the etchant species down the trenches depends on the deposition phase. The lag was higher for a larger ratio of etching to deposition time. The fact that ion bombardment of the CF@sub x@ polymer releases F atoms can be the reason for this change in lag behavior. Incorporation of the model into the SPEEDIE profile simulator will be shown.

11:40am **MM+PS-MoM11 Pattern Shape Effects and Artefacts in Deep Silicon Etching***, **J. Kiihamaki**, S. Franssila,* VTT Electronics, Finland

Deep silicon etching in inductively coupled plasma (ICP) reactor offers high etch rate, nearly vertical profile, and good selectivity against most common masking materials. Crystal orientation independent ICP etching can replace area consuming KOH wet etch in many micromechanical applications. We have etched various test structures with patterns of different sizes and shapes, using different etch chemistries and etch times. The widths of etched patterns range from submicron to over 100 µm, the etched depths were up to 500 µm. Long narrow features are etched faster than wide short features, indicating three dimensional nature of RIE-lag. Aspect ratio dependent etch rate is also present, further complicating design rule - process interactions. The difference in etch rate of a rectangular hole with respect to a trench of same width increases with aspect ratio and can be up to 20%. Typically narrow trenches have positive angled sidewalls and as trenches get wider the profile turns into retrograde, which implies serious limitations to device design. Positive or vertical profiles can be achieved if etch rate is lowered to 1-2 µm/min. Amount of etchable area also affects profile. Coalescence of closely spaced trenches into a larger feature (due to retrograde profile and/or undercutting) causes both etch rate and profile to change. Large area structures connected to narrow trenches assist the etching of the narrow trenches over considerable distances. To fully utilise the benefits of ICP etching, the design rules must be tailored for each application, because of various pattern shape effects.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+SS-MoM
Tribology, Adhesion and Interfacial Forces

Moderator: J.E. Houston, Sandia National Laboratories

8:20am **NS+SS-MoM1 Nanotribological Interactions: Hard and Soft Interfacial Junctions***, **U. Landman**,* Georgia Institute of Technology **INVITED**

Certain aspects of the dependence of materials properties on their size will be addressed, particularly at the nanometer length scale where new behaviour emerges when the physical dimensions of the system approach, or are reduced below, a characteristic length relevant for the phenomenon or physical process being probed. We focus on computer simulation studies of formation mechanisms, structural, mechanical, electronic, transport, dynamic and rheological properties of nanoscale hard (solid nanowires) and soft (confined liquid) interfacial junctions. These issues are central to research in nanotribology, that is explorations of the atomic and molecular scale origins and methods of control of friction and lubrication, and are relevant to modern miniaturization technologies. Work supported by DOE and AFOSR.

9:00am **NS+SS-MoM3 Measuring Nanocontact Adhesion and Deformation***, **J.B. Pethica**,* University of Oxford, United Kingdom **INVITED**

Nanoscale probe techniques such as nanoindentation and AFM have given new insight into contact mechanics, and hence into adhesion and tribology problems. Almost all local mechanical, and several electrical parameters of the component surface materials can be measured. The key is a reliable determination of the test probe displacement (lateral as well as normal) as a function of applied forces. Accurate determination of storage and loss moduli in thin polymer films, along with their frequency and temperature variation, will be described as one example of these capabilities, and of the associated stringent experimental requirements. During the approach to contact, sensitive force-distance spectroscopy, close to atomic scale spatial resolution, allows mapping of the interaction potential between the surfaces. Some of the outstanding problems will also be discussed. These include the effect of adsorbates, especially on the onset of irreversible or dissipative deformation, and the determination of contact area in systems which are anything other than clean and homogeneous.

9:40am **NS+SS-MoM5 Adhesive Interactions and Damage Mechanisms in Scanning Probe Microscopy: A Study by Interfacial Force Microscopy***, **J.F. Graham**, O.L. Warren, P.R. Norton,* University of Western Ontario, Canada

It is often observed that contact mode scanning probe imaging with hard tips at loads of 10's of nN will damage soft surfaces, such as those of polymers. We have studied the origin of damage mechanisms on cellulose acetate (CA) calibration grids with the interfacial force microscope (IFM) using parabolic tungsten probes of 100 to 200 nm radius and forces of ~ 75 nN. The parabolic geometry of our W tips possesses a smooth profile at the apex with no sharp or discontinuous edges that can cause exceedingly high and damaging local stresses. The CA grid (elastic modulus ~ 2 GPa) can be imaged many times with a clean tungsten tip (modulus ~370 GPa) without visible damage, provided the maximum static force does not exceed that for plastic deformation of the CA. This force is readily and quantitatively determined by the IFM. After determination of a force (f) versus distance (d) curve (from which the nanomechanical properties are derived) during which the plastic limit of the CA was exceeded, contact mode imaging at the same force which had previously caused no damage, produced rapid, irreversible damage to the CA surface. It was also observed that there was a distinctive adhesion event (in the sense that it was not related to capillary forces) in the withdrawal curves of those f-d curves which preceeded damage. Further, occasionally we observed a sub-micron polymer particle on the surface after operation of the IFM in the tapping mode after an indentation experiment. This specific adhesive interaction (as well as the capillary forces) was eliminated by carrying out the measurements under hexadecane. The origin of the damage mechansim therefore appears to be: 1. the adhesive transfer of polymer to the tip; 2. the formation of adhesive contacts between this polymer "coated" tip and the CA surface; 3. repetitive formation and breaking through shear forces of polymer-polymer contacts at the interface.

10:00am **NS+SS-MoM6 Friction and Adhesion in the Attractive Regime***, **A.R. Burns**, J.E. Houston, R.W. Carpick,* Sandia National Laboratories

Recent molecular level measurements and simulations have shown a strong connection between adhesive bonding forces and energy dissipation in sliding friction. In order to observe this directly, we have constructed a scanning force microscope with de-coupled lateral and normal force sensors to simultaneously observe the onset of both friction and chemical bond formation. Furthermore, by using a mechanically-stable interfacial force sensor,@footnote 1@ we are able to map the entire attractive interaction between the probe tip and the sample surface. Measurements made on self-assembling alkanethiol films with chemically different head groups show that friction can be directly attributed to bond formation and rupture well before repulsive contact. Thus we are able to separate chemical friction from more traditional mechanical sources of energy dissipation.@footnote 2@ @FootnoteText@ @footnote 1@ S. A. Joyce and J. E. Houston, Rev. Sci. Instrum. 62, 710 (1991). @footnote 2@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

10:20am **NS+SS-MoM7 Tribology and Mechanical Properties of Langmuir-Blodgett Monolayers***, **K.J. Wahl**, W.R. Barger, S. Asif,* Naval Research Laboratory

Mechanical properties of contacts with nanometer-scale dimensions are important in understanding the behavior of microscale sliding contacts. Monolayer films provide a model system to study fundamentals of relationships between adhesion, friction and mechanics. In this study, we deposited monolayers of distearoyl phosphatidyl ethanolamine (DSPE) and dioleoyl phosphatidyl ethanolamine (DOPE) (both mixed and single component) on freshly cleaved mica by the Langmuir-Blodgett technique. We use atomic force microscopy to examine morphology, adhesion and shear (sliding) behavior as well as modulation techniques to investigate mechanical properties of the monolayers as a function of deposition pressure. Measurements of film elastic/viscoelastic mechanical response via force modulation techniques are compared and contrasted with the surface compressional modulus determined during film deposition as well as to mechanical properties via nanoindentation.

10:40am **NS+SS-MoM8 Deformation and Friction of Organic Monolayers**, ***J.D. Kiely***, *J.E. Houston,* Sandia National Laboratories

The use of organic monolayers as lubricating films has received considerable attention recently, especially with regard to their potential use in micromachine applications. We have used the interfacial force microscope (IFM) to characterize, on the nanometer scale, tribological properties of alkanethiol self-assembled monolayers on Au and monolayers of octadecyltrichlorosilane and perfluorodecyltrichlorosilane on Si. The IFM is similar to the atomic force microscope (AFM) but is distinguished by it use of a quantitative, mechanically stable, zero-compliance force sensor which allows us to measure both normal and frictional forces in a controlled fashion (i.e., without 'snap-to-contact'). We quantitatively relate monolayer deformation (chracterized by using the IFM in a nanoindentation mode) to friction, and find that, in the absence of appreciable adhesion/adhesion hysteresis, friction is very well correlated with deformation hysteresis. Additionally, we have identified the effects of wear, monolayer preparation procedure, and the environment (e.g., UV exposure and humidity) on tribological properties. This work was supported by the U.S. Department of Energy under Contract DEAC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

11:00am **NS+SS-MoM9 Structure-Dependent Viscoelasticity During Alkane Thiol Monolayer Growth**, ***N.D. Shinn***, *T.M. Mayer, T.A. Michalske,* Sandia National Laboratories

Organic monolayers adsorbed on contacting surfaces (e.g., as micromachine lubricants) modify both the chemistry and the mechanical properties of the interface. Whereas the chemistry can be predicted from the terminal functionality of the individual molecules, the viscoelastic properties reflect inadequately understood molecular ensemble dynamics. For example, the isomorphic self-assembled monolayers of methyl-terminated alkane thiol homologues [HS(CH@sub 2@)@sub n-1@CH@sub 3@ denoted as C@sub n@] have complex shear moduli that vary by orders of magnitude. We are using Acoustic Wave Damping (AWD) techniques and spectroscopic ellipsometry to elucidate the structure-dependent viscoelasticity of alkane thiols on polycrystalline Au(111) quartz crystal microbalance substrates. Multi-frequency analysis yields the complex shear modulus of equilibrium structures and a high-sensitivity oscillator circuit @footnote 1@ permits simultaneous measurement of the adsorption kinetics and energy dissipation during monolayer growth from the gas phase. Monolayer elasticity increases with alkane chain length. Co-adsorbed physisorbed molecules, chemisorbed two-dimensional fluid phases, and the nucleation and growth of condensed-phase islands each contribute to dissipation in the growing monolayers. Short chain (n < 10) thiol monolayers grow via Langmuir kinetics into a two-dimensional gas phase followed by slow condensation into ordered domains. However, the C@sub 12@ thiol exhibits surprising precursor-mediated kinetics and a highly viscous initial phase. Thiol dimerization is considered as a mechanistic explanation for the observed differences. 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@ K. Wessendorf, Sandia Nat. Labs. (patent pending).

11:20am **NS+SS-MoM10 Lubrication Brought to Light: Optical Signatures of Nanomechanical Effects in Organic Thin Films**, ***R.W. Carpick***, *D.Y. Sasaki, S. Singh, A.R. Burns,* Sandia National Laboratories

The properties of organic lubricant films composed of hydrocarbon chain molecules is currently of great interest, as the detailed molecular response of these films to mechanical stress remains to be understood. Molecular films of polydiacetylenes are composed of ordered hydrocarbon chains attached to a chromophoric polymer backbone. These materials exhibit strong fluorescence emission and optical absorption which can be altered by mechanical stress (mechanochromism), providing the opporutunity to exploit the optical response as a signature of specific molecular behavior. Furthermore, structurally distinct chromatic phases ("blue" and "red" phases) of the film can be produced by a combination of Langmuir-Blodgett deposition and photopolymerization. We have studied the response of these films to mechanical stress at the nanometer level using a novel scanning force microscope. The instrument combines near-field optical detection with a displacement-controlled (non-compliant) normal force sensor and a decoupled lateral force sensor. Nanomechanical properties, including local elastic modulus, adhesion, and friction are compared for different chromatic phases of the film. We examine the modes of film deformation at the molecular level by monitoring the fluorescence emission while varying the mechanical stress applied to a nanometer-sized contact area. * 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.

11:40am **NS+SS-MoM11 In-situ Investigation of the Influence of a Mechanical Load on the Orientation of Organic Monolayers with Second Harmonic Generation**, *M. Gurka,* ***F. Eisert***, *M. Buck, M. Grunze,* University of Heidelberg, Germany

Understanding mechanical properties of ultrathin organic films is of fundamental importance due to their vital role in numerous technological applications such as hard disc drive lubrication or as moulde release agents in the injection moulding process. The relationship between macroscopically applied forces and processes taking place on the molecular scale can be studied in situ by photon-based techniques. Second harmonic generation (SHG) is a nonlinear optical technique which allows to investigate the effect of normal and shear forces on the order and orientation of confined monolayers. We have set up a model experiment consisting of an SHG-active silane film self-assembled onto a glas prism. A pressure in the range of 30 - 50 MPa is applied to the monolayer by pressing a quartz lens against the prism. Changes of the film structure are monitored by in situ polarization dependent SHG experiments. The SHG signal reflects the response of the SHG-active endgroup of the monolayer to the mechanical load and allows to determine the average tilt angle of the monolayer and also the in-plane symmetry of the molecular layer. During loading we observe only a minor change in the mean tilt angle of the endgroup whereas shear forces cause the molecules to align.

Organic Electronic Materials Topical Conference
Room 327 - Session OE+EM-MoM

Organic Thin Film Devices I: Light Emitters

Moderator: A. Kahn, Princeton University

8:20am **OE+EM-MoM1 Polymers for Optoelectronics**, ***N. Peyghambarian***, University of Arizona **INVITED**

Tailoring of organic molecules and polymers has enabled the recent development of multifunctional materials such as photorefractive polymers and organic electroluminescent materials. This talk will review: (i) the development of thermally stable photorefractive polymers with infrared and their application to imaging through scattering media using holographic time-gating techniques; (ii) the fabrication of photorefractive polymer-dispersed liquid crystals; (iii) the demonstration of ultra-bright electroluminescent devices using new Al-based cathodes; (iv) the fabrication of micro-pixel arrays of organic light-emitting devices for displays; (v) the demonstration of optically pumped organic laser structures based on conjugated polymers.

9:00am **OE+EM-MoM3 High Efficiency Three Color Stacked Organic Light Emitting Devices**, ***P.E. Burrows***, *G. Parthasarathy, G. Gu, S.R. Forrest,* Princeton University; *T. Zhou,* Universal Display Corporation **INVITED**

Vacuum deposited organic light emitting devices (OLEDs) based on "small molecule" organic semiconductors have demonstrated adequate efficiency and lifetime for commercial monochrome flat panel display applications. For full color display applications, vertically stacked OLEDs (SOLEDs) offer increased resolution and aperture ratio over conventional, side-by-side patterned pixels. The SOLED consists of separate red, green and blue elements grown in a vertical stack by sequential vacuum deposition. The elements emit light co-axially through semi-transparent electrodes enabling any combination of three colors to be emitted from the entire area of the device. In this paper we present recent improvements in the color, efficiency and operating voltage of SOLEDs. A typical SOLED is a 13 layer device comprised of organic semiconductors, metal oxides and metal thin films. Understanding and controlling microcavity effects in the stacked device is therefore essential to generate a pixel with well separated and adequately saturated colors. We present an analytical model of weak microcavity effects in SOLEDs and apply the results to fabricate a three color pixel with minimal directionality and good color separation. We also discuss a higly transparent, metal-free cathode which defeats the microcavity effects by reducing reflections within the stack.

9:40am **OE+EM-MoM5 Excited-State Electronic Structure of Conjugated Polymers and Oligomers: Characterization of the Luminescence and Two-Photon Absorption Properties***, **J.L. Brédas,*** University of Mons-Hainaut, Belgium **INVITED**

Conjugated polymers and oligomers present remarkable semiconducting and nonlinear optical properties. They can for instance be incorporated as the active element in new generations of organics-based field-effect transistors, light-emitting diodes, or photovoltaic cells; much work is also devoted to designing chromophores with enhanced second-order or third-order optical response. In this talk, we discuss the results of correlated quantum-chemical calculations aimed at characterizing the electronic structure of these excited states that are responsable for the luminescence and nonlinear optical properties. We focus on polyparaphenylene vinylene and its derivatives; these polymers are widely exploited in polymer-based light-emitting diodes. We describe the nature of the lowest singlet excited states involved in the absorption and emission processes. We then discuss the major influence of interchain interactions; by considering polyphenylenevinylene chains carrying different substituents, we show that some combinations lead to exciton transfer (which is good for luminescence) and others to charge transfer (which is good for photovoltaics). The second (brief) part of the talk deals with the design of novel donor-acceptor phenylenevinylene oligomers which display unprecedented two-photon absorption cross-sections. Some examples of potential applications will be briefly described.

10:20am **OE+EM-MoM7 Gain, Amplified Spontaneous Emission and Lasing in Semiconducting Polymers**, *M.D. McGehee, R. Gupta, E.K. Miller,* ***A.J. Heeger,*** University of California, Santa Barbara **INVITED**

Because of the high absorption coefficients, the high density of chromophores, and the Stokes-shifted luminescence, luminescent semiconducting polymers have potential as low threshold laser media. Optically pumped amplified spontaneous emission has been demonstrated in submicron films of ¼-conjugated polymers as the active materials. Resonant structures appropriate for photopumped lasers include microcavities, distributed feedback (DFB) substrates, and whispering gallery mode micro-discs and micro-rings. Photopumped stimulated emission and lasing have been observed in a growing number of highly luminescent polymers with emission wavelengths that span the visible spectrum. Progress in the areas of polymer lasers will be reviewed and the possibility of electrically pumped diode lasers (fabricated from semiconducting polymers) will be explored.

11:00am **OE+EM-MoM9 XPS and AFM Investigation of Stability Mechanism of tris-(8-hydroxyquinoline) Aluminium Based Light-Emitting Devices***, **Q.T. Le**, F.M. Avendano, E.W. Forsythe, L. Yan, Y. Gao,* University of Rochester*; C.W. Tang,* Eastman Kodak Company

Stability is an essential issue in the application of organic light-emitting devices (OLEDs). We have investigated the indium tin oxide (ITO) surface for operated and un-operated OLEDs that consist of ITO/phenyl-diamine (NPB)/tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@)/Mg:Ag with NPB thickness varied from 0 to 300 Å using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques. The ITO surface was exposed by removing the organic and metal layers with dichloromethane, an organic solvent in which NPB and Alq@sub 3@ are highly soluble. Electroluminescence (EL) characterization demonstrates that the NPB layer substantially enhanced the stability. XPS analysis shows that for the device made without NPB and after 90 hours of operation, there exists an insoluble organic material on the ITO surface. This organic material is not observed on the ITO of un-operated cells nor of the operated NPB-containing devices. Lateral force AFM also shows a striking difference between the ITO surface of devices with and without NPB after operation. The XPS and AFM results suggest that the organic residue is the degradation product of Alq@sub 3@ that act as quenching sites at the ITO/Alq@sub 3@ interface, which may lead to the early failure of the single layer devices. This work was supported in part by DARPA DAAL 0196K0086 and NSF grant DMR-9612370.

11:20am **OE+EM-MoM10 A Comparison of the Change in the Valence Electronic Structure of p-sexiphenyl Thin Films upon Doping with K and Cs***, N. Koch,* Technische Universität Graz, Austria*; **J.-J. Pireaux**, L.M. Yu,* Facultés Universitaires Notre-Dame de la Paix, Belgium*; R.L. Johnson,* Universität Hamburg, Germany*; G. Leising,* Technische Universität Graz, Austria

Thin films of the electroactive conjugated material para-sexiphenyl (6P) were doped with potassium and cesium under ultra-high vacuum conditions. The changes in the valence electronic structure of 6P upon increasing dopant exposure were followed with synchrotron ultraviolet photoelectron spectroscopy (UPS), and are compared subsequently. For doping with Cs, new occupied electronic states are only found in the energy gap at 5.8 and 3.6 eV (with respect to the vacuum level); they lie well below the Fermi level, and can be interpreted to negative bipolaron states in 6P. The experimental findings are different when doping with K; for very low doping levels, a finite density of valence states (DOVS) is observed at the position of the Fermi-level E@sub F@ . Higher doses of K lead to a shift of E@sub F@ closer to the vacuum level, and out of the DOVS. This observation could be interpreted in terms of a polaron to bipolaron transition of the charged species of 6P with progressive doping. But also a different interpretation will be proposed, in a manner that bipolarons are formed from the beginning of the doping experiment.

Plasma Science and Technology Division
Room 318/319/320 - Session PS-MoM

Feature Evolution

Moderator: J.L. Cecchi, University of New Mexico

8:20am **PS-MoM1 The Independence of Feature Profile Evolution on Mask Charging During Chlorine Plasma Etching of Si (100)***, K.H.A. Bogart, F.P. Klemens, V.M. Donnelly, **J.T.C. Lee,*** Bell Laboratories, Lucent Technologies

Non-ideal feature profiles including sidewall undercutting or bowing and microtrench formation at the feature bottom are often observed for crystalline (100) silicon (Si) with silicon dioxide (SiO@sub 2@) masks etched in pure chlorine (Cl@sub 2@) plasmas. Localized charging of the mask with respect to the underlying Si has been suggested as one possible cause for flawed profiles. Cl@sub 2@ plasma etching of Si (100) wafers (150 mm p-type, 4-200 @OMEGA@cm) with an insulating SiO@sub 2@ mask and patterned Si (100) wafers without a mask were compared directly to determine the effect of mask charging on the resulting feature profile. Etching was performed in a TCP plasma reactor (250 and 500 W rf source and 150 W rf bias power) at 2 and 10 mTorr Cl@sub 2@ . The pattern (nested and isolated lines and trenches) was transferred into the no-mask Si wafers by etching through a SiO@sub 2@ mask with a hydrogen bromide plasma, producing trenches with nearly vertical sidewalls and flat trench bottoms. The SiO@sub 2@ mask was removed in aqueous hydrofluoric acid, and the line and trench pattern was further propagated into the Si wafer by etching in Cl@sub 2@ plasmas under various conditions. In the latter case, the pattern through which etching proceeded was composed only of Si and was not insulating, but conductive. Therefore, localized charging of the patterned Si did not occur. Cross sectional scanning electron micrographs were used to compare feature profiles. In general, wafers etched with the insulating SiO@sub 2@ mask had line and trench profiles with bowed or tapered sidewalls and pronounced microtrenches. Wafers etched in the absence of the insulating SiO@sub 2@ mask showed nearly identical feature profiles. Therefore, localized charging of the insulating SiO@sub 2@2 mask is not a primary cause of sidewall bowing or microtrenching for Cl@sub 2@ plasma etching of Si under these conditions.

8:40am **PS-MoM2 Is Notch Formation Chemical or Physical?***, **N. Hershkowitz**, A.K. Quick,* University of Wisconsin, Madison

There is debate in the etching community about what mechanisms are most important in the formation of notches in phosphorous-doped poly-Si lines during Cl@sub 2@ plasma etching. Some researchers claim that the notch is formed by ion deflection due to differential charging. Others claim that the ion deflection causes only the removal of SiCl@sub 2@ passivating films which then allows neutral etching of the notch. They claim that stress at the poly-Si/SiO@sub 2@ interface opens up the poly-Si lattice to enhance the neutral etch rate. The goal of this talk is to help clear up this controversy. An experiment was performed in which poly-Si line and space patterns were etched in the presence of an electron beam to reduce differential charging. An electron beam of the correct energy and current density was found to suppress notch formation, indicating that this phenomenon is charge related. Analysis of the notch shape for a floating and 13.56 MHz RF biased substrate (without the electron beam) showed a characteristically larger notch opening for the biased case due to the low-energy peak in the bimodal ion energy distribution function. This shape difference provided evidence that the notching phenomenon is mainly from ion deflection. In addition, scanning electron microscope images of the inside of the notch showed ion tracks that could not have been made by neutrals. These findings, along with the notch supression in the electron beam are proof that the dominant etching species are ions. This work is supported by National Science Foundation Grant #EEC-8721545.

9:00am **PS-MoM3 Feature Evolution Simulations of Silicon Trenches***, **H.H. Hwang**, D. Bose,* Thermosciences Institute*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center

Understanding how an evolving microfeature is affected by process parameters, such as those that are controlled by knobs on the reactor panel, is of great interest. This is possible only if the feature level model is coupled to a reactor level model. We have developed a level set theory based profile evolution model to simulate the moving gas-solid interface between the semiconductor and plasma. This approach is an alternative to string algorithms which suffer from looping problems and are not easy to implement in three dimensions. Our model includes both the isotropic and anisotropic components of etching, and considers reemission of neutrals and ions inside the trenches. We have also developed a comprehensive reactor model which can provide the necessary input parameters for the level set simulation. The multidimensional reactor analysis code solves the complete set of Navier-Stokes equations for plasma transport, neutral species dynamics, gas flow, heat transfer, and Maxwell's equations for power deposition from an external source in a coupled manner to provide concentrations, fluxes, and energies of various species as a function of process parameters. We have validated the reactor model against available experimental data for N@sub 2@ plasmas (10 mTorr, 100 sccm) in a 300 mm etch ICP reactor. The current analysis shows that the model reproduces plasma properties, such as electron density, temperature, and their variations, with reasonable accuracy. We will present results from the feature profile simulation in pure chlorine plasmas in an ICP reactor at 1-10 mTorr and 20-100 sccm, based on the calculations generated from the reactor model. Comparisons to experimental data will also be presented. Support for Bose and Hwang provided by NASA contract NAS2-14031 to Eloret.

9:20am **PS-MoM4 An Integrated Multi-Scale Modeling Approach to Predicting Ionized PVD Step Coverages***, **D.G. Coronell**, P.L.G. Ventzek, V. Arunachalam, C.-L. Liu,* Motorola*; D.E. Hanson, J.D. Kress, A.F. Voter,* Los Alamos National Laboratory

Ionized PVD has emerged as a promising technology for inlaid metallization over high aspect ratio features. However, the high cost of process and tool development and the need to forecast the extendibility of ionized PVD processes to smaller features and new materials represent major challenges. Computer-aided process development is an increasingly important means of addressing these challenges. Here we demonstrate how models describing phenomena at several length scales can be integrated to better understand, control, and predict the influence of process settings on ionized PVD step coverages. The relationship between the process variables and the flux of material to the wafer is determined using a detailed equipment scale plasma model.@footnote 1@ The ion flux information is subsequently funneled through a sheath model where the angular and energy distributions of the ions are computed for input to a feature scale model. This is a critical link in the integrated model as it enables a clear understanding of the relationship between equipment level settings and process performance at the feature scale level. An important component of the ionized PVD feature scale model is the description of the interaction of the energetic ions with the feature surface. The ion-surface interaction models were formulated from atomic scale molecular dynamics analyses where the angular and energy-dependent sticking probabilities, sputter yields, and directional characteristics of reflected and sputtered atoms were computed.@footnote 2@ The multi-scale model was applied to ionized Cu PVD where the effects of wafer bias, pressure, target power, and coil power on step coverage are illustrated for various feature geometries. As the feature sizes decrease, a judicial selection of process conditions is required in order to properly engineer the optimal mix of ionization and resputtering according to the model predictions. @FootnoteText@ @footnote 1@ See AVS '98 paper by Ventzek et al. @footnote 2@ See AVS '98 paper by Kress et al.

9:40am **PS-MoM5 Notch Formation by Stress Induced Etching of Polysilicon***, J.P. Chang, **H. Sawin**,* Massachusetts Institute of Technology

We have demonstrated that notch formation during over-etching of polysilicon is in part caused by stress enhanced spontaneous etching and is not solely a result of feature charging. Mechanical stresses applied to patterned polysilicon samples were shown to be effective in enhancing or reducing the extent of notching formation. The tensile stress at the polysilicon-oxide interface enhances spontaneous etching of polysilicon by reactive neutrals and leads to the notch formation. Non-uniform stress fields are observed within the patterned lines and large localized stresses are induced at the interface, especially the corner adjacent to the substrate. Stress concentration at the polysilicon-oxide interface can enhance the surface kinetics of etching, thereby causing notching. Notching has been attributed to the electric-field-induced ion trajectory distortion and the subsequent etching of polysilicon by these ions near the polysilicon-oxide interface. The large local charging potential at the silicon dioxide surface is caused by the difference in the directionality of ions and electrons; i.e. the isotropically directed electrons charge the photoresist sidewalls negatively and the directional ions charge the underlying oxide positively during overetch. For submicron features, the potential necessary to deflect low energy ions (<45eV) to form notches is ~500V/µm (5V/100Å) on an oxide surface. However, the magnitude of this field is within a factor of two to the breakdown voltage for bulk oxide, ~1000V/µm. Such a large field is likely to cause leakage along the surface, reducing the field and thereby preventing the deflection of ions to the extent needed to form notches. Even through bulk oxide, leakage is significant for 100Å thick oxide above applied voltages of 5V.

10:00am **PS-MoM6 The Influence of Insulator Charging on Ion Scattering and Feature Evolution During Plasma Etching***, **M.A. Vyvoda**, D.B. Graves,* University of California, Berkeley

As aspect ratios of structures etched during semiconductor device fabrication increase, the flux of scattered ions from sidewall surfaces can become a significant component of the total ion flux to the feature bottom. Previous work@footnote 1@ has suggested that details of this scattering can strongly affect the ultimate shape of the feature bottom and therefore the success or failure of the etch process itself. However, relatively few studies describe a systematic investigation of the effects of insulator (e.g., hardmask) charging on ion scattering and feature profile evolution even though it is known that such charging can perturb ion trajectories and therefore affect ion scattering behavior.@footnote 2@ Using numerical simulations of electron and ion dynamics within trench structures in order to self-consistently calculate the local charging potential on insulating surfaces, combined with realistic ion scattering distributions from feature sidewalls,@footnote 3@ we show that charging of insulating materials during the etching of both semiconductors and insulators can have a large impact on the ion flux distribution along the feature bottom. Parameters varied in the simulation include mask angle, ion angular and energy distribution function, electron temperature, and trench aspect ratio. In general, under conditions of relatively low ion energy, narrow ion angular distribution function and near-vertical mask sidewalls, ion trajectories can be significantly perturbed by insulator charging, resulting in different ion flux distributions on the feature bottom. The coupling between the perturbation of ion trajectories incident upon feature sidewalls and the subsequent scattering characteristics of these ions is especially important. These results show that under certain combinations of independent variables, neglecting ion trajectory perturbation due to charging can lead to qualitative as well as quantitative errors in the prediction of local etch rates. @FootnoteText@ @footnote 1@ T.J. Dalton et al., J. Electrochem. Soc., 140(8), Pp. 2395 (1993); @footnote 2@ M. Schaepkens and G.S. Oehrlein, Appl. Phys. Lett., 72(11), pp.1293 (1998); @footnote 3@ C.F. Abrams and D.B. Graves, submitted to J. Vac. Sci. Technol. A (1998)

10:20am **PS-MoM7 Feature Profile Evolution during the High Density Plasma Etching of Patterned Polysilicon***, **A.P. Mahorowala**, H. Sawin,* Massachusetts Institute of Technology

The two-dimensional Monte Carlo profile evolution simulator developed was used to explain the origin of artifacts such as double faceting of photoresist masks and feature bottom trenching observed during the high-density plasma etching of polysilicon, and to study the effects of feature charging on profile evolution. A designed set of experiments was performed earlier on photoresist patterned polysilicon samples on a Lam TCP 9400SE etcher varying the top power, bottom power and Cl@sub 2@ gas flow rate. The catalog of SEM micrographs generated suggested strong dependencies of the artifacts mentioned above on feature aspect ratio, product formation rate and product residence time in the etching chamber.

In particular, the surface composition at the top of the photoresist lines was found to govern the top facet angle; greater the deposition of silicon-based etching by-products, the less steep the facet. The lower facet angle was found to be controlled by the feature aspect ratio and the sticking probabilities and fluxes of the depositing materials. Feature bottom trenching was strongly linked to sidewall bowing. Trenching was found to begin when the passivating species were unable to prevent the sidewalls from bowing; the focussing effect of the curved sidewalls on the directional ions was determined to cause trenching. Finally, the realistic feature charging problem incorporating bulk conduction and surface leakage was solved to understand its role in profile evolution. For example, the high potentials developed near the feature bottom corners were found to reduce the energies of the ions striking the corners and correspondingly lower the etching rates.

10:40am **PS-MoM8 Modeling of Finite 3-Dimensional Features in High Density Plasma Etching@footnote 1@***, **R.J. Hoekstra**, M.J. Kushner,* University of Illinois, Urbana-Champaign

The development of 2-dimensional profile simulators for fabrication of microelectronics devices has significantly progressed in recent years enabling modeling of etch profile evolution under many different processing conditions. Submicron device development and increasing device density leads to more complex and innately 3-dimensional features which require improved dimensionality in profile simulators. Two issues of concern are: 1) To what degree can 2-d simulators can be applied to modeling 3-d structures? and 2) What systemmatic perturbations to 2-d profiles are cause by 3-d structures (such as finite length trenches)? In this paper, results for the Monte Carlo Feature Profile Model (MCFPM) will be used to investigate the these issues. There are 2-d and 3-d versions of the MCFPM which are identical with the exception of increased dimensionality. Comparisons are made of profiles predicted by the 2-d and 3-d MCFPM for finite length trenches and square vias for etching of poly-Si in an ICP reactor using Cl@sub 2@. The aspect ratio of the trench and the angular spread of the ion flux were varied. In the center of "long" trenches (e.g., 1 µm x 4 µm) profiles from the 2-d model are similar to those from the 3-d model except that the etch rate is lower due to increased shadowing of reactants. As the ends of the trenches are approached (that is, one is near "3-plane" corners) increased sidewall sloping and curvature is predicted from the 3-d models compared to the 2-d model. This necessitates a greater amount of over-etching to fully clear these features than predicted by 2-d models. The effects of angular spread and asymmetry of the ion flux, and redeposition of etch products were examined to determine their role in 3-d profile evolution. With redeposition, we found that narrow ion angular distributions were more sensitive to being near 3-plane corners, resulting in more variation in transverse etch profiles along the trench. @FootnoteText@ @footnote 1@Work supported by SRC and NSF.

11:00am **PS-MoM9 Charging Effects in Profile Evolution during Etching of Silicon in High-Density Plasmas***, **G.S. Hwang**, K.P. Giapis,* California Institute of Technology

Charging effects are particularly important when high-density plasmas interact with patterned semiconductor surfaces containing mixed conducting and insulating layers. We employ the Direct Simulation Monte Carlo method to investigate the influence of mask charging by the electron shading effect on profile evolution of polysilicon during etching in a Cl@sub 2@ plasma. We compare simulation results with and without charging as a function of ion temperature and mask thickness. We find that microtrenching and sidewall bowing are significantly affected by mask charging as a result of ion trajectory deflection by the local electric field between the mask sidewalls. The magnitude of the effect depends strongly on mask aspect ratio and shape. Differences in profile evolution during etching of nested and isolated lines could also be attributed to charging. The results reaffirm that feature-scale modeling can no longer exclude mask charging effects.

11:20am **PS-MoM10 Effect of Residual Chlorine (Cl) Atoms for Notching Formation in a High Density Plasma Reactor***, **H.C. Lee**, Y.-B. Kim, S. Beckx, S. Vanhaelemeersch,* IMEC vzw, Belgium

Notching at the bottom corner of the etched polysilicon feature has been known as charging problem due to the electron shading effect,@footnote 1@ especially at the outermost line of the nested lines. Most of the experiments@footnote 2@ and simulations@footnote 3@ were conducted in a high density plasma reactor using Cl@sub 2@ chemistry. However, notching still occurs in the RIE reactors with symmetrical shape. We believe that notching can be formed due to the combination of plasma charging and preferable reaction between Si and Cl atoms. In this study, notching was investigated in terms of polymerization and chemical reaction between Si and Cl or Br atoms in a TCP 9400 high density plasma reactor. Mixed chemistry of HBr/Cl@sub 2@ and HBr/He-O@sub 2@ was used as a main etch step and over etch step respectively. From the TEM inspection of etched polysilicon profiles, the thickness of polymer which deposited on the sidewall decreases along down the sidewall. Much thicker polymer was detected at the top portion of the sidewall than the ones at the bottom. Thus, bottom sidewall exposed to the plasma without the protection layer against Cl atoms. Sidewall polymer was analyzed by angle resolved XPS in order to understand the polymer composition. TOA (Take of Angle) was varied from 15° to 90° which is normal to the horizontal gate oxide surface. Cl2p peaks were detected from the TOA35° to TOA65° which means most of Cl bonds are located at the sidewall of the feature. Si was also detected in the form of SiO@sub 2@ at the same TOA regime. At the TOA90°, however, intensity of Cl2p was very low, which explains that no Cl residues are on the etched gate oxide surface. It can be concluded that a lot of Cl atoms still remain on the sidewall even if it is not used during the over etch. In the meantime, Br3d peaks were detected whole range of TOA. With very low reaction probability of Br to Si, Br in the sidewall polymer also works as a protection layer. Consequently, notching has not been found in one step etching using HBr/He-O@sub 2@. Without the protection layer, 50nm thick SiO@sub 2@ was used as a mask material instead of photoresist, notching was increased dramatically. Residual Cl atoms play a major role in notching formation with combination of very thin polymer layer at the bottom corner of the features. @FootnoteText@ @footnote 1@K. Hashimoto: JJAP, 32, P6109, 1993. @footnote 2@T. Nozawa et al.: JJAP, Vol. 34, P2107, 1995. @footnote 3@G.S. Hwang and K.P. Giapis, Proceeding of P2ID, P63, 1997.

11:40am **PS-MoM11 A General Predictive Semi-Empirical Feature Profile Simulator***, **D.J. Cooperberg**, V. Vahedi,* Lam Research Corporation

A multiple process, semi-empirical, 2-dimensional, feature profile evolution simulator has been developed and is being used to conduct mechanistic studies of processes including oxide etch, silicon etch, PECVD, and IPVD. The feature surface is advanced with a shock-tracking algorithm@footnote 1@. The simulator employs a Monte Carlo based scheme for determining particle fluxes to the surface. Trajectories of ions, depositing and etching species are followed. Etching and depositing agents are modeled using a sticking coefficient model. A Langmuir site balance model is employed at the discretized feature surface to compute rates. For oxide etch, an algorithm for simultaneous etching and deposition has been implemented which allows for the modeling of a steady-state fluorocarbon film during etching@footnote 2@. Physical sputtering, ion-assisted etching and scattering of ions at the feature surface are modeled along with redeposition of sputtered material. Ion energy and angular distributions can be supplied to the profile simulator from self-consistent sheath models or simulations. Parameters such as stickling coefficients, sputter and etch yields which are associated with each material (i.e. photo-resist, oxide, polymer, metal) within a feature have been determined in part by experiment. Polymer deposition experiments have been performed to determine polymer sticking coefficients and study the role of ion-assisted deposition. Sputtering experiments have been performed to carefully measure angular and energy dependence of sputter yield on resist and oxide. Experimental results from IPVD have also been used to determine the yield and threshold for physical sputtering. Parameters not yet measured through experiment have been chosen with the use of a calibration routine which determines the values which lead to optimal agreement between simulation and digitized SEM data. The mechanistic and the semi-empirical calibration approaches have given our profile simulation tool a predictive capability. Feature characteristics such as taper, bow, necking, etchstop, facet angles, step-coverage and trenching are captured with appropriate process parameters. @FootnoteText@ @footnote 1@Hmamguchi S., "Mathematical methods for Thin Film Deposition Simulations", in "Modeling of Film Deposition for Microelectronic Applications," Thin Films, vol. 22, ed. by S. Rossnagel, (Academic Press Inc., San Diego, 1996), pp. 81-115 @footnote 2@ Rueger, N.R.; Beulens, J.J.; Schaepkens, M.; Doemling, M.F.; Mirza J.M.; Standaert, T.E.F.M.; and Oehrlein, G.S., Role of steady state fluorocarbon films in the etching of silicon dioxide using CHF@sub 3@ in an inductively coupled plasma reactor. Journal of Vacuum Science Technology A (Vacuum, Surfaces, and Films), July-Aug. 1997, vol.15, (no.4):1881-9.

Surface Science Division
Room 308 - Session SS1-MoM
Issues in Surface Electronic Structure

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **SS1-MoM1 The Physical Origin of Surface Relaxation@footnote 1@*, T. Zhang,*** University of Tennessee, Knoxville*; J.-H. Cho,* Oak Ridge National Laboratory*; E.W. Plummer,* University of Tennessee, Knoxville*; Z. Zhang,* Oak Ridge National Laboratory

The subtantial difference in the valence charge distributions between sp and df metals can be so large that for hcp (0001) surfaces, the first inter-layer spacing of berillium will expand while that of zirconium will contract. This difference in relaxation can be traced to a difference in the direction of the traditional Smoluchowsky charge smoothing at the two surfaces. The failure of the Finnis-Heine (FH) picture in explaining material dependence of surface relaxation lies in its neglect of this critical difference in valence charge distributions. This work is supported by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464 @FootnoteText@ @footnote 1@ Tianjiao Zhang, Jun-Hyung Cho, E.Ward Plummer, Zhenyu Zhang, submitted to Physical Review Letters @footnote 2@ R. Smoluchowsky, Physical Review,60,661(1941) @footnote 3@ M W Finnis and Volker Heine, J. Phys. F: Metal Phys., 4, L37(1974)

8:40am **SS1-MoM2 Unoccupied States vs Coverage in Alkali Metals on Mo(110) by Auger Decay, NEXAFS, and Bandmapping*, E. Rotenberg,*** *C.M. Lee,* Lawrence Berkeley National Laboratory*; S.D. Kevan,* University of Oregon

In recent years, the nature of the chemical bonding between alkali metals (AMs) and metal substrates has been intensely debated. For many alkalis on metals, the workfunction rapidly falls with coverage, reaching a minimum at about 1/2 monolayer before recovering somewhat up to saturation. The key issue is whether this work function change directly reflects a strong change in the charge distribution around the AM, as proposed by Langmuir and Gurney (LG) over 60 years ago, or whether the charge distribution somewhere else (in the substrate or in the space between adsorbate and substrate) dominates the workfunction change. Using localized, core-hole processes at the AM (near edge xray absorption fine-structure spectroscopy (NEXAFS) and Auger decay) we can now infer the alkali s-level occupation as a function of coverage, and correlate this with other measurements such as bandmapping and workfunction measurements. Measurements were performed for Li or K on Mo(110). At low coverages (below about ~0.1 ML) we find no occupied states at the AM atoms. At somewhat higher coverages, we observe a reoccupation of the AM valence orbital. This reoccupation, however, appears largely complete before the workfunction minimum occurs. Therefore, we conclude that there is a significant change in AM valence occupation with coverage, roughly following the LG model (donation of charge from AM to the substrate at low coverage, followed by backdonation at higher coverages). However, the workfunction change cannot be explained only by our measurements of the AM valence occupation, but instead has additional contributions from redistribution within the substrate.

9:00am **SS1-MoM3 Auger Photoelectron Coincidence Spectroscopy of Ag and the Ag/Cu(100) Surface Alloy*, D.A. Arena,*** *R.A. Bartynski,* Rutgers, The State University of New Jersey*; Q. Qian,* New Jersey Institute of Technology*; S.L. Hulbert,* Brookhaven National Laboratory

The question of atomic versus band-like contributions to the core-valence-valence (CVV) Auger line shape in Ag remains a controversy. Theoretical predictions are ambiguous as the correlation energy, U, is comparable to the 4d valence band width, W. Using Auger-photoelectron coincidence spectroscopy (APECS), we measured the line shape of the Ag M@sub 4,5@VV and N@sub 2,3@VV Auger transitions from single crystal Ag. In addition to a dominant atomic-like component, both spectra show a significant contribution from band-like decays. However, the N@sub 2,3@VV spectrum cannot be accounted for within the Cini-Sawatzky theory, suggesting that dynamical effects of the very rapid 4p core hole decay influences the lineshape. Furthermore, the N@sub 2,3@VV transition exhibits a much larger low energy tail that may be of the same origin. We have also measured the Ag CVV Auger spectra for 0.1ML Ag/Cu(100) to investigate the electronic structure of this prototypical surface alloy. In contrast to theoretical predictions, the Auger lineshape suggests that the Ag d-band shifts towards the Fermi level.

9:20am **SS1-MoM4 Photoelectron Spectroscopy Studies of Adhesion, Alloying and Segregation in the Platinum - Tungsten Bimetallic System*, J.J. Kolodziej,*** *T.E. Madey,* Rutgers University*; J.W. Keister, J.E. Rowe,* North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation, and Auger electron spectroscopy, are used to study Pt films on W (211). It is found that the films grow in layer-by-layer mode at 300 K. As a function of Pt film thickness four different Pt 4f@sub7/2@ photoemission peaks are observed, corresponding to a single monolayer of Pt/W, a Pt interface layer, Pt surface atoms and Pt bulk atoms. A single monolayer of Pt is stable up to the onset of desorption. In contrast, when multilayer Pt films are annealed above 600 K, substrate W atoms diffuse in the Pt overlayer to form an alloy. Evidence for a dilute alloy, in which the W 4f@sub7/2@ signal from the W impurity in a Pt host is found to have a binding energy 1 eV higher than bulk W, is observed up to 900K. The evolution of the bimetallic Pt - W sample as a function of Pt coverage and annealing temperature is diagnosed by analysis of intensities and angular dependencies of the W 4f@sub7/2@ and Pt 4f@sub7/2@ features. In all cases a single monolayer of Pt "skin" covers the alloy film. The data provide detailed information on energetics of adhesion, segregation and alloying in an early d - late d transition metal system.

9:40am **SS1-MoM5 Electronic Structure of Sn/Ge(111) along the @sr@3 x @sr@3 to 3x3 Phase Transition***, J. Avila,* LURE and CSIC, France*; A. Mascaraque,* Universidad Autonoma Madrid, Spain*; G. LeLay,* CRMC2-CNRS, France*; E.G. Michel,* Universidad Autonoma Madrid, Spain*;* ***M.C. Asensio,*** LURE and CSIC, France

The @sr@3 x @sr@3-Sn/Ge(111) structure undergoes a phase transition to a 3x3 phase at low temperature,@footnote 1@@footnote 2@ which has been interpreted as a charge-density-wave@footnote 1@ where electron localization gives rise to strong correlation effects.@footnote 2@ We report an angle-resolved photoemission investigation on the band structure and the Fermi vector of this interface along the phase transition. The electronic bands at room temperature exhibit a prominent surface state originated from Sn p@sub z@ orbitals, dispersing 0.3 eV with minima at K points. The Fermi vector obtained from these data is close to 0.3 Å@super -@@super 1@, much smaller that the calculated value.@footnote 1@ The surface state band splits at low temperature in two dispersing bands with strong 3x3 periodicity, at variance with previous data.@footnote 2@ The observation of these two bands correlates with the appearance of two components in the shallow Sn core levels. These data together with several other evidences support that the phase transition is of the order-disorder type. The mechanism driving the phase transition will be discussed in view of different theoretical models. @FootnoteText@ @footnote 1@J.M. Carpinelli et al, Phys.Rev.Lett. 79, 2859 (1997). @footnote 2@A. Goldoni and S. Modesti, Phys.Rev. Lett. 79, 3266 (1997).

10:00am **SS1-MoM6 Surface Electronic Structure of Wurtzite GaN(0001)1x1 Studied with Angle-Resolved Photoemission*, Y.-C. Chao,*** *C.B. Stagarescu, J. Downes, K.E. Smith,* Boston University*; D. Hanser, M. Bremser,* North Carolina State University*; R.F. Davis,* North Carolina State University, US

The surface electronic structure of the n-type, Si-doped, wurtzite GaN(0001)1x1 surface has been studied in detail with angle-resolved photoemission. The GaN film was grown on a AlN buffer layer on a 6H-SiC(0001) Si-face, on-axis substrate using a low-pressure metalorganic vapor phase epitaxy technique. A very sharp 1x1 LEED pattern was observed from the surface after the cleaning by repeated cycles of sputtering with nitrogen ions and annealing in ultra-high vacuum. The photoemission spectra reveal a previous unidentified highly dispersive surface-state band. The dispersion of this surface state has been determined along the [@GAMMA@KM] azimuthal direction of the 1x1 surface Brillouin zone. At @GAMMA@ point, the surface state is located at ~2 eV below the valence band maximum. For small emssion angles, this surface state rapidly disperses towards the VBM by ~1 eV. As the emssion angle is increased, the state starts to disperse downward and moves into the projected bulk band gap close to the K point. The identification of this state as originating from a surface band is confirmed by exposure of the surface to activated hydrogen. The intensity of emission from the surface state decreases dramatically following H exposure. This work was supported in part by the National Science Foundation under grant umber DMR-95-04948.

10:20am **SS1-MoM7 Fermi Surface and Metallization of the Ag/Si(111)7x7 Interface***, **J. Avila,*** LURE, Centre Universitaire Paris Sud and ICMM, France*; M. DeSeta,* III Univerista di Roma, Italy*; M.C. Asensio,* LURE, Centre Universitaire Paris Sud and ICMM, France

The determination of the metallization onset of metal/semiconductor interfaces is an important goal for diverse applications as well as for its fundamental interest. In this field, the early stage of nucleation and growth plays an essential role in determining the final morphology and electronic structure of the interfaces. In this work, we address this particular issue for the epitaxial growth of silver overlayers on Si(111)7x7 surfaces studied by LEED, Photoelectron Diffraction and High Energy Resolution Angular Resolved Photoemission. The films were prepared by Ag deposition at room temperature and the silicon substrates were chemically treated previously to be introduced to the ultra high vacuum system. The evolution of the valence band as a function of the silver coverage, at particular high symmetry points of the reciprocal space, has put clearly in evidence the onset of the metallization of this interface. The presence of Si features even at 4 silver monolayers is consistent with the existence of Ag islands since the first layers. The Fermi Surface of the Ag/Si(111)7x7 interface, measured in situ, shows the coexistence of two domains of Ag(111) rotated 60° each others. In addition, the valence bands recorded along the @GAMMA@K, @GAMMA@M and @GAMMA@M' azimuths are in excellent agreement with band theoretical calculations.

10:40am **SS1-MoM8 Analysis of High-Index Si(001) Surfaces by Reflectance-Difference Spectroscopy***, **L. Mantese,*** University of Texas, Austin*; Q. Xue,* Tohoku University, Japan*; D.E. Aspnes,* North Carolina State University

High-index Si surfaces are of interest as potential substrates for electronic device applications. The growth properties of these surfaces are expected to be superior to those of the commonly used (001) and (111) orientations. It is believed that higher concentrations of surface steps may lead to higher nucleation densities. In addition, these surfaces provide new opportunities for meeting the requirements demanded by increasingly complex structures. Here, we consider the surface-induced optical anisotropies (SIOA) of three high-index Si surfaces: (113), (114) and (115) representing offcut angles of 25.2, 19.5, and 15.8 degrees from (001) toward [110], respectively. The SIOA of these surfaces were measured first in their air-oxidized conditions, second as-cleaned by heating, and third following Ge deposition. In some instances previous results on lower index Si(001) surfaces offcut 6 and 10 degrees toward [110] are available for comparison. The air-oxidized surfaces show sharp derivative-type structures near the critical point energies of bulk Si, consistent the lower index Si(001) surfaces. We have previously interpreted these structures in terms of photon-induced localization of the excited electronic states, which results from final-state correlation effects ordinarily discarded in conventional descriptions of optical absorption in solids. Spectra of clean reconstructed surfaces show a broad feature near 3 eV and a small step-related structure near the (E@sub 0@',E@sub 1@) transition of bulk Si. Atomic H exposure decreases the amplitude of the broad 3 eV feature suggesting it to be a dangling-bond-related state. In contrast, H exposure of Ge-deposited Si surfaces sharpens and enhances features below 3 eV while structures near the critical point energies of bulk Si remain. The optical response of Si(114) is consistent with its STM analysis, which indicates that this is the highest-index surface to demonstrate a terrace-plus-step morphology.

11:00am **SS1-MoM9 HRPES Study of Acetylene Adsorption and Reaction with Si(100)-2x1 Surface***, **S.H. Xu,*** Y. Yang, H. Cruguel,* Montana State University*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; G.J. Lapeyre,* Montana State University*; J.T. Yates Jr.,* University of Pittsburgh

The adsorption and reaction of acetylene with Si(100)-2x1 surface has been studied using high resolution photoemission measurement the Si 2p, C 1s and valence band(VB)spectra as a function of acetylene coverage and post annealings at several temperatures. After the clean Si(100) surface is exposed to 0.5 ML acetylene, the surface state in valence bands is totally gone. Meanwhile, there is only one interface component in the Si 2p core line. These results indicate that the asymmetry of Si dimers is gone after acetylene adsorption, which is in excellent agreement with the tetra-@sigma@ model proposed by our previous photoelectron holographic results.@super [1]@ Significant changes in the electronic structure(Si 2p, C 1s and VB) are found after subsequent annealing of a saturation overlayer. Annealing at lower temperatures can induce a bit of acetylene desorption but most of the molecules decompose to C@sub 2@H@sub x@ (x=1, 0) and H species. After annealing at above 650 °C, there develops a surface state in valence bands and a Si 2p surface core-level component indicating some restoration of a Si(100)-2x1 structure. The C 1s line shows a single component indicating that a SiC compound forms on the Si surface. Both of the reacted components of the Si 2p and C 1s lines show that the SiC species form cluster-like feature. At the same time, the surface core-level components indicate that the clean surface Si dimers reappear on the silicon surface. This work is supported by NSF. The ALS of LBNL is supported by the DOE. [1]. G. J. Lapeyre et al., to be published.

11:20am **SS1-MoM10 The Electronic Structure of Nanosized Mg Clusters on MgO Surfaces: Characterization with MIES***, **J. Günster**, J. Stultz, S. Krischok,* Texas A&M University*; P. Stracke, V. Kempter,* Technische Universitat Clausthal, Germany*; D.W. Goodman,* Texas A&M University

MgO films (2nm thick) were grown on Mo and W substrates with "in situ" investigation by MIES and UPS(HeI). Apart from the valence band emission no additional spectral features could be detected with electron spectroscopies. The oxide surface was exposed to Mg atoms (substrate temperature between 100 K and RT). An additional peak, not seen in UPS, located within the bandgap developed in MIES, located about 2.3eV above the top of the valence band with ca. 1.5eV FWHM at the lowest exposures. Both the energetic position and the peak width depended (weakly) on the exposure time. This additional emission could be detected in MIES until its intensity fell below a level of 10 ppm of that from the valence band. We attribute this additional emission to the formation of small, non-metallic Mg clusters. For small exposures these are 2D clusters.@footnote 1@ It is remarkable that the energetic position of the cluster emission closely matches that expected for the ionization of surface Fs+ / Fs-centers.@footnote 2@ Indeed, the existence of Mg-induced F-type centers an MgO has recently been detected by both ESR@footnote 3@ EELS.@footnote 4@ Therefore, we suggest that in the initial phase of Mg exposure F-type point defects are produced when the Mg adsorbs close to extended defects, such as steps, corners etc. These point defects may play an important role as nucleation sites for the cluster formation. @FootnoteText@ @footnote 1@C.T. Campbell: Surf. Sci. Rep. 27 (1997) 1 @footnote 2@L.N. Kantorovich, J.M. Holender, M.J. Gillan: Surf. Sci. 343 (1995) 221 @footnote 3@E. Giamello, A. Ferrero, S. Coluccia, A. Zecchina: J. Phys. Chem. 95 (1991) 9385 @footnote 4@K.-M. Schr@um o@der, D. Peterka, H. Pfn@um u@r: DPG Fr@um o@hjahrstagung Regensburg, and to be published in Surf. Sci.

11:40am **SS1-MoM11 Scattered and Recoiled Ion Fractions From Cd- and S-Terminated CdS(0001) Surfaces***, L. Houssiau,* ***M. Liu****, J.W. Rabalais,* University of Houston*; J. Wolfgang, P. Nordlander,* Rice University

Scattered and recoiled ion fractions from CdS(0001) and CdS(000-1) surfaces have been determined by means of time-of-flight scattering and recoiling (TOF-SARS) spectrometry. An acceleration tube placed between the sample and the CEM detector enabled separation of the ions and neutrals. By applying a positive (negative) high voltage on the tube, the negative (positive) ions are accelerated, giving rise to neutral and ion peaks in the TOF spectra. On the Cd-terminated surface, 4 keV Ne@super +@ ions scattered at an incident angle @alpha@ = 11° through a scattering angle @theta@ = 50° exhibit a pronounced angular dependence, i.e. the lowest ion fractions (Ne@super +@/Ne@super 0@) are observed along the close packed atomic rows and . On the S-terminated surface however, the same experiment exhibits the opposite angular dependence, i.e. the highest ion fractions (Ne@super +@/Ne@super 0@) being now observed along the close packed rows. 4 keV Kr@super +@ ions were also used to study the S recoiled ion fractions. On the Cd-terminated surface, the lowest S@super -@ ion fractions are found along both the and rows. On the S-terminated surface, the lowest S@super -@ ion fractions are found along the rows, but the highest ion fractions are found along the rows. The final charge state of the ejected atoms is determined by electron tunneling between the surface and the atom as it leaves the surface. This process has been modeled using ab initio calculations of the potentials in the CdS surfaces. In conclusion, it is found that the ion fractions and their angular dependence are extremely sensitive to the nature of the surface terminating layer. This is important in determining the microscopic reactive sites on surfaces.

Surface Science Division
Room 309 - Session SS2-MoM
Molecular Adsorbates on Metals

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

8:20am **SS2-MoM1 An X-ray Absorption Study of Saturated Hydrocarbons Physisorbed on Metal Surfaces***, K. Weiss,* ***C. Wöll,*** Ruhr-Universität Bochum, Germany

Monolayers of linear and cyclic saturated hydrocarbons (n-hexane, cyclohexane, n-octane, n-hexatriacontane) physisorbed on several metal surfaces (Cu(111), Au(111), Ru(0001) and Pt(111)) have been investigated by K-edge X-ray absorption spectroscopy (XAS). Whereas the corresponding multilayer data qualitatively resembles the core excitation spectrum observed for the free molecules, a strong quenching of the Rydberg R-resonance at 287.7 eV is observed for molecules in direct contact with the substrate. The intereaction with the metal surface is found to result in the formation of a new, sharp resonance which is assigned to a novel surface-induced Rydberg state. In addition the broad feature observed in the saturated hydrocarbon monolayer XAS-spectra at 285.1 eV is identified as a transition into metal-molecule hybrid orbitals, indicating a significant chemical interaction between saturated hydrocarbon and the metal surface. This C-H-activation is shown to correlate with the well-known soft C-H--stretch modes seen in IR-spectroscopy for many saturated hydrocarbon/metal surface combinations.@footnote 1@ @FootnoteText@ @footnote 1@G. Witte, K. Weiss, P. Jakob, J. Braun, K.L. Kostov, and Ch. Wöll, Phys. Rev. Lett. 80, 121, (1998)

8:40am **SS2-MoM2 An Atom Specific Probe of the Surface Chemical Bond Using X-ray Emission Spectroscopy***,* ***J. Hasselstrom,*** *A. Fohlisch, O. Karis, A. Nilsson,* Uppsala University, Sweden*; M. Nyberg, L.G.M. Pettersson,* Stockholm University, Sweden*; J. Stohr,* IBM Almaden Research Division

When a molecule is adsorbed on a metal surface by chemical bonding new electronic states are formed. The direct observation and identification of these states is still an experimental challenge. In this contribution we will show how X-ray Emission Spectroscopy (XES), in spite of its inherent bulk sensitivity, can be used to investigate adsorbed molecules. We have applied XES to CO and NH@sub 3@ adsorbed on single crystal Cu surfaces. These molecules have lone pair orbitals in its @sigma@-systems and adsorb with these towards the substrate. Due to the localization of the core excited intermediate state, XE spectroscopy allows an atom specific probe of the valence electrons, i.e. the molecular contributions can be separated from those of the substrate. In combination with ab initio calculation, new details of the chemical bond formed at the surface can be revealed. It is, for CO adsorbed on Cu(100), found that the surface chemical bond formation can be related to the @pi@-system interacting with the metal d band. The overall interaction of the @sigma@-system, i.e. the 5@sigma@ lone pair, is found to be repulsive. In contrast, the @sigma@-system, involving the 3a@sub 1@ lone pair, of ammonia is found to comprise the main covalent contribution to the adsorption energy of the NH@sub 3@/Cu(110) system; the degenerated 1e orbitals, often referred to as the N-H @pi@-system preserve much of its molecular character. Our results indicate that the different bonding mechanisms can be related to the energy position of the lone pair valence orbitals as compared to the metal bands, and furthermore to the corresponding symmetries of the lowest unoccupied molecular orbitals.

9:00am **SS2-MoM3 The Role of Steps and Kinks in Catalytic Activity***,* ***L. Ford,*** *P. Blowers, R. Masel,* University of Illinois, Urbana

In the literature, there is the idea that steps and kinks are active sites for chemical reactions, but the experimental data is far from convincing. In this paper we see if there is a correlation between step and kink density and reactivity for a number of simple decomposition and hydrogenation reactions on platinum. We have examined the decomposition of ethylene, methanol, methylamine, ethanol, propanol, NO, the hydrogenation of ethylene, and the hydrogenolysis of ethylene, methanol, ethanol on Pt(111), Pt(110)(1x1), Pt(110)(1x2), Pt(100)-hex, Pt(100)(1x1), Pt(210), Pt(511), Pt(331). We find that in general stepped surfaces have different reactivity than closed packed planes, but some stepped surfaces are more active than Pt(111) while other stepped surfaces are less active than Pt(111). There is no correlation between step and kink density and catalytic activity. Calculations are done to understand the variations. We find that in general stepped surfaces relax to more stable geometries. The relaxation process lowers the electronic coordination number of the atoms in the surface of the catalyst so after relaxation, there is not a large difference in the coordination of atoms in stepped surfaces and Pt(111).

9:20am **SS2-MoM4 Face Specificity and the Role of Metal Adatoms in Molecular Reorientation at Surfaces***, C.C. Perry, S. Haq,* University of Liverpool, United Kingdom*; B.G. Frederick,* University of Maine, U.K.*;* ***N.V. Richardson,*** University of St. Andrews, Scotland, U.K.

Using Reflection Absorption Infrared Spectroscopy (RAIRS), the coverage dependent reorientation of the benzoate species on the (110) and (111) faces of copper is compared and contrasted. Whereas on Cu(110), benzoate reorients from flat-lying to upright orientation with increasing coverage, on Cu(111), at all coverages, benzoate is aligned normal to the surface. The formation of periodic, flat-lying copper-benzoate structures has been attributed to the availability of metal adatoms, which differs dramatically between the (111) and (110) faces. We discuss the face specificity of molecular orientation by comparing calculated formation energies of adatom-vacancies from ledges and kink sites on (100), (110), and (111) faces. Further support for this model is given by the evaporation of sodium, either by pre- or post-dosing, onto low coverage benzoate/Cu(111), which induces benzoate to convert from perpendicular to parallel orientation. Likewise, coevaporation of Cu while dosing benzoic acid onto the Cu(111) surface also results in a majority of flat-lying benzoate species. Finally, for adsorption on the p(2x1)O/Cu(110) reconstruction, benzoate occurs only as the upright species, which is consistent with reducing the copper mobility and availability on the (110) face. We therefore suggest the possible role of metal adatoms as a new mechanism in controlling adsorbate orientation, and therefore face specificity, in surface reactions.

9:40am **SS2-MoM5 Theoretical Studies of Surface Reactions on Metals: I. Ethyl to Ethylene Conversion on Platinum; II. Photodissociation of Methane on Platinum***,* ***J.L. Whitten,*** North Carolina State University **INVITED**

An embedding method designed to provide a molecular level understanding of adsorbate energetics and surface reaction mechanisms is presented. Electronic structures, including relativistic effects, are described by an ab initio formalism that permits an accurate determination of energies and adsorbate structure.@footnote 1@ Applications to catalytic and photochemical reactions on transition metal surfaces are reported. I. In the catalytic conversion of ethyl adsorbed on platinum surfaces to ethylene, the minimum energy pathway for the transfer of hydrogen to the metal surface is calculated. A detailed description of the transition state is presented. II. In the photodissociation of methane physisorbed on platinum, results are reported for a methane molecule interacting with an embedded cluster model of Pt(111). Configuration interaction theory is used to sort out states resulting from electron attachment to methane from lower energy states that correspond to metal excitations. Energies of the ground and excited states of the Pt(111)CH@sub 4@ complex are calculated as a function of geometrical distortions and the distance of methane from the surface. Key steps in the photodissociation process are described. @FootnoteText@ @footnote 1@ J. L. Whitten and H. Yang, Surf. Sci. Repts., 218 (1996) 55.

10:20am **SS2-MoM7 Chemistry of SO@sub 2@ on Ru(001): Formation of SO@sub 3@ and SO@sub 4@***,* ***T. Jirsak,*** *J.A. Rodriguez, S. Chaturvedi, J. Hrbek,* Brookhaven National Laboratory

The interaction of SO@sub 2@ with Ru(001) at 300 and 100 K was studied using synchrotron-based high-resolution photoemission, INDO/S MO calculations, and a thermochemical analysis based on the bond-order conservation Morse-potential (BOC-MP) formalism. At 300 K and small exposures of SO@sub 2@, sulfur dioxide completely decomposes (SO@sub 2@ -> S@sub a@ + 2O@sub a@). Several coordination modes for adsorbed SO@sub 2@ were examined using INDO/S and the BOC-MP formalism. It was found that adsorption geometries in which the molecule is di-coordinated via O,O or S,O are the most probable precursors for dissociation. For large exposures of SO@sub 2@ at 300 K, SO@sub 3@ and SO@sub 4@ species appear on the Ru(001) surface confirming thus the theoretical predictions derived from the BOC-MP method which indicate that formation of SO@sub 3@ and SO@sub 4@ can take place only when the number of empty adsorption sites is limited. This prediction was also proved during the adsorption of SO@sub 2@ on a O/Ru(001) surface with @theta@@sub O@ = 0.25 ML, producing similar types of species as at saturation of SO@sub 2@ on Ru (S@sub n@+O, SO@sub 4@ and S). When a Ru surface partially covered by sulfur (@theta@@sub S@ = 0.2 ML) was exposed to molecular oxygen at 300 K, formation of SO@sub 3@ and SO@sub 4@ species was not observed. Experiments performed at a surface temperature of 100 K showed a very rich surface chemistry. Five different surface species were observed after SO@sub 2@ dosing: atomic S, S@sub n@+O, SO@sub 2@, SO@sub 3@ and SO@sub 4@. The S 2p spectrum of a Ru(001)surface saturated at 100 K is dominated by a very intensive peak of a multilayer of SO@sub 2@, which entirely disappeared upon annealing to 160 K. Further annealing to 260 K leaves mainly atomic S and SO@sub 4@ on the surface and the latter is completely decomposed by 350 K.

10:40am **SS2-MoM8 Low Temperature STM Imaging of Furan Molecules on Pd(111)***, C.A. Pearson,* ***S. Chiang****, A. Loui, D.N. Futaba,* University of California, Davis

The cyclotrimerization reaction of acetylene to benzene is known to proceed readily in ultra high vacuum on the Pd(111) surface. Thermal desorption spectroscopy has measured furan (C@sub 4@H@sub 4@O)@footnote 1@ and thiophene (C@sub 4@H@sub 4@S)@footnote 2@ desorbing from the Pd(111) surface following the coadsorption of acetylene with oxygen and sulfur respectively. Using low temperature scanning tunneling microscopy (STM), we have imaged furan molecules adsorbed on the Pd(111) surface. Dosing and imaging of the sample was performed at 200 K. While no changes were evident with low energy electron diffraction (LEED), we observed localized ordering with the STM for monolayer coverage. Furan molecules form ordered rows in three different domains oriented 120° apart. The ordered regions are roughly 50 Å to 100 Å in size. Higher resolution images show individual molecules within the rows. Measurements of the intermolecular spacing in the images provide information about the molecular tilt on the surface. Images of individual molecules will also be compared with predicted theoretical STM images from extended Hückel molecular orbital theory. @FootnoteText@ @footnote 1@R.M. Ormerod, R.M. Lambert, Cat. Lett. 6, 121 (1990). @footnote 2@A.J. Gellman, Langmuir 7, 827 (1991).

11:00am **SS2-MoM9 Conformation and Orientation of Methyl Pyruvate on Ni(111)***,* ***P.H. McBreen****, M. Castonguay, J.R. Roy,* Université Laval, Canada

Both the orientation and molecular conformation of adsorbed layers are determining factors in a variety of properties including chemical reactivity. The question of surface orientation and conformation are particularly important for methyl pyruvate since it possesses both a keto and an ester carbonyl and it can undergo cis-trans isomerization. Its hydrogenation to methyl lactate is one of the very few well documented cases of enantioselective heterogeneous catalysis. To the best of our knowledge this is first report of an investigation of the intrinsic adsorption of this prochiral molecule on a metal surface using surface science techniques. RAIRS data shows that methyl pyruvate is chemisorbed on Ni(111) at all coverages with its molecular plane perpendicular to the surface. Two different adsorption conformations are detected. The full monolayer is found to be exclusively in the bidentate cis-conformation.The results, and DFT calculations, indicate that the keto cabonyl metal surface interaction is stronger than the ester carbonyl metal surface interaction. Comment will be made on the fact that the observed molecular orientation and conformation are at odds with the model usually assumed in rationalizations of the enantioselective hydrogenation of methyl pyruvate.

11:20am **SS2-MoM10 Negative and Positive Adsorbate-Induced Reflectance Changes: Formic Acid on Cu(100)***,* ***C.-L. Hsu****, E.F. McCullen, R.G. Tobin,* Tufts University

Adsorption on metal surfaces typically reduces the broadband reflectance of the surface, an effect that is usually attributed to diffuse scattering of the conduction electrons by the adsorbate. The resistance of the film typically increases. On the other hand, a dielectric film typically increases the broadband reflectance of a metal. Both effects are observed for the adsorption of formic acid (HCOOH) on epitaxial Cu(100) films at 125 K. Both the dc resistance and the infrared reflectance at 1500 cm@super -1@, away from any vibrational resonances, were measured during dosing. Upon initial exposure to formic acid, the film's resistance increases by 1% and its reflectance decreases by 0.5%. With continued exposure, leading to the growth of a multilayer formic acid film, the reflectance begins to increase and ultimately reaches a level more than 10% greater than the clean-surface reflectance. The resistance, however, scarcely changes after adsorption of the first monolayer. While the results are qualitatively consistent with expectations, there are discrepancies. The resistance and reflectance changes in the monolayer region are not proportional, and the increase in reflectance with thickness is more rapid than expected.

11:40am **SS2-MoM11 Ordering of Chemisorbed PF@sub 3@ on Cu(001)***, J. Braun, L.V. Goncharova, G.G. Bishop, A.V. Ermakov,* Rutgers University*; D.-M. Smilgies,* Rutgers University, US*;* ***B.J. Hinch,*** Rutgers University

PF@sub 3@ adsorbs molecularly on many transition metal surfaces with P bonded at 'on top' positions. On close packed Pt, Ni and Ru crystal faces, PF@sub 3@ has been reported to adsorb with a high density @sr@3 x @sr@3 structure. In these cases steric interactions are believed to be strong enough to prevent rotational motion of the molecules about an axis parallel to the surface normal. On Cu(001), between 140K and 200K, a saturated(4x2) structure with at least two 90° rotated domains has been observed with both helium atom scattering and LEED. We shall discuss the implications of free rotational motion of these molecules in the c(4x2) and a close-packed, uniaxially-compressed, near-hexagonal phase that is found at higher coverages and lower temperatures. Evidence for PF@sub 3@ decomposition on Cu at temperatures above 500K will also be presented.

Thin Films Division
Room 310 - Session TF-MoM
Transparent Conductive Oxides

Moderator: T.J. Coutts, National Renewable Energy Laboratory

8:20am **TF-MoM1 Atmospheric Pressure Chemical Vapor Deposition of Transparent Conducting Films of Fluorine-Doped Zinc Oxide***, H. Liang,* ***R.G. Gordon,*** Harvard University **INVITED**

Transparent conducting fluorine doped zinc oxide was deposited as thin films on soda lime glass substrates by atmospheric pressure chemical vapor deposition (CVD) at substrate temperatures of 480@super o@C to 500@super o@C. The precursors diethylzinc, tetramethylethylenediamine and benzoyl fluoride were dissolved in xylene, and this solution was nebulized ultrasonically and then flash vaporized by a carrier gas of nitrogen preheated to 150 @super o@C. Ethanol was vaporized separately, and these vapors were then mixed to form a homogeneous vapor mixture. Good reproducibility was achieved using this new CVD method. Uniform thicknesses were obtained by moving the heated glass substrates through the deposition zone. The best electrical and optical properties were obtained when the precursor solution was aged for more than a week before use. The films were polycrystalline and highly oriented with the c-axis perpendicular to the substrate. More than 90% of the incorported fluorine atoms were electrically active as n-type dopants. The electrical resistivity of the films was as low as 5x10@super -4@ ohm-cm. The mobility was about 45 cm@super 2@/V-s. The electron concentration was up to 3x10@super 20@/cm@super 3@. The optical absorption of the films was about 3-4% at a sheet resistance of 7 ohms/square. The diffuse transmittance was about 10% at a thickness of 650 nm. Amorphous silicon solar cells were deposited using the textured fluorine doped zinc oxide films as the front electrode. The short circuit current was increased over similar cells made with fluorine doped tin oxide.

9:00am **TF-MoM3 Effects of Layered Structure on Properties of Transparent Conductive Films of ZnO/ZnO:Al***,* ***K. Tominaga****, T. Murayama, Y. Sato, I. Mori, T. Ushiro, T. Moriga, I. Nakabayashi,* The University of Tokushima, Japan

Recent data for transparent conductive films show that film resistivity seems to saturate at 10@super -4@ ohm-cm or above. This circumstance is common in ZnO and ITO films. To overcome this difficulty, approaches different from conventional parameter controls should be examined. In ZnO film preparation, we tried additional Zn adding during the film deposition. Recent investigations showed that the additional Zn during the sputtering of ZnO:Al target (doped 2 wt% aluminum oxide) induced an increase of both carrier concentration and Hall mobility. As the result, film resistivity was decreased. This suggested that an incorporation of oxygen deficient ZnO phase (ZnO:O@sub v@) in ZnO:Al phase improves the film crystallinity of ZnO:Al and decreases defects in ZnO:Al. This effect may be observed in general for the case of layered films of ZnO:Al and ZnO. To confirm this, we produced a multilayered film of ZnO:Al and ZnO:O@sub v@ film and investigated the role of the inserted ZnO:O@sub v@ layer in electrical conduction and optical property. Films were deposited by alternative sputtering method, where a ZnO:Al(2 wt%) target and a conductive ZnO target which only contains native donors were sputtered alternatively in pure Ar gas at 1 mTorr for a definite time. This process was succeeded to deposit a definite film thickness. The results showed that the film resistivity is decreased by inserting ZnO:O@sub v@ layer. This is due to an improvement of doping efficiency of Al donors in ZnO:Al layer by inserting ZnO:O@sub v@, in addition to carrier redistribution between two layers.

9:20am **TF-MoM4 Chemical State Effects on Doped ZnO Film Properties***,* ***G.J. Exarhos****, L.-Q. Wang, C.F. Windisch, Jr.,* Pacific Northwest National Laboratory

Zinc oxide is representative of the class of transparent conducting oxides which exhibit high transmission at visible wavelengths and concurrent low electrical resistivity. The resident conductivity and associated long wavelength reflectivity of these II-VI semiconductor films arises from the introduction of defect levels within the bandgap generated during the deposition process itself or during subsequent processing. In this work, films are prepared by means of rf-sputter and solution deposition methods. The deposition parameters are varied in order to increase conductivity in films which incorporate multivalent cationic dopants (Ga@super +3@, In@super +2@, Cu@super +2@, Au@super +3@, Pt@super +4@,...) within the wurtzite lattice. Post deposition modification of films on silica, Si, Al, or Pt substrates involves annealing in Ar/4% H2 or cathodic reduction in an electrochemical cell. Electrochemical film modification is carried out in aqueous solution (pH 7) or in an organic solvent such as CH@sub 3@CN. As-deposited and modified films are characterized using a cadre of analytical methods including XPS, AFM, TEM, XRD, Raman spectroscopy, and Electrochemical Impedance Spectroscopy. EIS measurements enable selective characterization of polarization effects within the oxide film and localized chemistry at the film-solution interface as a function of applied potential. The defect structure of the oxide is readily probed by means of in situ Raman spectroscopy during electroreduction. Results indicate that the LO Raman E@sub 1@ mode intensity, linewidth, and resonance frequency are particularly sensitive to the nature and concentration of defect states present in the film. Based upon these studies, a surface hydroxyl species is proposed to explain the observed reversible changes in conductivity. Such measurements complement the XPS studies which probe dopant oxidation state. Insight into film properties stability is based upon the electrochemical studies and measured variations in film properties upon subsequent annealing.

9:40am **TF-MoM5 Photoemission Spectroscopy Analysis of ZnO Films for Display Applications***, E.W. Forsythe, Y. Gao,* University of Rochester*;* ***G.S. Tompa****, L.G. Provost,* Structured Materials Industries, Inc.*; J. Doyle,* Advanced Display Systems

An important factor in the performance of most displays is the quality of at least one transparent conductive oxide contact layer. Presently, indium tin oxide (ITO) is predominantly used because it is an accepted standard and has a great deal of invested development. However, for several reasons, including work function, physical stability, and band alignment, ITO is not always the ideal contact layer for a given display technology. We will report the physical properties of ZnO based films prepared by metal organic chemical vapor deposition (MOCVD) using ultraviolet and x-ray photoemission spectroscopy (UPS and XPS). In addition, the surface characteristics of the films are modified with series of cleaning and polishing steps. Using UPS, the work function for ZnO is 4.23eV. XPS results show an oxide layer more than 5nm on the surface of the as-received MOCVD films, with a small fraction of Zn and Ga. This oxide layer is removed by a cleaning and plasma treatment, which enhances the conductivity of the ZnO films. Finally, we will report atomic force microscopy results before and after cleaning and polishing as well as chemical etching results. This work was supported in part by DARPA DAAL01-96-K-0086, NSF DMR-9612370.

10:00am **TF-MoM6 Transparent and Conductive Multicomponent Oxide Films Prepared by Magnetron Sputtering***,* ***T. Minami****,* Kanazawa Institute of Technology, Japan **INVITED**

Recently, multicomponent oxides composed of combinations of binary compounds or ternary compounds have attracted much attention as new materials for transparent and conductive thin films. This paper introduces transparent conducting multicomponent oxide films prepared with varied chemical compositions by magnetron sputtering. It was found that most multicomponent oxides composed of combinations of binary compounds contained at the least one ternary compound; highly transparent and conductive films could be prepared in the ternary compound. In addition, if binary or ternary compounds which produced transparent and conductive films when prepared by magnetron sputtering were used as the starting materials, transparent and conductive films composed of combinations of these binary or ternary compounds could be also produced from all compositions in the resulting multicomponent oxides. In addition, it was found that most of the properties of transparent conducting multicomponent oxide films were mainly determined by the metal element contained in the oxide. It can be concluded that transparent conducting multicomponent oxide films are suitable for specialized applications because their electrical, optical and chemical properties as well as physical properties such as band-gap energy, refractive index and work function can be controlled by changing the chemical composition.

10:40am **TF-MoM8 Improvement of Microstructure of Indium-Tin-Oxide Films by Thin Film and Surface Technologies***,* ***Y. Taga****, T. Satoh, M. Ishii, T. Ohwaki,* TOYOTA Central Research & Development Labs., Inc., Japan

A rapid progress has been made in the practical device applications of flat panel displays (FPD) such as liquid crystal display, electroluminescence display, etc. In accordance with this trend, strong demands have been actually appeared in the quality of transparent conductive films such as indium-tin-oxide (ITO). Up to now, a lot of studies have been devoted mainly to the electrical and optical properties of ITO films. However, it becomes clear that microstructure of ITO films gives an important influence on the performance and durability of FPD's. In this paper, we tried to improve the microstructure of ITO films by controlling the sputter deposition and plasma treatment conditions in thin film preparation. Furthermore, we investigated the effect of microstructure of ITO films on the electrical properties of Ta-Sn-O films in the system of Al/Ta-Sn-O/ITO layered structure in inorganic electroluminescence displays. It was found that the microstructures of ITO films changed drastically with oxygen partial pressure in Ar-O@sub 2@ sputtering gas; i.e., with increasing oxygen partial pressure, grain size become small and surface morphology become smooth. Measurements of I-V characteristics in Al/Ta-Sn-O/ITO revealed that the leakage current at low electric field has been diminished by the improvement of microstructure of ITO films.

11:00am **TF-MoM9 Work Function Modification of Indium Tin Oxide***,* ***S.M. Tadayyon****, K. Griffiths, P.R. Norton,* University of Western Ontario, Canada*; C. Tripp, Z. Popovic,* Xerox Research Centre of Canada, Canada

Indium-tin-oxide (ITO) is a transparent conducting material widely used in electronic devices such as flat panel displays, solar cells, IR detectors and OLED's where it is used as the hole injecting electrode. It is desirable to have an electrode possessing as high a work function as possible, and so extensive investigations into properties and modification of ITO have been undertaken. The objective of the present study is the possible modification of ITO work function (WF) using evaporated metal overlayers. We have therefore studied gold overlayers because of the high WF of gold, and its inertness. ITO films on glass substrates (resistance ~ 10 Ohms/sq) were cleaned with a UV-ozone treatment before entry into a UHV system. Auger electron spectroscopy (AES) was used to determine the surface composition. The change of work function (WF) of the surface (± 10mV) was determined by a Kelvin probe technique and correlated with the absolute coverage (@theta@) of Au in the range 0<@theta@ 5x10@super 15@ Au cm@super -2@. The final WF values were not very different from the non-UV-ozone treated samples. Studies on bulk Au and ITO covered by Au in a single deposition, showed that the low final WF value in the sequential experiments was attributable to adsorption of hydrocarbons from the 5x10@super10@ torr vacuum, and that useful increases in WF are attainable on transparent ITO electrodes

11:20am **TF-MoM10 Application of High Speed Four-Parameter Stokes Vector Spectroscopy to the Characterization of Textured and Specular Transparent Conducting Oxide Thin Films***,* ***P.I. Rovira****, R.W. Collins,* Pennsylvania State University

A rotating-compensator multichannel ellipsometer has been used to measure the four unnormalized Stokes vector elements associated with the polarization state of polarized light reflected from both specular and textured transparent conducting SnO@sub 2@:F films. This technique provides not only the ellipsometry angles (@PSI@, @DELTA@), but also the reflectance R and the degree of polarization p. With a photodiode array detector, spectra in (@PSI@, @DELTA@), R, p) having 100 points from 1.5 to 3.75 eV can be collected with a minimum acquisition time of ~32 ms. In contrast to rotating-polarizer multichannel ellipsometry which tends to be inaccurate when @DELTA@ equals 0° or ±180°, or p<1, the rotating-compensator approach provides high accuracy measurements of the phase shift @DELTA@ over its full range (-180° to 180°) even when p<1. Therefore, this new configuration permits us to make accurate ellipsometric measurements for SnO@sub 2@:F films on glass substrates, which is the structure of choice for large area device applications such as photovoltaics. In addition to conventional microstructural characterization using the ellipsometry angles (@PSI@, @DELTA@), we have incorporated light scattering due to the textured surfaces into the analysis using the reflectance and degree of polarization. From the latter analysis, information on the SnO@sub 2@:F texture can be extracted. The results are consistent with direct images by scanning electron microscopy and atomic force microscopy. A comparison of the degree of polarization measured for the specular and textured SnO@sub 2@:F films suggests that deviations in p from unity for the latter are due to the detection of light multiply-scattered by the texture into the specular direction. Finally, the rotating-compensator multichannel ellipsometer developed here can be readily adapted to real time analysis of solar cells prepared on textured transparent conducting oxide films in commercial processes.

11:40am **TF-MoM11 Transparent Conductive Oxides with Improved Performance for Plastic Flat Panel Displays***, **C.I. Bright**,* Delta V Technologies

The major use of Transparent Conductive Oxides (TCO) is in Flat Panel Displays (FPD). One of the major issues preventing the use of a plastic film substrate for FPD is its moisture and oxygen permeability. The permeation of water and oxygen limits the long-term stability of the display device. Another issue with plastic substrates is the low conductivity of the TCO that must be deposited at a low temperature. The Polymer MultiLayer (PML) process for vacuum evaporation of organic monomers and in-situ e-beam or UV polymerization has been shown to produce excellent substrate smoothing and when combined with other layers, outstanding barrier properties on plastic films, e.g., polypropylene and polyester (PET). Oxygen and moister permeation rates for an aluminum film with PML base coat, are one to two orders of magnitude lower than with just an aluminum layer alone. Similarly, permeation rates with PML plus an aluminum oxide layer, are another one to two orders of magnitude lower than PML with aluminum. Thus, it is proposed to combine a PML base coat and the necessary TCO transparent electrode layer, to form a barrier and solve the permeability problem of plastic substrates. This PML base coat layer should also provide a pristine surface for nucleation of the deposited TCO. Therefore, the surface resistivity of the TCO should be lower, for a given film thickness, due to its improved microstructure. The experimental results for an evaporated acrylic base coat on PET substrate, follow by DC sputtering of ITO from a ceramic target in a single pass through a web coater, are reported. Results for ITO sputtered directly onto the PET substrate without the smoothing base coat are also reported. The optical, electrical and barrier properties for both constructions were measured and compared. Three-layer constructions are also considered with, for example, a silicon dioxide barrier layer deposited either onto the PET substrate, TCO or on the base coat. The potential benefits of these configurations are compared with the two-layer configuration results reported.

Vacuum Metallurgy Division

Room 328 - Session VM+TF-MoM

Ionized-PVD: Processes, Properties, and Applications

Moderator: S.L. Rohde, University of Nebraska, Lincoln

8:20am **VM+TF-MoM1 Ionised PVD and Filtered Arc Deposition; Processes, Properties and Applications***, **P.J. Martin**, A. Bendavid,* CSIRO, Australia*; H. Takikawa,* Toyohashi University, Japan **INVITED**

Recent innovations in vacuum arc deposition have resulted in the development of the filtered arc source as a deposition tool for a range of technologically important materials. The vacuum arc was recognised early on as a potentially useful source of energetic, ionised material and a practical high rate method for depositing thin films with bulk properties and the deposition of new materials. The inherent problem of microdroplet contamination was overcome by several approaches, the toroidal magnetic duct being the most prevalent. The present state of the art of filtered arc deposition (FAD) is discussed in terms of the current understanding of the emitted fluxes, the properties of the materials deposited by these devices and new applications.

9:00am **VM+TF-MoM3 Transport of a Cathodic-Arc Plasma Through a Linear-Solenoid Macroparticle Filter***, **B.P. Cluggish**, B.P. Wood,* Los Alamos National Laboratory

A long standing problem in the use of cathodic arcs for deposition of coatings is the production of micron sized droplets, or "macroparticles," of the cathode material. These macroparticles hit and stick to the substrate, causing defects in the coating. One widely used method for "filtering out" the macroparticles is to guide the arc plasma through a solenoidal "magnetic duct" (a metal tube with an axial magnetic field.) The macroparticles travel in straight lines and thus hit and stick to the walls of the duct, rather than reaching the substrate. Unfortunately, most of the plasma ions are lost as well. For this reason, we are performing measurements to understand the transport of the plasma through a duct. The ion flux is found to decay exponentially along the length of the duct, and the magnetic field is crucial for reducing the ion losses. However, increasing the field strength above 50 G has no effect on the ion losses. Furthermore, unlike previous researchers @footnote 1@, we find that applying a positive voltage to the duct has little effect on the ion losses. We have developed a computer simulation which reproduces our results, and predicts that the injection conditions at the entrance to the duct are crucial in determining the ion losses. This work supported by the U.S. D.O.E. @FootnoteText@ @footnote 1@ A. Anders, S. Anders, and I. G. Brown, J. Appl. Phys., vol. 75, pp. 4900-4905, 1994

9:20am **VM+TF-MoM4 Characterization of Magnetron-Sputtered Partially Ionized Deposition as a Function of Metal and Gas Species***, **M.M.C. Allain**, D.B. Hayden, D.R. Juliano, D.N. Ruzic,* University of Illinois, Urbana-Champaign

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 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 attached to a pulley system that allows the ion and neutral deposition rates to be determined along the substrate plane. The ionization fraction of the flux incident onto the QCM can then be determined as a function of position. The ionization rate is a sensitive function of the metal's ionization potential (IP). The electron energy distribution in the plasma is affected by the metal being sputtered and the working gases' ionization and excitation potentials (EP). While keeping the magnetron power, rf coil power, target to substrate distance and pressure constant, the ionization fraction, as a function of position, has been measured. The electron temperature and density are measured using a Langmuir probe. The target metals analyzed in design of this experiment are aluminum(IP=5.98eV), copper(IP=7.72eV), and titanium(IP=6.82eV). The working gases will be krypton(IP=13.99eV, EP=1.702eV), argon(IP=15.76eV, EP=2.55eV), neon(IP=21.56eV, EP=3.52eV), and helium(IP=24.58eV, EP=5.36eV). An analytic model is compared to the experimental results.

9:40am **VM+TF-MoM5 Effects of Coil dc Potential on Ion Energy Distribution Measured by an Energy-resolved Mass Spectrometer in Ionized Physical Vapor Deposition***, **E. Kusano**, T. Kobayashi, N. Kikuchi, K. Fukushima, T. Saitoh, S. Saiki, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

In ionized physical vapor deposition, ion energy distribution is crucial to obtain films with desired properties. The energy distribution is supposed to be affected by the plasma potential that relates to the coil dc potential induced by an applied rf power. In this study, ion energy distribution of ionized Ti particles and Ar discharge gas has been measured by an energy-resolved mass spectrometer for various coil dc potential. The sputtering cathode used in the experiment was a conventional magnetron sputtering source with a Ti target (55mm@phi@). The cathode was coupled with an rf coil (60mm@phi@, made of Cu) generating an additional plasma in the region between the target and the substrate. The mass spectrometer was a Balzers PPM421 plasma monitor. The orifice to the ion optics was 0.1mm@phi@ and electrically grounded. The coil dc potential was controlled by changing the resistance of the resistor in the LCR circuit connecting the coil to the ground. The results showed that the energy of Ti@super +@ and Ar@super +@ was enhanced from a few eV to more than 100eV as a coil rf power increased from 0 to 200W for a constant cathode dc current. By changing the resistance of the LCR circuit, the peak of the energy spectra shifted from about 160eV for the resistance of 0@OMEGA@(the coil was grounded) to about 100eV for the resistance of 1k@OMEGA@. In addition, it was found that the total energy of Ti@super +@ or Ar@super +@ arriving to the spectrometer increased as the resistance decreased. The results suggest that the coil potential to the ground affect the plasma potential and thus the energy distribution of ions arriving to the electrically grounded substrate through the plasma sheath.

10:00am **VM+TF-MoM6 Modeling of Large Cluster Synthesis***, **A. Hosseini-Tehrani**, F.K. Urban III,* Florida International University

The original idea of the ionized cluster beam (ICB) thin film deposition technique was based upon producing, ionizing and accelerating beams of atoms clusters from vaporized material onto a substrate in a vacuum environment, using a supersonic jet source. Simulation of this process using classical nucleation theory and one dimensional gas flow equations will be presented. This approach is an extension of previous methods used for simulation of condensation of water vapor during supersonic expansion in nozzles and simulation mechanism of large clusters from vaporized solid materials. Zinc cluster sizes predicted by the model are in qualitative and quantitative agreement with our experimental results. Simulation results will be presented for different materials as well. Recently, other methods of synthesizing clusters and nanoparticles, using different types of cluster source, like magnetron sputtering mounted in a cooled chamber, have come under development. We are in the process of extending the model for the magnetron sputtering gas aggregation cluster source and will present new results for this process.

10:20am **VM+TF-MoM7 Combined Monte Carlo and Fluid Sputter Transport Model in an Ionized PVD System with Experimental Plasma Characterization***, **D.R. Juliano**, D.B. Hayden, M.M.C. Allain, D.N. Ruzic,* University of Illinois, Urbana

A code has been developed to model the transport of sputtered material in a modified industrial-scale magnetron. The device has a target diameter of 355 mm and was designed for 200 mm substrates. The chamber has been retrofitted with an auxilliary RF inductive plasma source located between the target and substrate. The source consists of a water-cooled copper coil immersed in the plasma, but with a diameter large enough to prevent shadowing of the substrate. The RF plasma, target sputter flux distribution, background gas conditions, and geometry are all inputs to the code. The plasma is characterized via a combination of a Langmuir probe apparatus and the results of a simple analytic model of the ICP system. A Monte Carlo routine in the code then tracks high energy atoms emerging from the target as they move through the chamber and undergo collisions with the electrons and background gas. The sputtered atoms are tracked by this routine whatever their electronic state (neutral, ion, excited). If the energy of a sputtered atom decreases to near-thermal levels, then it exits the Monte Carlo routine as is tracked with a simple diffusion model. In this way, all sputtered atoms are followed until they hit and stick to a surface, and the velocity distribution of the sputtered atom population (including state information) at each surface is calculated, especially the substrate. Through the use of this simulation the coil parameters and geometry can be tailored to maximize deposition rate and sputter flux uniformity.

10:40am **VM+TF-MoM8 Plasma Diagnostics of Magnetic Field Assisted Ionized Magnetron Sputtering***, **J.H. Joo**,* Kunsan National University, Korea, South Korea

The effects of axial magnetic field generated by solenoid coil has been studied for controlling the capacitive coupling between RFI antenna and metallic chamber wall, which causes severe coil sputtering at high RFI power levels. From OES results, at small magnetic flux density of 8G, RFI plasma showed sharp drop of plasma potential and reduced emission from Cu coil. Also visually the RFI plasma was confined within the RFI coil area. We compared two types of coil materials, metallic and ceramic coated. The plasma potential varied very much with materials and RFI power, which will affect the incomming ion's energy distribution. Also pulsing the sputtering power was studied to control average electron temperature of the RFI plasma, where electrons are easily quenched by heavily sputtered metals. As time dependent measuring of the plasma parameters is not readily available, some metallic films were deposited with different duties and the resulting film properties were measured. There was a big difference in preferred orientations of the grown Ag films. And the effects of ceramic coating on the RFI antenna will be addressed in the view point of plasma diagnostics, electron temperatures, electron densities, plasma potentials, contaminations and the change when it is coated by sputtered metals. Also the impedance characteristics of the RFI plasma were measured by RFZ-60 impedance analyser to study the type of coupling in mixed plasmas of DC magnetron and RFI plasma.

11:00am **VM+TF-MoM9 Study of Thin Films Deposited from a Copper Beam Formed in an Argon Atmosphere Capable of Condensing Nanoparticles***, **F.K. Urban**, A. Khabari, A. Housseini-Tehrani, P. Griffiths, G. Fernandez,* Florida International University

Although thin films formed from beams of nanoparticles or clusters have been discussed since the early 1970s, the question of the usefulness of this method has remained open as few films of any significant thickness have been formed to date. Early attempts did not condense, could only condense a few "high vapor pressure" solids, or were so low rate as to make growth too slow to be of use. A new deposition system has been designed and built here along the lines of those of Averback and Haberland, as they appear to have the most promise. The new system was specifically designed for high rate with a high throughput intermediate pressure pump and 2 kW capable sputter source. Preliminary films of copper deposited onto single crystal silicon substrates show a small beam divergence of less than 1 degree total. The beam is highly non-uniform with maximum intensity on-axis, which drops rapidly to zero within less than 10 mm off axis. Deposits have been made using a 1 Torr Argon + Helium sputtering and condensation atmosphere followed by nozzle aperture extraction. Films are affected by the amount of He and by cooling of the sputter chamber walls using liquid nitrogen. Nothing appears (detectable optically) on the substrate using Ar and no cooling and increases in both factors result in films of generally increased thickness. Optically transparent films of copper have been deposited but are not yet understood. SEM, TEM, and AFM results of Cu and other films will be presented.

11:20am **VM+TF-MoM10 Novel (111)-Textured AlCu Growth by Ionized Metal Plasma (IMP) Ti Underlayer***, **J.-B. Lai**, L.-J. Chen,* National Tsing-Hua University, Republic of China*; C.-S. Liu,* Taiwan Semiconductor Manufacturing Company, Republic of China

(111)-textured AlCu is well known to possess better electromigration resistance than those of (200) and random orientations. In general, stronger (111)-textured AlCu can be obtained with the deposition of Ti underlayer compared with AlCu deposited directly on oxide or TiN underlayer. The improved texture is attributed to the small lattice mismatch between (0002)Ti and (111)AlCu. In this paper, (111)-textured AlCu (0.5 at. %) enhanced by Ti had been investigated using Auger electron spectroscopy, x-ray diffraction, transmission electron microscope, high-resolution transmission electron microscope, four-point-probe and EM test. Using thicker ion metal plasma (IMP) sputtered titanium underlayer was found to enhance the stronger growth of (111)-textured AlCu compared to conventional and collimated Ti films because of stronger (0002) textured-Ti was formed and hence the growth of (111)-textured AlCu was facilitated. However, TiAl@sub 3@, about 50 µm@OMEGA@-cm in resistivity, was found in the samples annealed at 400 °C. As the samples were annealed at 450 °C, a continuous but not smooth TiAl@sub 3@ precipitate layer was observed. If the precipitates of TiAl@sub 3@ were discontinuous and restricted to grain boundaries, the (111)-textured Al was destroyed and local joule heating caused the early failure of AlCu line. TiN, as a barrier layer, can retard the growth of TiAl@sub 3@. In our study, TiN/IMP-Ti was also found to enhance the stronger tendency of the growth of (111)-textured AlCu than TiN/collimated-Ti and TiN/conventional-Ti. The growth of (111)-textured TiN was enhanced by (0002)Ti. AlCu/TiN/IMP-Ti samples were observed to possess longer EM lifetime compared with those of AlCu/TiN/collimated-Ti (or conventional-Ti).

11:40am **VM+TF-MoM11 Plasma Polymerization of Fluorine Alloyed Amorphous Carbon Coatings***, **A. Vanhulsel**, J.-P. Celis,* KU Leuven, Belgium*; E. Dekempeneer, J. Smeets,* VITO, Belgium

This paper reports on the deposition conditions and characterization of plasma polymerized fluorocarbon coatings grown by an inductively coupled r.f. plasma (ICP) source, using CH@sub 4@ and CF@sub 4@ as precursor gases. SiH@sub 4@, H@sub 2@or Ar were further added to the plasma to investigate their influence on the coating properties. The coatings were characterized by XPS to determine the surface and bulk composition and combined with FTIR-spectroscopy to reveal the structure of the coatings. The mechanical properties (hardness and Young's modulus) were measured by nano-indentation. The surface energy was obtained by contact angle measurements with 2 different liquids. By varying the deposition conditions, we were able to deposit coatings with surface energies as low as 14 mN/m. With the appropriate feed gases and process parameters it is possible to adjust separately the polar and dispersive part of the surface energy. A low polar component of the surface energy corresponds to a high fluorine ,CF@sub 3@and CF@sub 2@ content at the surface of the coatings. The wetting behaviour of the coatings against water is mainly dependent on the polar component. The maximum contact angle achieved was 113°. By adding H@sub 2@ to the plasma, it is possible to minimize the polar component and maximize the dispersive component of the surface energy to obtain a relatively hard (3 GPa) coating with a hydrophobic nature (contact angle (H@sub 2@O) = 90°). The fluorocarbon coatings deposited in this system are not sensitive to atmospheric aging.

Vacuum Technology Division
Room 329 - Session VT-MoM
Vacuum Gauging, Outgassing and Leak Detection

Moderator: J.P. Looney, National Institute of Standards and Technology

8:40am **VT-MoM2 Data Evaluation of Gas-Analytic Mass Spectra: Special Aspects of Getter-Assisted Helium Analysis***, **U. Langer**, R. Dobrozemsky,* Vienna University of Technology, Austria

During the last years, a method for the decomposition of complex gas-analytic mass spectra has been developed at Research Center Seibersdorf.@footnote 1@ The method (termed Vector Mass Spectrometry - VMS) is based on the evaluation of data gathered by a quadrupole mass spectrometer (QMS) and a Bayard-Alpert gauge (BAG) during multiple spectrum scans with parameter variation. Although this method allows to analyze even complex mixtures of hydrogen and helium isotopes with accuracies in the percent range, it exhibits severe weakness if small He-amounts have to be measured in a hydrogen background. This particular problem can be overcome by selective pumping, as it has been applied in several labs for similar purposes. In a recent work we have shown that hydrogen reduction factors (i.e. relative He-enrichments) of up to about 50 can be achieved by a simple, orifice controlled SAES getter pump in combination with an additional BAG.@footnote 2@ By a mathematical trick it was possible to evaluate the data by means of the already well-established spectrum decomposition codes, based on a least-squares-fit routine. This method allows quantitative measurements of He-concentrations in the percent range in the presence of hydrogen isotopes. @FootnoteText@ @footnote 1@ R. Dobrozemsky and G.W. Schwarzinger, J. Vac. Sci. Technol. A10(4), 2661 (1992) @footnote 2@ U. Langer and R. Dobrozemsky, contributed paper, submitted to 14@super th@ International Vacuum Congress, Birmingham, UK (1998)

9:20am **VT-MoM4 Long Term Behavior of an Axial-Symmetric Transmission Gauge***, **H. Akimichi**, K. Takeuchi, Y. Tuzi,* ULVAC Corporation, Japan*; I. Arakawa,* Gakushuin University, Japan

An axial-symmetric transmission gauge (AT gauge) is an ionization gauge developed for the pressure measurements in ultrahigh and extreme high vacua. In the gauge, a Bessel-box type energy filter is placed between the ionizer and the ion collector to eliminate the effects of soft X-ray and electron stimulated desorption ions. The lower limit of the pressure measurement by the AT gauge is estimated to be 10 @super -12@ Pa. The sensitivity factor for hydrogen calibrated by the conductance modulation method was about 2 x 10 @super -3@ Pa @super -1@, and was constant in the pressure range from 10 @super -10@ to 10 @super -6@ Pa. We have examined the characteristics of the AT gauge such as the sensitivity factor, the outgassing rate, etc., over the period of 3200 hours. It was found that the condition of the continuous dynode type electron multiplier, which is used for the ion detection in pulse counting mode, was one of the most important factor that determine the gauge characteristics. The followings were noticed in our study: (1) the outgassing rate of the electron multiplier was higher than that of the ionizer and the energy filter, (2) the outgassing rate of the multiplier as received from the manufacturer was very high but decreased to acceptable level after a few days operation, (3) the outgassing rate of the multiplier increased after exposure to the atmospheric air but restored, (4) the temporal increment of the sensitivity factor was observed after the exposure to the atmospheric air and was assumed due to the change in the secondary electron yield of the electron multiplier, (5) the correlation between the residual current by the X-ray effect and the sensitivity factor of the gauge were observed.

9:40am **VT-MoM5 Ultra-high Vacuum Instrumentation Development Studies***, **C. Dong**, G.R. Myneni,* Thomas Jefferson National Accelerator Facility and Old Dominion University

Measurements of both total and partial pressure in the ultra high vacuum range are known to be limited by several effects including the x-ray limit, electron stimulated desorption, cathode evaporation and thermal and chemical effects at hot cathodes. In order to understand the contributions of these effects, ultra high vacuum instrumentation development studies are in progress at the Jefferson Lab in collaboration with Teledyne Brown Engineering-Hastings Instruments. These studies include the modification of extractor gauges and RGAs by replacing the hot filaments with Spindt field emitters. The sensitivities of the modified instruments are determined in the Jefferson Lab's vacuum gauge calibration apparatus. In this paper the sensitivities of the UHV instruments for nitrogen, helium and hydrogen with different cathode currents and for various electrode potentials are presented. In addition, the contributions of electron-stimulation desorbed ions are also measured with the help of a Watanabe ion spectroscopy gauge in an ion pump evacuated vacuum system and the results are also included here. This work supported by the U.S. DOE under contract No. DE-AC05-84ER40510

10:00am **VT-MoM6 Effect of Background Neutral Pressure on the m=1 Diocotron Mode Amplitude in a Pure Electron Plasma@footnote 1@***, E.H. Chao, R.C. Davidson, **S.F. Paul**,* Princeton University

The word "diocotron" was first used to describe instabilities in hollow electron columns which had shear in the angular flow velocity. These instabilities can occur in propagating nonneutral electron beams and layers and in low-voltage microwave generation devices such as magnetrons, traveling-wave tubes, and ubitrons. We use the word to generally refer to low-frequency electrostatic oscillations perpendicular to the magnetic field and have studied experimentally the mode with azimuthal mode number m=1. The diocotron mode is studied in a pure electron plasma confined in a Malmberg-Penning trap. The frequency of the mode is generally on the order of 100 kHz while the plasma frequency is on the order of 10 MHz and the electron cyclotron frequency is 100 MHz. The frequency of the m=1 diocotron mode in an infinite length column was predicted theoretically by Levy@footnote 2@, however, we find better agreement when the finite column length theories@footnote 3,4@ are used which predict an upward frequency shift from the infinite length case. The mode amplitude is affected by wall resistance as well as by the background neutral pressure. The resistive wall destabilization of the m=1 diocotron mode was predicted and experimentally verified by White@footnote 5@. Our measurements of the growth rate agree reasonably well with theoretical predictions. The m=1 diocotron mode is also predicted to be driven unstable in the presence of collisions with background neutrals@footnote 6@. However, we have found experimentally that increasing the background neutral pressure causes the amplitude of the m=1 diocotron mode to decrease as the column expands. @FootnoteText@ @footnote 1@Research supported by the Office of Naval Research. @footnote 2@R.H. Levy, Phys. Fluids 11, 920 (1968). @footnote 3@S.A. Prasad and T.M. O'Neil, Phys. Fluids 26, 665 (1983). @footnote 4@K.S. Fine and C.F. Driscoll, Phys. Plasmas 5, 601 (1998). @footnote 5@W.D. White, J.H. Malmberg, and C.F. Driscoll, Phys. Rev. Lett. 49, 1822 (1982). @footnote 6@R.C. Davidson and E.H. Chao, Phys. Plasmas 3, 3279 (1996).

10:20am **VT-MoM7 Ionization Gauge Errors at Low Pressures***, **B.R.F. Kendall**,* Elvac Laboratories **INVITED**

Factors affecting the accuracy of ionization gauge measurements at low pressures are reviewed. In hot-cathode gauges these include electron-stimulated desorption at the electron collector, forward and reverse X-Ray effects, Auger emission, outgassing, and various controller-related errors. In cold-cathode gauges they include nonlinearities below the "magnetron knee", plasma instabilities, and leakage currents. Case studies are given to illustrate many of these sources of error and their elimination. The case studies were gathered in the course of long-term stability measurements on over 30 ionization gauges at pressures ranging from 10@super-7@ to 10@super-11@ Torr. The investigation included Bayard-Alpert (both conventional and modulated), Extractor, Magnetron, Inverted Magnetron and Double Inverted Magnetron gauges. Recent measurements on Bayard-Alpert gauges with low-temperature (lanthanum boride) and cold (disordered tetrahedral carbon) emitters are also discussed. It is concluded that, with proper precautions, ten percent reproducibility in the 10@super-10@ Torr range is easily achievable with either hot-cathode or cold-cathode gauges. A combination of the two, mounted on a common vacuum flange, is particularly useful at very low pressures.

11:00am **VT-MoM9 Plasma Expansion in a Malmberg-Penning Trap as a Function of Background Pressure@footnote 1@***, **E.H. Chao**, R.C. Davidson, S.F. Paul,* Princeton University

Single species nonneutral plasmas have very robust confinement properties because the conservation of canonical angular momentum in a system with azimuthal symmetry provides a powerful constraint on the allowed radial positions of the particles. If no external torques act on the plasma, the plasma cannot expand radially to the wall. However, collisions with a background neutral gas will exert a torque on the rotating plasma thus allowing the mean square radius to increase. In the EDG experiment at the Princeton Plasma Physics Laboratory, a pure electron plasma is confined in a Malmberg-Penning trap and the radial density profile is measured as a function of time. The base pressure is 5*10@super -10@ Torr and purified helium is injected to pressures @>=@1*10@super -9@ Torr. The magnetic field is varied between 100 and 600 Gauss. Plasma densities up to 3*10@super 7@ cm@super -3@ are achieved and temperatures are on the order of 1 eV. This leads to a Debye length of about 1 mm while the plasma dimensions are 1-2 cm in radius and 15 cm in length. The expansion rate of the plasma in the presence of a background neutral gas has been studied theoretically by Davidson, et al.@footnote 2,3@ The expansion rates observed experimentally are faster than the theoretical prediction but the magnetic field scaling of the expansion rate is similar. In addition, using the measured radial density profiles along with a numerical code to calculate the axial density distribution, the decrease in electrostatic energy was calculated and compared with the predicted temperature rise in Ref. [3]. Finally, measurements of plasma expansion rates as a function of background gas pressure are in progress. @FootnoteText@ @footnote 1@Research supported by the Office of Naval Research. @footnote 2@R.C. Davidson and D.A. Moore, Phys. Plasmas 3 (1996) 218. @footnote 3@R.C. Davidson and E.H. Chao, Phys. Plasmas 3 (1996) 2615.

11:20am **VT-MoM10 Outgassing Measurements of Vacuum Compatible Stepper Motors***, **J.W. Weed**, R.S. Goeke, J.A. Romero,* Sandia National Laboratories

The $1.2B National Ignition Facility is currently being constructed at Lawrence Livermore National Laboratory in California. This high-power laser inertial confinement fusion device consists of 192 beams with large optical components in the vacuum environment. Over 1000 stepper motors will be used to perform automated alignment of the laser beams prior to shots. Gas load and contaminants from stepper motor outgassing can severely impact the performance and operation of the laser. We have measured the time dependent outgassing rate of "vacuum compatible" stepper motors from four different manufacturers. We have also obtained mass spectra of each motor. The results of these measurements will be presented and the impact on component performance will be discussed. Possible improvements to these commercial-off-the-shelf motors will be described. @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

Applied Surface Science Division
Room 307 - Session AS-MoA
Oxides and Insulators - Surface Characterization and Applications

Moderator: R.E. Davis, IBM Corporation, East Fishkill Facility

2:00pm **AS-MoA1 Aqueous Leachability of Single Crystal and Polycrystalline Calcium Titanate***, **Z. Zhang**, E.R. Vance,* Australian Nuclear Sci. and Tech. Organisation, Australia

Calcium titanate (CaTiO@sub 3@) constitutes about 20% of Synroc-C, a titanate-based ceramic designed for the immobilization of high level nuclear waste from Purex-type reprocessing. The chemical durability of calcium titanate in an aqueous environment is, therefore, an important issue. We have investigated the aqueous leachability of both single crystal and polycrystalline CaTiO@sub 3@ primarily using X-ray Photoelectron Spectroscopy (XPS). Static leaching tests were conducted in doubly deionized water at room temperature (RT), 90°C and 150°C for various periods of time. A reduction in the surface concentration of Ca (with respect to Ti) was observed after all leaching tests. The calcium leach rate of single crystal CaTiO@sub 3@ is found to be slightly lower than that of polycrystalline CaTiO@sub 3@ at all leaching temperatures. For both single crystal and polycrystalline samples, the calcium leach rate increases with increasing leaching temperature: the leach rate at 90°C is slightly higher than that at RT, while the leach rate at 150°C is substantially higher than that at 90°C. The effect of surface cation impurities, resulting from thermally induced segregation from the bulk, on the leaching behavior will be discussed. Other techniques employed in the study include Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) of CaTiO@sub 3@ surfaces before and after leaching tests, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Emission Spectroscopy (ICP-AES) of the leaching solutions. These results will also be shown.

2:20pm **AS-MoA2 XPS Investigations of the Chemistries of Soils***, **T.L. Barr**, E.E. Hoppe, S. Hardcastle,* University of Wisconsin, Milwaukee*; S. Seal,* University of Central Florida

The present study continues our XPS or ESCA investigations of silicate systems, particularly those in contact with biological materials. In the present case the investigations are extended to a detailed analysis of a wide variety of soil samples extracted from different locations around the world. The samples were selected from relatively pristine sites, pressed into wafers, and were examined without further modification. All of the materials were insulators and therefore analysis required extensive use of the electron flood gun. Careful XPS chemical shift arguments have bee achieved for many silicate minerals. These have been exploited in the present study along with the detailed XPS analysis of organo-funchtional groups rendered by Beemson and Briggs. As a result a fairly detailed simultaneous non-destructive description is provided of both the humus and silt components of these soil samples. Substantial variations in the composition are demonstrated and questions are raised about our classifications of fertility.

2:40pm **AS-MoA3 Problems in Surface Characterization of Oxides and Insulators***, **J. Cazaux**,* University of Reims, France **INVITED**

Most of the oxides are insulators in which charging effects and radiation damage effects often coexist when they are investigated with incident particles. In electron irradiated insulators, charge phenomena result from a competition between the secondary electron emission which contributes to a positive charging and the trapping of incident electrons which tends the specimen to be negatively charged. The initial charge distribution (and the electric field it induces) may be estimated but self regulation processes rapidly take place. The final state equilibrium is difficult to predict because it is a function of the nature and of the density of trapping centers that may pre-exist or that are induced by the irradiation and then negative charging may be observed at primary beam energies where a positive charging is expected from the total yield approach. Various specific mechanisms may be involved in the chemical change of irradiated insulators and most of them are electric field dependent. There is first the migration of the mobile species driven by the electric field build-up. There is also the dissociation of some electron/hole pairs generated by the transport of energetic (photo) electrons. The third cause of damage results from the ionization of core electrons followed by (intra or inter atomic) Auger transitions.Each transition finally leaves the excited atom with two electrons missing and the lack of conduction electrons (in insulators) prevents the initial charge of this atom or of its surroundings to be quickly restored. Halogen ions change sign while O@super-2@ ions become neutral and they may be desorbed into the vacuum when they are located close to the surface. Examples of microscopic (Electric image effects and Schottky barrier lowering) and macroscopic (electric field function) calculations will be given. These calculations are supported by a significant number of recent experimental results. Practical consequences to minimize these effects or to take benefit of them (nanolithography ; controlled surface modifications) will be suggested

3:20pm **AS-MoA5 ESCA Depth Profiling of Insulating Thin Film Structures***, **J.S. Hammond**, J.F. Moulder, D.J. Hook,* Physical Electronics, Inc.*; H.M. Dunlop,* Pechiney, Centre de Recherches de Voreppe, France

Recent advances in ion gun technology have allowed ESCA to surpass AES as the routine, quantitative depth profiling technique for thin film structures. To effectively utilize the potential of ESCA to provide chemical state information, accurate and reproducible charge neutralization for insulating and mixed insulator/conductor samples is required. Results will be presented comparing traditional, floating, and biased sample mounting techniques, to obtain an optimized process for reproducible, stable charge referencing. Depth profiling data will be presented from doped aluminum oxide thin films, architectural glass coatings, and silicon ONO thin films. Only by using the optimized charge neutralization approach can subtle acid-base chemistry in the aluminum oxide films and chemical states in the oxidized silicon films be elucidated.

3:40pm **AS-MoA6 Quantification of Nitrogen in Silicon Oxynitride Thin Films by XPS***, **J.R. Shallenberger**, D.A. Cole,* Evans East, US*; S.W. Novak,* Evans East

There has been a considerable effort in the past several years to incorporate nitrogen into oxides in order to improve the electrical properties of ultra-thin (2-10 nm) gate oxides. The nitrogen in-depth distribution, concentration and local bonding all affect the electrical properties of the dielectric layer. To date at least five different nitrogen environments have been reported in the XPS literature. All have the general formula: N(Si@sub x@O@sub y@H@sub z@), where x+y+z = 3 and x@<=@3, y@<=@1, z@<=@2. This paper focuses primarily on determining the concentration (to a detection limit of 1x10@super 13@ atoms/cm@super 2@) and local coordination of nitrogen in oxynitrides by XPS. Both Secondary Ion Mass Spectrometry and Nuclear Reaction Analysis are used as complementary tools for quantifying nitrogen; SIMS is also used to determine the in-depth N distribution.

4:00pm **AS-MoA7 XPS Characterization of Nitrogen Profile and Chemical States in Ultrathin Silicon Oxynitrides***, **J.P. Chang**, M.L. Green, V.M. Donnelly, R.L. Opila,* Bell Laboratories, Lucent Technologies

Continuous scaling of the gate dielectric thickness to @<=@ 40Å makes X-ray photoelectron spectroscopy (XPS) a viable technique for analyzing the composition and stoichiometry of a thin film and its interface with silicon, since the film thickness is comparable to the escape length of photoelectrons. Photoemission of various species is acquired at different take-off angles, and the maximum entropy method is employed to convert the angular dependent photoemission intensities to compositions as a function of depth.@footnote 1,2@ Angular resolved XPS (ARXPS) analysis permits nondestructive characterization of the nitrogen profile and interfacial compositions of ultrathin silicon oxynitride films grown by furnace oxidation. The incorporation of nitrogen in SiO@sub 2@ improves the electrical reliability and prevents boron penetration. In this work, nitric oxide (NO) and oxygen gases have been used to engineer the nitrogen profile in SiO@sub 2@ films. With furnace growth at 800°C, 1-4 at. % of nitrogen can be incorporated in the ultrathin (@<=@ 40Å) oxide films. Additional nitrogen can be incorporated by plasma ion nitridation. The nitrogen profile and nitrogen chemical bonding states are analyzed as a function of the depth to understand the mechanism of nitrogen incorporation during the NO/O@sub 2@ thermal growth process. Reoxidation of a thermal oxide grown in NO leads to a peak nitrogen concentration at the upper oxide interface, ideal to prevent boron penetration. Annealing of thermal oxide in NO leads to a peak concentration of nitrogen at the SiO@sub 2@/Si interface. Nitrogen bonds primarily to silicon at low total nitrogen content (1-4 at. %), but also bonds to oxygen at higher total nitrogen content. The improved reliability as determined by charge to breakdown (Q@sub bd@) measurement will be correlated with compositions and stoichiometry of the bulk film and its interfaces. The mechanism of nitrogen incorporation in NO or plasma ion nitridation will be discussed. @FootnoteText@ @footnote 1@G. C. Smith and A. K. Livesey, Surf. and Interface Anal. 19, 175 (1992). @footnote 2@N. Layadi, V. M. Donnelly, and J. T. C. Lee, J. Appl. Phys., 81, 6738 (1997).

4:20pm **AS-MoA8 Ultra Shallow Depth Profiling by ESCA and SIMS**, ***J.F. Moulder***, *S.R. Bryan,* Physical Electronics, Inc.

The next generation of semiconductor devices will contain shallow implants and other ultra thin structures. SIMS has been the traditional choice for analysis of these ultra thin layers. Because of the nature of these layers, significant challenges are being encountered in the interpretation and quantification of the SIMS data from them. A shallow 250eV boron implant for example, resides completely within the native oxide at the surface of a silicon wafer, complicating quantification by SIMS. ESCA depth profiles obtained with low energy ions (100-500V) and shallow photoelectron take-off angles provide quantitative chemical state information from these ultra thin film structures. ESCA and SIMS data will be presented from shallow boron implants and thin silicon oxy-nitride (ONO) structures. The data suggests that ESCA depth profiles may be very useful for calibrating and interpreting SIMS depth profiles of these ultra thin film structures.

4:40pm **AS-MoA9 Valence Band X-ray Photoelectron Spectroscopic Studies to Distinguish Between Oxidized Aluminum Species**, *J.A. Rotole,* ***P.M.A. Sherwood***, Kansas State University

The determination of the detailed chemical nature of oxidized aluminum species is an essential requirement for the study of many important practical aspects of aluminum metal. While thick oxidized films on aluminum metal can be easily characterized by X-ray powder diffraction when the films are crystalline, thin amorphous films are very difficult to characterize. In this paper a study of the valence band X-ray photoelectron spectrum of aluminum oxides, hydroxides and oxyhydroxides is reported using monochromatized aluminum K@alpha@ X-radiation. The valence band spectra obtained are shown to have significant differences for different oxidized aluminum species, and a spectrum that can be well understood by calculations. The calculated spectra are generated by cluster calculations using multiple scattered wave X@alpha@ calculations, together with spectra generated by band structure calculations. This study compliments earlier published studies from this research group using achromatic radiation, and the use of monochromatized X-radiation can be seen to allow a more conclusive distinction between the oxidized aluminum species.

5:00pm **AS-MoA10 Influence of Mg on the Oxide Formation on Al@footnote 1@**, ***D.R. Baer***, *C.F. Windisch, Jr., M.H. Engelhard, M.J. Danielson,* Pacific Northwest National Laboratory

In an effort to increase the strength of lightweight, non-heat treatable Al alloys, Mg is a common alloy addition. However, particularly due to changes in alloy structure and chemical distribution during processing and welding, these alloys can be susceptible to grain boundary dissolution, stress corrosion cracking or hydrogen induced cracking. In an effort to understand the influence of Mg segregation and second phase formation on the electrochemical behavior and corrosion behavior of Al, we have exposed freshly cleaned surfaces of Al, Mg-implanted Al and Al@sub 3@Mg@sub 2@ to a salt solution. These cleaned surfaces are moved to the solution through a transfer system that exposes the cleaned specimens only to vacuum or a nitrogen environment (with some water vapor) before immersion into the salt solution. The open circuit corrosion potential is measured for each sample. After a short exposure, the specimens are quickly rinsed with clean water, pumped to vacuum conditions and moved into a spectrometer for XPS analysis. Specimens are also analyzed by SEM imaging and AES in a different spectrometer. Measurements show that Mg influences the corrosion potential of the material and changes the nature of the film. When Mg is present in the alloy at levels of approximately 4 at%, the oxides that form are no longer smooth but rumpled. The outer oxide that formed during solution exposure contains no observable Mg, but regions below this alumina layer are rich in oxidized Mg. This film is compared to those that form on pure Al and the beta phase Al@sub 3@Mg@sub 2@. @FootnoteText@ @footnote 1@This research was conducted at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) with funding provided by the U.S. Department of Energy, Office of Basic Energy Sciences. The EMSL is a new DOE scientific user facility located at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. PNNL is operated by Battelle for the Department of Energy.

Biomaterial Interfaces Group

Room 326 - Session BI-MoA

Cell Solid-Surface Interactions

Moderator: D.E. Leckband, University of Illinois, Urbana-Champaign

2:00pm **BI-MoA1 Cell Solid-Surface Interactions Under Flow**, ***L.V. McIntire***, Rice University **INVITED**

Understanding the molecular mechanisms of cell-solid surface interactions is crucial for developing specific therapeutic strategies to control or modulate processes such as thrombosis, inflammation and cancer metastasis. In the vasculature or in blood contacting artificial devices these interactions occur under dynamic flow conditions. Primary adhesion or tethering of the flowing cells requires very special properties of the cell surface receptor and its ligand on the solid structure because of the very short contact times available for bond formation and the forces on those bonds due to fluid drag. Leukocytes utilize primarily members of the selectin family of receptors and their carbohydrate ligands for this first step - often resulting in a rolling interaction. For lymphocytes and monocytes, the integrin @alpha@@sub 2@ @beta@@sub 1@ is also capable of mediating primary adhesion under some flow conditions via its ligand vascular cell adhesion molecule (VCAM). Platelets utilize a receptor complex GPIb-IX-V for this tethering process. Secondary or firm adhesion is mediated by members of the integrin family on the cell surface, often after activation, in concert with their ligands on the solid. For leukocytes these are members of the @beta@@sub 2@ integrin family, while for platelets they are members of the the @beta@@sub 3@ integrin family. Methods for dissecting the specific molecular pathways involved for each step in the adhesion process for several cell types are given and the current state of our knowledge and potential applications are discussed.

2:40pm **BI-MoA3 Leukocyte Adhesion on Self-Assembled Thiol Monolayers under Flow**, ***V.A. Tegoulia***, *S.L. Cooper,* University of Delaware

The effect of specific chemical functionalities on the attachment of neutrophils, one of the cells responsible for host response to biomaterials, was investigated using self-assembled monolayers (SAMs) containing different terminal groups. A surface modification was used to incorporate a zwitterionic phosphorylcholine group on one of the surfaces. Adhesion was studied on surfaces preadsorbed with fibrinogen or albumin, under well defined flow conditions using a radial flow chamber and automated videomicroscopy. The general formula for the thiols used was HS-(CH@sub 2@)@sub 10@-X, where X=CH@sub 3@, CH@sub 2@OH, COOH, COOCH@sub 3@ and CH@sub 2@(OCH@sub 2@CH@sub2@)@sub 3@OH (EG@sub 3@). The phosphorylcholinated monolayer (PC, X=CH@sub 2@PO@sub 4@CH@sub 2@CH@sub 2@N(CH@sub 3@)@sub 3@ was prepared by phosphorylation of the hydroxyl terminated SAM. Contact angle measurements, ellipsometry and X-ray photoelectron spectroscopy (XPS) were used to characterize the SAMs. The amount of adsorbed protein on the surfaces was quantified using radiolabelled fibrinogen and albumin. Neutrophils were isolated from fresh human whole blood. Contact angle measurements, ellipsometry and XPS confirmed the presence of the SAMs. Phosphorous and nitrogen were detected on the phosphonated SAM. Neutrophil attachment was found to be higher at the low shear rates. Cell adhesion was increased on the hydrophobic CH@sub 3@ and the anionic COOH terminated surface. Cells were more activated on the COOH surface. The presence of the EG@sub 3@ and the PC moieties led to very low cell adhesion.

3:00pm **BI-MoA4 Smart Polymers for Bacterial Release**, ***L.K. Ista***, *V.H. Pérez-Luna, G.P. López,* University of New Mexico

Poly (N-isopropylacrylamide) (PNIPAAM) was used as a model system to demonstrate the utility of environmentally responsive, or "smart", polymers as agents for the release of bacterial biofilms. PNIPAAM was grafted onto the surface of polystyrene coupons by plasma-initiated in situ polymerization. The resultant grafted polymer exhibited the characteristic lower critical solubility temperature (LCST) of 32 @super o@C, as demonstrated by a change in water contact angle and was characterized by x-ray photoelectron spectroscopy. The surfaces were challenged with bacterial strains of marine (Halomonas marina) and medical (Staphylococcus epidermidis) importance as well as with natural sea water. Under experimental conditions, cells attached at temperatures above the LCST of PNIPAAM were released upon transfer to flow conditions below the LCST. The total release observed was greater than 90% of the initially attached cells. In addition, fouling and release could be repeated on the same sample several times, with a small loss in release efficiency upon each repetition.

3:20pm **BI-MoA5 Characterization of Biorecognition Surfaces*, B.D. Ratner,*** University of Washington **INVITED**

Biomaterials can now be surface-engineered to drive and control specific bioreactions in vivo and in vitro. Three examples will be presented: (1) surface-immobilized amino acids, peptides and proteins; (2) templates for protein recognition; and (3) surfaces that resist the deposition of biological materials and therefore act in a "stealth" fashion. These surfaces bring new challenges to surface analysis to deal with the molecular complexity, molecular orientation and 2D and 3D organization found on recognition surfaces. Static TOF-SIMS, XPS, IRAS, and AFM are allowing us to glean new information on such surfaces. This overview will highlight progress made in analysis of complex recognition surfaces and demonstrate relationships between surface structure and biological response.

4:00pm **BI-MoA7 Neuronal Networks as the Basis for Computational Systems*, J.J. Hickman,*** *M.S. Ravenscroft,* The George Washington University

We are using patterned Self-Assembled Monolayers (SAMs) to control the intrinsic and geometric properties of cell culture growth surfaces to create in vitro circuits of mammalian neurons and their processes. The ability to control the surface composition as well as other variables, such as growth media and cell preparation, all play important roles in neuronal pattern viability and cell fate. The use of serum-free medium makes examination of the culture substratum possible by surface analysis as the serum-free medium contains very small amounts of protein, thus the protein on the surface arises primarily from the cells and can be related to their morphology. The surfaces have been characterized by X-ray Photoelectron Spectroscopy (XPS) and imaging XPS using a FISONS 220i spectrometer and we have related the intrinsic properties of the SAM surfaces and the deposited protein layer to the neuronal cellular development. The electrophysiological signals produced by the neurons in response to artificial and spontaneous electrical stimuli has been recorded by patch-clamp electrophysiology. We are using these circuits to obtain a more fundamental understanding of neuronal circuit development as well as to develop new concepts of hybrid neuroelectric devices for biological computation applications. The continuing development of this technology by our group and other groups will be discussed, as well as the application of this technology for (a) obtaining an improved understanding of neuronal synaptic development, (b) formation of neuronal circuits, and (c) biosensor fabrication. The theory behind the creation of simple hybrid devices will also be explored.

4:20pm **BI-MoA8 Growth of Central Nervous System Cells on Microfabricated Pillars*, A.M. Perez,*** *S.W. Turner,* Cornell University*; N. Dowell,* New York State Department of Health*; L. Kam,* Rensselaer Polytechnic Institute*; J.N. Turner, W. Shain,* New York State Department of Health*; R.C. Davis, M. Isaacson, H.G. Craighead,* Cornell University

We are investigating the influence of microfabricated micrometer-size surface features on the attachment and growth of mammalian central nervous system cells. Columnar surface structures have been fabricated using photolithography and reactive ion etching to create arrays with varying sizes and separations. Features 1 µm in height and 1.0 - 5.0 µm in diameter separated by 0.5 - 4.0 µm have been patterened on silicon wafers. The patterned wafers possess 50 µm wide regions of pillars surrounded by smooth silicon surfaces. Several pillared surfaces were also chemically modified with biological polymers including polylysine and conjugated laminin to study the behavior of cells on chemically treated topography. Cells used for these studies include LRM55 astroglial cells, cortical astrocytes prepared from primary cultures, and hippocampal neurons. Cell growth was characterized by scanning electron and fluorescence microscopy while focal contacts and cytoskeletal elements were determined using techniques of vinculin immunocytochemistry and actin cytochemistry, respectively. Astroglial cells preferentially attached to the pillars as opposed to the smooth surrounding surfaces while neurons attached randomly. Cell densities both on and off the pillars have been measured using optical microscopy. The cell densities and morphologies varied according to the geometric features of the columnar surfaces.

4:40pm **BI-MoA9 Directed Neuron Attachment and Growth by Micrometer-Scale Chemical Patterning of Glass Substrates*, C.D. James,*** *R.C. Davis,* Cornell University*; L. Kam,* Rensselaer Polytechnic Institute*; H.G. Craighead, M. Isaacson,* Cornell University*; J.N. Turner, W. Shain,* New York State Department of Health, University of Albany*; G. Banker, G. Withers,* Oregon Health Sciences University

Directed neuron attachment and growth is a necessary technology for long-term, in vitro studies of synaptically interactive neurons. Research has shown that chemical cues can stimulate cell attachment and neurite outgrowth in neurons when cultured on chemically-modified bioactive surfaces. Specifically, the synthetic polypeptide polylysine has been shown to induce cell attachment, and the basement membrane protein laminin has been used to initiate neuronal process outgrowth as well as cell attachment. In this paper, we attempt to produce a method for using chemical cues to control the organization of neurons into defined networks in order to facilitate long-term studies of synaptic function and inter/intra-neuronal signal processing. We demonstrate a technique for chemically patterning glass substrates with polylysine and laminin using microcontact printing, an emerging tool for micrometer-scale chemical patterning of surfaces. Further, we show that these chemically patterned surfaces are biologically active, and that cell attachment and neurite outgrowth are stimulated in culture.

5:00pm **BI-MoA10 Characterization of Cellular Interfacial Forces with AFM*, T.J. Boland,*** Pennsylvania State University*; Y.F. Dufrene,* Universite Catholique de Louvain, Belgium*; W.R. Barger,* Naval Research Laboratory*; D.L. Allara,* Pennsylvania State University*; G.U. Lee,* Naval Research Laboratory

Biomaterial design depends on understanding the molecular basis of material-body interactions. Much is known about the molecules and cells involved in the body's response to foreign materials but it has been difficult to characterize the physical nature of their interaction. To this end, the interfacial properties of model films have been measured at the nanometer scale with atomic force microscopy (AFM). In specific, as a model for cell surfaces, mixed, uncharged phospholipid/glycolipid monolayers have been deposited on octadecyltrichlorosilane monolayers (OTS) using Langmuir-Blodgett (LB) deposition. The lipid films phase segregate allowing us to measure the relative surface properties of the different phases. Spectroscopic ellipsometry was used to characterize optical properties and thickness of each pure layer and the mixed bilayers in air and in water. As a model for a polymeric surface, AFM probes were functionalized with SH-(CH@sub 2@)@sub 15@-R, where R=CH@sub 3@, CH@sub 2@OH, COOH groups. The height, friction, mechanical properties and surface forces of the lipid phases were measured with these probes. The force curves are purely repulsion due to a dominant short-range force indicative of steric/ hydration interaction and the range of this force is dependent on the head group of the lipid. At high loading forces the probe is observed to snap into contact with the surface which we believe is a measure of the mechanical stability of the film. These measurements demonstrate that AFM can be used to directly characterize molecular interactions between model cell surfaces and model organic surfaces.

Electronic Materials and Processing Division
Room 316 - Session EM-MoA

Future Issues in Electronics and Photonics

Moderator: H.A. Atwater, Caltech

2:00pm **EM-MoA1 Pathways Toward Chemically Assembled Electronic Nanocomputers*, J.R. Heath,*** University of California, Los Angeles*; R.S. Williams, P.J. Kuekes,* Hewlett Packard Corporation **INVITED**

Many ideas for alternatives to CMOS-based VLSI manufacturing have been proposed as new paradigms for computer fabrication. These ideas include quantum computing, molecular computing, and chemically-assembled electronic nanocomputers. Of these three, only electronic nanocomputers can potentially build upon the foundation of CMOS architectures, and, as such, they hold the potential for relatively near-term realization. However, even the simplest of computational tasks have yet to be demonstrated for electronic nanocomputers. From a chemist's point of view, there are two major differences between anything fabricated chemically, and a current microchip. The current microchip is complex and is the result of manufacturing perfection, while anything that is chemically synthesized is likely to be ordered (crystalline) and imperfect. Thus, in many ways, the chemist's task is to design a system from which perfect complexity can be extracted from imperfect order. In this presentation, I will discuss an ongoing HP/UCLA project in which we are attempting to build an electronic nanocomputer. Architectural considerations will be stressed, and experimental progress towards building the nanocomputer will be discussed.

2:40pm **EM-MoA3 Room Temperature Silicon Single Electron Memory and Switch and Nanoimprint Lithography***, S.Y. Chou,* Princeton University **INVITED**

The paper presents two recent progresses in developing single electron devices that can operate at room temperature and one breakthrough in nanopatterning. The first is a single-electron MOS memory in crystalline silicon, that has a channel width (~10 nm) and a nanoscale polysilicon dot (~7 nm by 7 nm) as the floating gate embedded between the channel and a control gate.@footnote 1@ It is observed that storing one electron on the floating gate can significantly screen the channel from the potential on the control gate, leading to a threshold voltage shift. The second progress is a silicon single electron switch, that has a small silicon dot (~12 nm in diameter) inside the channel and separated from the source and drain by two thin tunneling barriers.@footnote 2@ As a gate modulates the electron population inside the dot, the drain current oscillates at room temperature. Each oscillation is attributed to electron tunneling through a discrete single electron level inside the dot. Finally, nanoimprint lithography is a new lithographic mehtod that has achieved sub-10 nm feature size with high throughput and low cost, paving the road for manufacturing silicon single electron devices.@footnote 3@ @FootnoteText@ @footnote 1@L. Guo, E. Leobandung and S.Y. Chou, Science, vol. 275, 649-651, 31 January, 1997. @footnote 2@L. Zhuang, L. Guo, and S.Y. Chou, IEDM, Dec. 8-10, 1997. @footnote 3@S.Y. Chou, P.R. Krauss, W. Zhang, L. Guo and L. Zhuang, J. Vac. Sci. Technol. B 15(6), 2897 (1997).

3:20pm **EM-MoA5 Terabit Integration: New Ideas, Need for New Materials***, **K.K. Likharev**,* State University of New York, Stony Brook**INVITED**

The electronics industry predicts that the current progress in scaling down silicon MOSFETs will lead eventually to dynamic random-access memories with a density of the order of 5 Gbits/cm@super 2@ and integration scale up to 64 Gbits. Further progress in this direction is, however, in doubt, mostly because of problems with the storage capacitance scaling. The situation may be changed by the recently proposed@footnote 1@ "crested" tunnel barriers, with an electrostatic potential maximum in the middle. In these barriers, applied voltage increases the barrier transparency much more quickly. Calculations have shown that crested barriers may combine long retention time (say, 10 years) with fast write/erase time (below 10 nanoseconds). This radical improvement may be used, first of all, in nonvolatile random-access memories ("NOVORAM"). Using dual-gate, nanoscale MOSFETs with ballistic electron transfer along undoped channels,@footnote 2@ NOVORAM cells are scaleable to a minimum feature size about 6 nm, corresponding to a memory density of 100 Gbits/cm@super 2@, and apparently integration scale up to 16 Tbits. Beyond this frontier, NOVORAM may be challenged by SET/FET hybrid memories@footnote 3@ with dynamic read-out using single-electron transistors (SETs) in background-charge-insensitive mode. Analysis shows that these memories may be scaled to the 2 nm minimum feature size, enabling integration up to 64 Tbits. Moreover, there is an opportunity to combine crested barriers and SET/FET hybrids in a system for electrostatic data storage with density beyond 100 Gbits per square inch. In my presentation at the meeting, I will describe these encouraging prospects in detail, and also discuss the requirements to materials for their practical implementation. @FootnoteText@ @footnote 1@K.K. Likharev, in: GOMAC'98 Technical Paper Digest, p. 35. @footnote 2@F. Pikus and K. Likharev, Appl. Phys. Lett. 71, 3661 (1997). @footnote 3@K.K. Likharev and A.N. Korotkov, in: Proc. of 1995 ISDRS, p. 355

4:40pm **EM-MoA9 Oxide-Confined Vertical Cavity Surface Emitting Lasers using Quantum Well and Quantum Dot Active Regions***, **D. Huffaker**,* University of Texas, Austin **INVITED**

There is increasing interest in low power optoelectronics including ultralow threshold semiconductor lasers for use in optical interconnect applications. The oxide-confined vertical cavity surface emitting laser (VCSEL) is a potential candidate for such applications because of the promising device results which have been demonstrated to date. At the University of Texas we have focused on minimizing optical loss from the lasing mode by lateral index confinement and high contrast mirrors. This talk will overview our device structures, the selective oxidation processing and low threshold quantum well VCSEL results. The low loss VCSL cavity may be especially important in realizing 1.3µm VCSELs grown on a GaAs substrate using an InAs/GaAs QD active region as the QDs have limited gain at this long wavelength. To date, we have achieved a 1.15µm GaAs-based VCSEL using the InAs/GaAs QDs. We will also discuss very recent data characterizing ultranarrow electroluminescence spectra from a large ensemble of quantum dots at very low current densities.

The Science of Micro-Electro-Mechanical Systems Topical Conference
Room 324/325 - Session MM+VT-MoA
Vacuum MEMS and Microanalysis

Moderator: C.C. Wong, Sandia National Laboratories

2:00pm **MM+VT-MoA1 Polysilicon Sealed Vacuum Cavities for MEMS***, **J.D. Zook**, W.R. Herb,* Honeywell*; Y.C. Ahn, H. Guckel,* University of Wisconsin **INVITED**

Sealed vacuum cavities are highly useful in silicon-based micro-electrical-mechanical structures (MEMS). They serve as the reference chambers for absolute pressure sensors and provide enclosures for high-Q mechanical resonators. A process for fabricating sealed vacuum cavities in polysilicon was developed and described by Burns and Guckel in 1988.@footnote1@ The cavities are produced by the sacrificial etching of SiO@sub 2@. The vacuum is generated by the out-diffusion of hydrogen following the polysilicon sealing step. As an additional precaution the devices are coated with silicon nitride. The process was first applied to the fabrication of piezoresistive pressure transducers with a polysilicon diaphragm and a vacuum cavity used as a pressure reference. In 1989 a multi-level polysilicon process was used to fabricate resonant microbeams and to demonstrate that high mechanical Q values require a hard vacuum inside the cavity.@footnote 2@ The micromachined polysilicon resonant microbeams are sensitive strain transducers that provide the basis for temperature, pressure, strain, acceleration and vibration sensors. The polysilicon microbeams are fabricated monolithically on single crystal silicon microstructures, are sealed high vacuum shell enclosures and are characterized by high mechanical Q, typically between 20,000 and 100,000, with recent values as high as 220,000. Two devices have been running continuously for 7 years with no observable change in Q, i.e., no change in the vacuum level. The most recent use of the vacuum encapsulation process has been for fiber optic sensors which combine the advantages of silicon microfabrication with those of optical fiber communication.@footnote 3@ The microbeams are optically excited into resonance by either an optothermal mechanism or a photovoltaic mechanism. They can be driven by modulated light or can be self-resonant. The vibration of the beam modulates the light reflected back into the fiber, which is then detected using a photodetector. Fiber optic sensors also have advantages for aerospace because of their light weight and EMI immunity. A network of 16 optically resonant microbeam temperature sensors driven and read by the same laser was recently demonstrated. Optically driven self-resonant microbeams have been operating continuously for 4 years without measureable change in Q. The most recent demonstration of the vacuum integrity of the polysilicon cavities has been the high temperature operation of the microbeams. Operation up to 510 C for several hours resulted in no loss of vacuum as evidenced by the Q of the resonators after they were returned to room temperature. Thus polysilicon-based vacuum-encapsulated devices are potentially suitable for fiber-optic-based sensors that withstand harsh environments, including high temperature. The value of Q is determined not only by residual gas in the cavity but also by the end losses and by electrical losses induced by the vibrating polysilicon capacitor composed of the microbeam and the bias electrode. By measuring Q as a function of dc bias, the electrical contributions to Q can be subtracted, providing an upper limit on the partial pressure of residual gas in the vacuum cavity. @FootnoteText@ @footnote 1@D. W. Burns, Ph. D. Thesis, Dept. Mat. Sci., UW, Madison, WI (1988). @footnote 2@J. J. Sniegowski, Ph. D. Thesis, Dept. Nuc. Eng. and Eng. Phys., UW, Madiso n,WI (1989). @footnote 3@J. D. Zook, D. W. Burns, W. R. Herb, H. Guckel, J. W. Kang and Y. C. Ahn, S ensors and Actuators A52 (1996) pp. 92-98.

2:40pm **MM+VT-MoA3 Wafer Level Vacuum Packaging for MEMS***, **R.W. Gooch**, T.R. Schimert, W.R. McCardel, B.A. Ritchey,* Raytheon Systems Co.

Many types of MEMS devices require a vacuum environment for operation. Some such as uncooled bolometer IR detectors and imagers, and resonant reed devices require 10 mTorr or lower for optimal performance. Packaging cost associated with traditional materials, packages, and processes needed to achieve the vacuum requirements remains the primary barrier to high volume products. Wafer level vacuum packaging transfers the packaging operation into the wafer fab. It is a product neutral enabling technology for commercialization of MEMS for home, industry, automotive, and environmental monitoring applications. Proof of principle has been demonstrated with bolometer IR detectors on 1- inch piece parts sawed from Si wafers. The lid part contained an etched cavity and was joined to the device part with a solder seal. Less than 10mTorr pressure was measured in a cell volume of 4 cubic mm. A 120x160 IR bolometer array and a resonant reed MEMS device are being designed to be packaged in wafer form using this process. Progress toward these goals will be described. This work is supported in part by DARPA/ ETO, Elias Towe program manager and Al Pisano MEMS program manager.

3:00pm **MM+VT-MoA4 A Dual Sensor Vacuum Gauge: Advanced Micromachined Thin Film Pirani Sensor Combined with a Piezoresistive Sensor***, **D.H. Baker**, R.A. Outlaw,* Teledyne Hastings Instruments*; D. Rosenblatt,* Rosenblatt Associates

A new dual sensor vacuum gauge which employs an advanced thin film micromachined Pirani sensor combined with a B ion implanted Si piezoresistive sensor has been developed. The two sensors are mounted on a single header and welded into a small volume (2 cc), 316 stainless steel envelope which can withstand an over pressure of 1000 psi. The instrument is UHV compatible and can detect pressure from 1000 Torr down to less than 1x10@super -5@ Torr. It is shock resistant, altitude insensitive, and bakeable to 250°C. The gas composition insensitive piezoresistive sensor permits cross over to the gas composition sensitive Pirani, thus establishing the calibration of the Pirani in the gas environment at the crossover pressure. Design criteria leading to the present sensor configurations are discussed. In particular, material selection and heat transfer solutions for the fully contiguous membrane and the various suspended geometric designs are presented. Membrane stress levels characteristic of each design are also discussed. Finally, thermal and electronic noise limitations are considered to establish the ultimate sensitivity of the instrument.

4:00pm **MM+VT-MoA7 The Knudsen Compressor as a Micro and Macroscale Vacuum Pump Without Moving Parts or Fluids***, **S.E. Vargo**, E.P. Muntz, G.R. Shiflett,* University of Southern California*; W.C. Tang,* Jet Propulsion Laboratory

Microelectromechanical systems (MEMS) are rapidly becoming integral components of space missions and are finding an increasing utilization in commercial applications. Several current lander, probe and rover missions under study at NASAs Jet Propulsion Laboratory (JPL) focus on utilizing MEMS based instruments for science data gathering. These small instruments and NASAs new commitment to faster, better, cheaper missions has brought about the need for novel approaches to satisfying mission requirements. For example, a miniaturized mass spectrometer is currently under development at JPL that is designed to provide in-situ gas composition analyses of planetary atmospheres. This device utilizes a micromachined quadrupole array to provide comparable performance to a commercial large-scale unit but with much less mass, power and volume. However, the miniaturized mass spectrometer system lacks a vacuum pump that can meet future mission requirements. One attractive candidate for a vacuum pump is the Knudsen Compressor that is under collaborative development at the University of Southern California (USC) and JPL. The Knudsen Compressor is a vacuum pump that operates on the rarefied gas dynamic phenomenon of thermal transpiration, which is the development of a pressure difference between two volumes of gas via a temperature difference between the ends of small channels joining the volumes. A laboratory-scale Knudsen Compressor has previously been tested at USC@footnote 1@ with its success leading to the design and fabrication of a micromechanical version. This device has two overwhelmingly attractive features over miniaturized or mesoscale vacuum pumps - no moving parts and no fluids. The Knudsen Compressor is applicable in MEMS instruments as well as to larger, more standard pumping applications.@footnote 2@ The paper will include calculations of pumping speed, power usage, size and ultimate pressure for several applications of the Knudsen Compressor. @FootnoteText@ @footnote 1@Vargo, S.E. and Muntz, E.P. (1997): An Evaluation of a Multiple-Stage Micromechanical Knudsen Compressor and Vacuum Pump. In: Rarefied Gas Dynamics, Proceedings of the 20th International Symposium on Rarefied Gas Dynamics, Peking University Press, p995-1000, Beijing. @footnote 2@Pham-Van-Diep, G., Keeley, P., Muntz, E.P., Weaver, D.P. (1995): A Micromechanical Knudsen Compressor. In: J. Harvey and G. Lord Ed. Rarefied Gas Dynamics, Oxford University Press, 715-721.

4:20pm **MM+VT-MoA8 Novel Microvalve with Low Leakage***, **M. Hirano**, K. Yanagisawa,* Nippon Telegraph and Telephone Corporation, Japan*; S. Nakano,* NTT Advanced Technologies Corporation, Japan*; M. Shoji,* Nippon Telegraph and Telephone Corporation, Japan

Microvalve, being capable of precisely controlling fluid flow, is necessary in various industrial fields such as chemical analysis. This paper reports the novel microvalve with very low leakage, which was fabricated by silicon micromachining techniques. The valve is a micromachine constructed on a silicon substrate chip, and it uses a valve cap supported by a suspension spring and a valve seat with a 50-µmm-diameter bore to control fluid flow. Normally closed valve is obtained by applying compressive stress to the suspension spring @footnote 1@. Piezoelectric actuator bends the suspension spring, resulting in opening and closing the valve. The silicon substrate chip, on which the microvalve was fabricated, was suitably mounted on the specially designed holder, to which inlet and outlet lines are connected. The leak or flow conductance of the microvalve was precisely determined by measuring the pressure change in the gas flow system designed for precisely determining the leak and flow rate @footnote 2@. The measurements show that the valve has a very low leak rate of 5.8 x 10@super -10@ Pam@super 3@/s. This reduced leakage was due to tight contact between the cap and seat, which was obtained by nanometer-scale flat valve surfaces and self-alignment of the cap and seat-bore based on the fabrication techniques we have developed @footnote 1@. It is concluded that the flat surfaces result from the flat substrate of the sacrificial SiO@sub 2@ film deposited by RF magnetron sputtering, and from the homogeneous dry-etching at our amorphous surfaces by ion-beam milling. @FootnoteText@ @footnote 1@ K. Yanagisawa, H. Kuwano, and A. Tago, Microsystem Technologies 2. 22 (1995). @footnote 2@ M. Hirano, K. Yanagisawa, H. Kuwano, and S. Nakano, Trans. IEE of Japan 117-E, 622 (1997).

Manufacturing Science and Technology Group
Room 317 - Session MS-MoA

Contamination Free Manufacturing

Moderator: A.C. Diebold, Sematech

2:00pm **MS-MoA1 Green House Effect and LSI Process Technology***, **K. Okumura**, T. Ohiwa,* Toshiba Corporation, Japan **INVITED**

While LSI devices contribute to saving energy, their fabrication consumes large amounts of electric power and PFC gases. This paper will discuss the new LSI process technology to alleviate such negative aspects. Among the process tools, especially the furnaces and dry pumps consume a large quantity of electric power. The fast temperature processor (FTP), which realizes ramp temperature up and down at high speed, succeeds in maintaining temperature at 300 - 400 °C and ramping up to 800 - 900 °C only when processing. This leads to a 30 - 50 % power reduction compared to the conventional furnace which constantly maintains its temperature at 800 - 900 °C. Dry pumps with an inverter controlled DC motor drive consume half as much power as conventional induction motor drive systems. Furthermore, quick response of the DC motor without over-current makes it possible to turn it on only when necessary and off during machine idling, which leads to 15 - 80 % less power. In RIE and CVD machines, as much as 10 - 15 SLM of purge N@sub 2@ gas is used in order to prevent clogging of dry pumps by by-products. Pure N@sub 2@ gas generation also requires a vast amount of electric power. Therefore, reduction of N@sub 2@ gas is another effective approach. A dual in-line cold trap was newly developed for this. It consists of two traps. One traps by-products before the dry pump, and the other can be flashed meanwhile. Improving the efficiency of gas usage leads to reduction of PFC consumption. A new gas circulation system was developed, which pumps the exhausted gas still containing usable process gas into the RIE reaction chamber to be reused. Because many kinds of PFC gases after plasma processing eventually change to the most stable CF@sub 4@ gas, recycling of CF@sub 4@ gas is a key point. We have developed a dual trap system which operates at liquid N@sub 2@ temperature. It is capable of trapping CF@sub 4@ gas exhausted from an RIE reaction chamber. This system has the possibility of distillation of PFC gas by the appropriate control of regeneration temperature.

2:40pm **MS-MoA3 Ultra-Low-Temperature Growth of High-Integrity Silicon Oxide and Nitride Films by High-Density Plasma with Low Bombardment Energy***, **K. Sekine**, R. Kaihara, Y. Saito, M. Hirayama, T. Ohmi,* Tohoku University, Japan

As semiconductor devices are scaled down to smaller dimensions, conventional processing temperature such as 900°C will be incompatible with the desired device structure. For example, conventional high-temperature gate insulator formation process changes the impurity profile previously formed in the substrate. Moreover, it is necessary to introduce metal substrate SOI device for future high speed (>1GHz) ULSI device. To realize the metal substrate SOI device, all of manufacturing processes have to be done at below 550°C. Thus gate insulator also must be formed below

550°C. Therefore lowering growth temperature of high-integrity gate insulator is a key for future metal substrate SOI device fabrication. High integrity ultra-thin silicon oxide and nitride films can be obtained at 430°C by direct oxidation and nitridation of silicon surface. Such a low temperature oxidation and nitridation could be realized by employing newly developed high-densit!y plasma system with low ion bombardment energy less than 7eV and high plasma density above 10@super12@cm@super-3@. The electrical properties of these films are nearly the same level as those of thermally grown films. This technology becomes very promising for fabricating feature metal substrate SOI devices and silicon nitride gate MISFET.

3:00pm **MS-MoA4 Low-Temperature Large-Grain As-Deposited Poly-Si Formation by Microwave-Excited PECVD Using SiH@sub 4@/Xe**, ***W. Shindo**, S. Sakai, T. Ohmi,* Tohoku University, Japan

We have achieved as-deposited large-grain polycrystalline silicon at a temperature of 300°C by plasma enhanced CVD using SiH@sub 4@/Xe. The grain size evaluated by X-ray diffraction is 25nm, which is believed to be the largest grain size among 100nm-thick as-deposited poly-Si films fabricated by various methods at low temperature. High-density (>10@super 12@cm@super -3@) plasma having very low electron temperature (approximately 1eV) excited by microwave irradiation was used for the film growth. Plasma density and electron temperature dominate ion flux density and ion kinetic energy incident on the substrate surface, respectively. Thus, high-flux and low-energy ion bombardment (

3:20pm **MS-MoA5 Balanced Electron Drift Magnerton Plasma Source for Uniform SiO@sub 2@ Etching**, ***R. Kaihara**, T. Ohmi,* Tohoku University, Japan*; H. Komeda,* Sharp Corp., Japan*; Y. Hirayama,* Tokyo Electron Yamanashi Ltd., Japan*; M. Hirayama,* Tohoku University, Japan

Magnetron etcher using dipole ring magnet has demonstrated its high selectivity with lower micro-loading effects. When parallel magnetic field is applied by dipole ring magnet, the uniformity V@sub dc@ and ion flux is degraded by ExB drift of secondary electrons on the wafer. The inherent non-uniformity causes crucial problems such a charge up damage and etching non-uniformity. In order to improve non-uniformity of V@sub DC@, gradient magnetic field has been employed in a magnetron etcher using dipole ring magnet. Almost uniform V@sub DC@ profile can be achieved by optimizing the magnetic field profile. Even though optimizing magnetic field profile is effective, there is some problems such as restricted process window and non-uniformity of ion flux. On the other hand, we applied RF(100MHz) to upper annular electrode in order to improve non-uniformity of V@sub DC@ and ion flux. The electron drifts can be balanced between the upper annular electrode and the lower electrode. Uniformity of V@sub DC@ (±4V) and ion flux (±3%) are simultaneously obtained by the balanced electron drift (BED) magnetron etcher. Excellent etching profile of 0.15µm contact hole is also obtained uniformly on 200mm wafer.

3:40pm **MS-MoA6 Influence of Wafer Back Surface Finish on Dry Etching Characteristics**, ***S. Muramatsu**, K. Ando, H. Nanbu, H. Miyamoto, T. Kitano,* NEC Corporation, Japan

Process tolerance and controllability have become more severe with the scaling down and integration of devices. Wafer back surface finish is a factor affecting the process conditions such as dry etching and rapid thermal annealing. In this study, the correlation between back surface roughness and dry etching characteristics was investigated. The back surface roughness was changed from Ra=0.41 nm to 50.1 nm by final back surface treatments (mechanochemical polishing or chemical etching). Contact-hole etching with CHF@sub 3@ gas was performed for interlayer CVD oxide deposited on the front surface of wafers. The etching rate for a smooth back surface (0.41 nm) was increased by 1.1 times over that for a rough back surface (50.1 nm). During contact-hole etching, the wafer temperature of the smooth back surface was10°C lower than that for the rough back surface. This is due to the difference in electrostatic chucking (Ra=80-120nm) force during contact-hole etching. When the smooth back surface wafer was used, the adhesion area between the dry-etching stage and the wafer back surface increased because the back surface roughness was small. Consequently, the wafer can be cooled down sufficiently and the etching rate dominated by gas absorption was increased. As well as the etching rate, the position where residual gas was deposited inside the contact hole was governed by the degree of the wafer back surface finish. These experimental results indicate that the roughness of the wafer back surface should be well controlled for fabricating advanced devices.

4:00pm **MS-MoA7 Precise Control of Gas Ratio in Process Chamber**, ***Y. Shirai**, O. Nakamura,* Tohoku University, Japan*; N. Ikeda, R. Dohi,* Fujikin Inc., Japan*; T. Ohmi,* Tohoku University, Japan

In 300mm wafer generation, many kinds of single wafer processing will be necessary to establish higher process uniformity on a wafer. For achieving low cost production, it is necessary high-rate processing such as wafer/min including load-unload time. Process gas distribution system is one of the most critical issues for process uniformity and high-rate processing. Especially, high quality and uniformity of film formation process strongly depends on initial gas distribution in a process chamber. We have developed advanced integrated gas system and studied process gas ratio in process chamber using FT-IR method. We have prepared two types of integrated gas distribution system. One is the conventional system consists of MFC and air operate valve, the other is the advanced system consists of new pressure flow controller with electric valve. This new pressure flow controller built on the principle that the flow rate is directly proportional to the upstream pressure if the upstream pressure is more than two times of downstream pressure. We have introduced three kinds of process gases into a process chamber. The conventional system shows over shoot phenomena. The process gas concentration increase more than two times of the steady state. In addition, it takes more than 20 seconds to be steady state of gas ratio and chamber pressure after the valve operation. On the other hand, the advanced system does not show over shoot phenomena. The steady state of gas ratio and chamber pressure can be obtained within 2 seconds after the valve operation.

4:20pm **MS-MoA8 Clean Aluminum Oxide Formation on Surface of Aluminum Cylinder in an Ultraclean Gas Sampling System**, ***Y. Ishihara**, N. Itou, T. Kimijima, T. Hirano,* NIPPON SANSO Corporation, Japan

Because it is difficult to obtain enough space for a gas-analysis system in semiconductor manufacturing lines, gas purity is usually confirmed by an ex-situ analysis of gas sampled inside the gas-sampling cylinder (sampler). In order to analyze a trace impurities, it is necessary to significantly reduce the contaminants generated in sampler and to fabricate a surface and/or material with an extremely low outgassing rate. We have produced a sampler made of pure Al produced during plasma oxidation in 3% O@sub 2@/Ar after the EX process.@footnote 1@ Nevertheless, the H@sub 2@ concentration in N@sub 2@ or Ar sealed at 0.58MPa in the sampler increased from below 1ppb to 8ppb after 168hours. The CO and CO@sub 2@ concentration in O@sub 2@ also increased. Wet cleaning was carried out in the sampler in the plasma oxidation state by DI water for 72hours at a flow rate of 2L/min. After wet cleaning, the sampler was annealed at 423K for 72 hours in N@sub 2@ without exposure to air. We have confirmed that amorphous @gamma@-Al@sub 2@O@sub 3@ film with a thickness over 0.5µm was formed on the inner surface of the sampler using cross-sectional TEM observation. We have observed that the H@sub 2@ concentration in Ar or N@sub 2@ was maintained below 1ppb, the detection limit of the GC, for 168hours. The CO and CO@sub 2@ concentration in O@sub 2@ were also sufficiently low. These results suggest that the amorphous @gamma@-Al@sub 2@O@sub 3@ film formed by a series of treatments as already mentioned function as a gas-barrier film with an anti-catalytic property. @FootnoteText@ @footnote 1@H. Ishimaru, J.Vac.Sci.Tech., A7(3) 2439 (1989)

4:40pm **MS-MoA9 Gradational Lead Screw Pump Development**, ***K. Ando**,* T.D.Giken Co., Ltd., Japan*; I. Akutsu,* DIAVAC Limited, Japan*; T. Ohmi,* Tohoku University, Japan

Because the silicone device industry is innovating their production processes toward the larger wafer size and the higher process speed, a vacuum pump is required higher pumping speed through ranges of the both viscous and molecular flow. There has been no known conventional pumps that have been developed so as to vacuum a chamber down to 0.01 Torr with stable exhaust velocity over the entire region including the molecular flow region. All of them provide stable pumping speed only down to 0.1 Torr. The "GLS Pump" unlike these conventional pumps demonstrated the high pumping capability of 0.0004 Torr and the pumping speed of 3600L/M over the viscous and molecular flow ranges. The improved performance is attributable to the GLS employed for the rotor design. The pump utilizes a small amount of oil. The mass analyzer test(max. mass number 120) revealed that there is no evidence of the reverse diffusion in the pressure range above 0.002 Torr with a small amount of N2gas injected. In summary, the GLS Pump has enough displacement and large intake conductance. Low reverse diffusion is in practical operation. The pumping speed is high. The power consumption is low. The byproduct is transferred and ejected from the exhaust port through the operation mechanism. The radical deposit is minimized if the case temperature is maintained at 150°C. Although manufacturing this pump requires high level of skill, the pump structure is rather simple and the maintenance is easy hence it will increase the mean time between maintenance and reduce the maintenance cost. The detail report will be prepared on the characteristics of the GLS, the pump structure, and the performance attributes.

5:00pm **MS-MoA10 Etching and Cleaning of Silicon Wafers using HF Vapor Process in the Non-Condensed Etching Regime***, **Y.-P. Han**, H. Sawin,* Massachusetts Institute of Technology

We have studied oxide etching mechanisms of HF vapor etching process in two regimes: the condensed regime (liquid phase) and the 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. The rate limiting steps of the etch rate have been studied at various conditions by changing the temperature of the reactor, the partial pressure of the reactants and the flow rate. The etching rate of oxide in the non-condensed regime was mainly limited by the surface reaction rate at higher temperature, but the mass transfer rate became more important at lower temperature. We also have investigated the cleaning of Na from silicon wafer in HF vapor process. It was observed that Na contamination on thick thermal oxide films was typically removed by HF vapor process. On thinner oxide films, i.e. 1-2 nm native oxide, only part of the contaminated Na was typically removed by this process. The addition of SiF4 to the HF/H2O process, i.e. HF/H2O/SiF4 was found to improve the cleaning efficiency of Na from silicon surfaces. The volatile product is believed to be Na-OSiF3.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+EM+SS-MoA

Cross-sectional Scanning Tunneling Microscopy of Semiconductors

Moderator: M. Weimer, Texas A&M University

2:00pm **NS+EM+SS-MoA1 Scanning Tunneling Microscopy Studies of Atomic-Scale Structure In Semiconductor Heterostructures***, **E.T. Yu**, S.L. Zuo,* University of California, San Diego **INVITED**

Engineering of advanced heterostructure and nanoscale semiconductor devices requires a detailed understanding of the structure and properties of semiconductor materials and devices at the atomic to nanometer scale. Cross-sectional scanning tunneling microscopy provides unique and powerful capabilities for characterization of structural morphology and electronic properties in semiconductor epitaxial and device structures with spatial resolution at or near the atomic scale. In conjunction with results obtained using complementary characterization techniques, such studies can provide valuable insights into the relationships among epitaxial growth conditions, atomic-scale compositional structure, and various aspects of device behavior. We will discuss a number of recent applications of cross-sectional scanning tunneling microscopy to the characterization of III-V compound semiconductor heterostructures. Studies of InAsP/InP heterostructures, currently of interest for optoelectronic devices operating at 1.3-1.55 microns, have revealed that extensive nanoscale compositional clustering occurs, with As-rich and P-rich clusters bounded preferentially by {111} planes forming in the InAsP alloys. Related studies of InNAsP/InP heterostructures, in which low concentrations (~1-2%) of N are incorporated, have provided information about the influence of N on heterojunction band alignments. And STM images of InAsP/InAsSb superlattices of interest for midwavelength infrared emitters have revealed nanoscale compositional fluctuations in these materials consistent with previously reported observations by electron diffraction of partial ordering in InAsSb alloys.

2:40pm **NS+EM+SS-MoA3 Growth Asymmetry in InGaAsP/InAsP Superlattices Studied by Scanning Tunneling Microscopy***, **B. Grandidier**, H. Chen, R.M. Feenstra,* Carnegie Mellon University*; R.S. Goldman,* University of Michigan*; C. Silfvenius, G. Landgren,* Royal Institute of Technology, Sweden

InGaAsP based multiple quantum well structures are increasingly used to fabricate optoelectronic devices. However the strain can lead to lattice relaxation processes during the growth which degrades the optical properties of these structures. To understand the differences in the photoluminescence efficiency of several superlattices composed of InGaAsP quaternary wells, we have investigated a series of InGaAsP/InGaP and InGaAsP/InAsP superlattices using cross-sectional scanning tunneling microscopy (xSTM). These superlattices were grown by metalorganic vapor phase epitaxy, with different number of periods and with or without InP interlayers inserted in the barrier. For InGaAsP/InGaP superlattices, the individual well and barrier layers are well resolved in the xSTM images. In contrast, for InGaAsP/InAsP superlattices, the InGaAsP quantum well and preceding InAsP barrier layers can be clearly seen, whereas the subsequent InAsP barriers are severely intermixed with the quantum wells. Possible mechanisms for this intermixing are described. In addition, the contrast observed in both types of superlattices has been related to the strain which exists in the layers; the compressively strained InAsP barrier protudes outwards from the (110) cleavage plane whereas the tensilely strained InGaP barrier contracts inwards. Finite element computations are used to quantify these elastic relaxation effects of the cleavage surface.

3:00pm **NS+EM+SS-MoA4 Microstructure of Mixed-Anion Interfaces Examined with XSTM@footnote 1@***, **J. Harper**, M. Weimer,* Texas A&M University*; D. Zhang, C.H. Lin, S.S. Pei,* University of Houston

The quality of the interfaces between the nearly-lattice-matched 6.1 Å materials (InAs, GaSb, and AlSb) is important for a number of applications, including the development of mid-IR lasers, long-wavelength photodetectors, and resonant-tunneling devices. Cross-sectional scanning tunneling microscopy (XSTM) is a powerful tool for characterizing the heterojunctions in these structures, which pose special challenges for molecular beam epitaxy (MBE) because of the mixed-anion nature of this material system. We have observed a white-noise component in the roughness spectrum of the GaSb-on-InAs interface with XSTM that is associated with the presence of interface point defects; these defects most likely arise from thermodynamically favored anion exchange reactions that occur during the crossover from arsenide to antimonide growth. Abruptness of the InAs-on-GaSb interface, on the other hand, is limited by antimony segregation that causes compositional grading within the arsenic layers. We have quantitatively characterized the Sb fraction as a function of distance from the arsenide-on-antimonide heterojunction, and find this compositional grading is well described by an exponential profile. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation (DMR-9633011).

3:20pm **NS+EM+SS-MoA5 X-STM Study of InAs/In@sub 1-x@Ga@sub x@Sb/InAs/AlSb Laser Structures@footnote 1@***, **W. Barvosa-Carter**, M.J. Yang, L.J. Whitman,* Naval Research Laboratory

Strained-layer heterostructures involving the 6.1 Å family of III-V semiconductors (including InAs, GaSb, and AlSb) are being investigated for use in a growing number of high-speed and opto-electronic devices. Recently it was shown in InAs/In@sub 0.73@Ga@sub 0.28@Sb/InAs/AlSb mid-IR structures that the photoluminescence (PL) intensity and x-ray superlattice diffraction quality are strongly dependent on MBE growth temperature. These characteristics were shown to be optimized within a rather narrow growth temperature range (410-460°C) and much worse outside of that range. Although the quality of the interfaces in these structures is expected to play a crucial role in determining device performance, little is known about the actual atomic-scale structure of the interfaces. We present an atomic-resolution cross-sectional STM (X-STM) study of these laser structures in order to directly correlate atomic-scale features, such as interface roughness and layer intermixing, with material quality as measured by PL and x-ray measurements on the same samples. Two such laser structures have been examined, one grown at the optimum temperature and another grown at a higher temperature. Interface roughness appears to be larger in the higher temperature structure. In addition, intermixing occurs at the AlSb-on-InAs interfaces which results in electronic structure differences between the InAs-on-AlSb and AlSb-on-InAs interfaces as observed by X-STM. Based on our X-STM results, we will discuss the atomic-scale sources of device degradation, and present possible routes towards improvement of the growth of these laser structures. @FootnoteText@ @footnote 1@ Funded by the Office of Naval Research and the Air Force Research Laboratory.

3:40pm **NS+EM+SS-MoA6 Kinetics of Anion Cross Incorporation in Type-II Heterostructures Characterized with XSTM@footnote 1@***, **J. Steinshnider**, J. Harper, M. Weimer,* Texas A&M University*; D. Zhang, C.H. Lin, S.S. Pei,* University of Houston

We have used cross-sectional scanning tunneling microscopy (XSTM) to examine MBE material quality in the mixed-anion InAs/GaSb/AlSb system under growth conditions (including the use of cracked arsenic and antimony sources) similar to those presently employed for type-II quantum well and interband cascade lasers. Two apparently different anion defects are noted within the antimonide layers. The demonstration of a linear correlation between the defect densities observed with STM and the arsenic valve setting during antimonide-layer growth establishes background arsenic incorporation as the common origin for both of these defects.@footnote 2@ The distribution of As substitutional defects in a (110) cleavage plane is analyzed by way of the two-dimensional pair correlation function. We observe a pronounced attractive correlation in the [110] direction, parallel to the Sb dimer bonds of the (1x3) reconstructed growth surface, whereas the distribution in the orthogonal [001] direction is essentially random. This anisotropic correlation reflects the kinetics of arsenic dimer incorporation during growth and not the equilibrium distribution associated with strain-mediated repulsive interactions. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation (DMR-9633011). @footnote 2@ J. Harper, M. Weimer, D. Zhang, C.H. Lin, and S.S. Pei, JVST B 16, in press (1998).

4:00pm **NS+EM+SS-MoA7 Low Temperature Cross-Sectional Scanning Tunneling Microscope-Induced Luminescence of GaN**, ***S. Evoy,*** *C.K. Harnett,* Cornell University*; S. Keller, U.K. Mishra, S.P. DenBaars,* University of California, Santa Barbara*; H.G. Craighead,* Cornell University

The GaN system is of interest for applications in the green, blue, and UV spectral regions. Advances in device development have been made in spite of issues such as dislocation densities and defect induced visible luminescence. These issues prompted interest in spatially resolved luminescence studies of the material. Scanning tunneling microscope-induced luminescence (STL) offers nanometer scale resolution and control of the injection bias. In-situ cleaving and cross-sectional imaging is of particular interest for nanoscale luminescence studies of GaN heterostructures and interfaces. We recently reported the first low temperature STL of GaN, and the first STL images of this material. We now report the low temperature cross-sectional STL of MOCVD-grown GaN. Optical interference filters are used for semiquantitative spectral analysis. Room temperature top-view experiments reveal faint visible emission at tip biases above 1.5 V, with no clear evidence of UV luminescence. However, a sharp increase of emission in the 350±35 nm range is observed under liquid He cooling at biases above 3 V. The room temperature visible emission may be related to surface issues, suggesting that low temperature is required for the analysis of intrinsic bulk luminescence. Cross-sectional experiments are performed on in-situ cleaved samples. Incompatible cleaving planes between the GaN and the sapphire produce 200-400 nm wide vertical features, yielding an edge roughness of 30-50 nm. Behavior of luminescence is similar to what was observed in top-view. However, close to the sapphire interface, the 350±35 nm band-edge emission is undetected even at low temperature. Images show strong correlation between the remaining visible emission and the cleaved-induced artifacts. We are currently working on our cleaving technique in order to improve the quality of the edge. The technique will also be applied to the study of GaN heterostructures such as InGaN/GaN quantum wells.

4:20pm **NS+EM+SS-MoA8 Cross Sectional STM Study on MBE-grown Si/Ge(111) Interface**, ***H. Hirayama,*** *M. Ohmori, K. Takayanagi,* Tokyo Institute of Technology, Japan

We studied the (111) cross sectional surface of MBE grown Si/Ge(111) samples. Samples were cleaved in ultra-high vacuum, and their (111) cross s ection were investigated in-situ by using STM. On the as-cleaved surface, 2x1 reconstruction were observed at both Si and Ge side. After annealing, 2x1 reconstruction changed to 7x7 and c(2x8) on the Si and Ge layer, respec tively. At around the interface, 7x7 reconstruction changed to c(2x8) reco nstruction in moving from Si to Ge side. But, the transition from 7x7 to c(2x8) was not abrupt. The transient region of the width of c.a.200nm was obs erved. In the transient region, adatoms arranged with 2x2 and c(2x4) shor t range orderings. Patchy domains of 7x7 reconstruction, which was accompa nied with (110)- oriented grooves and non-double layer height steps, were a lso observed in the sea of 2x2 and c(2x8) arrangement of adatoms. In a det ailed analysis of adatom arrangement, we found that the non-double layer hei ght step was caused by the glide in the (111) plane parallel to the substr ate. The groove was triggered by partial dislocations at the edge of the gild region. The strain field with the glide-induced step and grooves modifi ed the surface strain locally, and caused patchy 7x7 domains.

4:40pm **NS+EM+SS-MoA9 Scanning Tunneling Microscopy Characterization of the Depletion Zone of a Si Lateral pn Junction**, ***M.L. Hildner,*** *R.J. Phaneuf, E.D. Williams,* University of Maryland, College Park

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are used to characterize lateral pn junctions fabricated on silicon (100) surfaces. Two separate device structures , one with p@super +@-n and the other with n@super +@-p abrupt junctions, were examined. The STM images of the first set of devices show both an electronic feature and a structural groove on each side of the ion implanted p-type regions. The groove is an etching artifact of the implantation mask fabrication process and was easily avoided in making the second set of devices which show only a similar electronic feature. The electronic feature widens with applied reverse bias with a voltage dependence that closely matches that expected for the depletion zone. However, the width of the electronic feature is much smaller than that of the depletion zone. The STS measurements show that the tip-junction system can be modeled as a series of non-equilibrium metal-insulator-semiconductor (MIS) diodes formed with a semiconductor of spatially variable carrier density. From this model, we qualitatively describe the electronic feature as confined to that portion of the depletion region in which the biasing sense of the MIS junction is switched from the biasing sense when the junction is in the lightly doped neutral region. Thus, the electronic feature commences, as the tip is moved from the lightly doped neutral region into the depletion region, when the majority carrier changes (from electrons to holes for the lightly doped n devices). This work has been supported by the Laboratory for Physical Science, with partial support from the NSF-MRSEC.

Organic Electronic Materials Topical Conference
Room 327 - Session OE+EM-MoA

Organic Thin Film Devices II: Transitors and Transport

Moderator: P.E. Burrows, Princeton University

2:00pm **OE+EM-MoA1 Organic Thin Film Transistors**, ***T.N. Jackson,*** The Pennsylvania State University **INVITED**

Over the past several years the performance of organic thin-film transistors (OTFTs) has improved dramatically and it now appears likely that they will find application in displays or other low-cost large-area electronic applications. Small molecule materials such as oligothiophenes and oligoacenes have shown the most progress. When deposited by thermal evaporation onto substrates held at elevated temperature these materials often form thin films with strong molecular ordering; such ordering may be important for obtaining large field-effect mobility and other desirable electrical characteristics. In particular, pentacene thin films deposited at a few Å/s onto substrates held at 50 - 100 °C typically have micron-sized grains, and OTFTs using pentacene as the active layer have demonstrated field-effect mobility as large as 1.5 cm@super 2@/V-s, current on/off ratio larger than 10@super 8@, near zero threshold voltage, and subthreshold slope less than 1 V/decade; all these characteristics are similar to those typically observed for a-Si:H thin film transistors (TFTs). Polymeric semiconducting materials are also of interest since they may offer a simple path to solution-processable devices. Thin films of these materials can often be solvent cast which leads to films that are less well-ordered than evaporated small molecule films; however, field-effect mobility near 0.05 cm@super 2@/V-s has been demonstrated for alkyl-substituted soluble polythiophenes. In addition to all-organic applications, OTFTs show promise for integration with a-Si:H TFTs. The field-effect mobility of p-channel OTFTs and n-channel a-Si:H TFTs are similar and integrated organic/a-Si:H devices can provide a simple complementary circuit technology.

2:40pm **OE+EM-MoA3 Fast Electronic Transport in Organic Molecular Solids?**, ***N. Karl,*** Universität Stuttgart, Germany **INVITED**

The fundamental aspects of electronic charge transport in organic solids will be reviewed and some specific features of this class of materials highlighted. Examples of appropriate measurement techniques - such as time-of-flight (TOF), field effect transistor (FET), and surface acoustoelectric travelling wave (SAW) techniques - as well as of characteristic results - such as magnitude, temperature dependence and anisotropy of intrinsic charge carrier mobilities - will be presented. While ample basic knowledge has been gained from well-defined ultrahigh purity single crystals, where mobilities of several hundred cm@super 2@/Vs could be reached (see e.g. ref. 1), understanding of the electronic properties of organic thin films is often unsatisfactory. Different kinds and degrees of structural disorder, residual foreign molecules, and a sensitivity to accidental doping by ambient donor or acceptor molecules (such as e.g. O@sub 2@) frequently not only lead to ill-defined irreproducible or nonstationary properties but also to slow transport. Sample preparation under well-controlled conditions and careful sample characterization by sensitive methods of structural and trace impurity chemical analysis are the prime prerequisite not only for further progress in fundamental research, but also for the development of innovative applications. Needless to say that proper selection of material parameters, such as sufficient stability and specific molecular architecture-based functions, is necessary for designing promising molecular-electronic systems, but the complementary aspect of efficient charge carrier transport, which is a superordinated consideration in most applications, may necessitate optimization compromises. @FootnoteText@ @footnote 1@ "Organic Semiconductors" in: Landolt-Börnstein (New Series) Group III, Vol.17i, pp 106-218 (Springer-Verlag, Berlin, New York 1985).

3:20pm **OE+EM-MoA5 Soluble and Processable Oligothiophenes and Analogues as Semiconductors for Thin Film Transistors***, **W. Li**, H.E. Katz, A.J. Lovinger, K.R. Amundson,* Bell Laboratories, Lucent Technologies

There has been rapid progress in the synthesis and fabrication of organic semiconductors for field effect transistors (FETs) useful for plastic-based electronics. Conjugated oligomers, such as oligothiophenes and their derivatives, have been shown to be effective semiconducting layers for FETs. We and others have utilized these compounds primarily as vapor-deposited solid films. Recently, our investigation has been extended to liquid phase fabrication of organic FETs. We have synthesized a series of soluble and processable oligothiophenes and related compounds. Thin film FETs cast from solutions of these compounds showed both high field-effect mobilities (ca. 0.03 cm@super 2@/Vs) and relatively high on/off current ratios (>10@super 3@). We find that the film continuity and field-effect mobility are strongly dependent on solvents and dielectric substrates used as well as other casting conditions. Detailed synthetic routes and transistor characteristics, as well as approaches to devices with higher on/off ratios will be presented.

3:40pm **OE+EM-MoA6 Field Effect Conductance of 1-6 Monolayer Thick Crystals of Organic Semiconductors***, E.L. Granstrom, T.W. Kelley, **C.D. Frisbie**,* University of Minnesota

We describe two types of field effect measurements on organic semiconductor single crystals that are as thin as a single molecular layer. In these studies, crystals of the semiconductors pentacene or sexithiophene are grown by vacuum sublimation onto SiO2, ranging in thickness from 1-6 monolayers with lengths and widths on the order of a micron. In one experiment, individual crystals are contacted with source and drain electrodes fabricated by electron-beam lithography; heavily doped Si underneath the SiO2 serves as a gate electrode. Field effect conductance and carrier mobility are measured as a function of temperature (30-300 K) and the number of discrete molecular layers in the crystals. We find that measurements on these thin crystals are extremely sensitive to carrier trapping and offer a potential approach to dynamic recording of the effects of individual trapping events on source-drain current. A second experiment uses a conducting atomic force microscopy (AFM) probe as a positionable source or drain contact to crystals contacted by a fixed electrode at the other end.@footnote 1@ This configuration allows variation of the source-drain separation and 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 general, the conjunction of AFM imaging methodology with transport measurements facilitates correlation of transport properties with specific, well-defined organic semiconductor structures. @FootnoteText@ @footnote 1@Loiacono, M. J.; Granstrom, E. L.; Frisbie, C. D. J. Phys. Chem. B 1998, 102, 1679.

4:00pm **OE+EM-MoA7 Charge Injection and Transport in Organic Films***, **D.K. Murti**,* Xerox Research Centre of Canada, CANADA

Charge injection and transport is important in many diverse organic electronic devices. For example, electroluminescent devices for display and organic photoreceptors for digital printers depend on injection and transport. In this presentation, the primary focus will be on the organic photoreceptor. Organic photoreceptors consist of a metal film with layers of organic photoconductor and molecularly doped polymers. Charge injection and transport at metal-phthalocyanine interfaces and phthalocyanine-molecularly doped polymer interfaces will be discussed in this presentation. In the photoinduced discharge technique, the surface is initially corona-charged and then followed by discharge of the surface potential with photogenerated carriers that are injected from phthalocyanine and transported in the tetraphenylbenzidine (TPD) doped polycarbonate film. Photoinduced discharge measurements indicate that photogenerated holes can be injected from phthalocyanine into TPD without charge trapping. Hole mobility and the electric field dependence were measured with the time-of-flight technique. In this technique, the drift of a sheet of holes injected from the phthalocyanine film is time-resolved; the transit time is determined in order to calculate the hole mobility at an applied electric field. Hole mobility showed dependence on the electric field with a mobility of about 1x10 @super -5@ cm@super 2@ / V.s at an electric field of 1x10 @super 4@ V/cm. Kelvin probe was used to determine the contact potential difference and changes in the work function of phthalocyanine and TPD. The relative work functions of phthalocyanine and TPD are 5.2 eV and 4.7 eV respectively based on Kelvin probe measurements. This indicates no barrier for hole injection as observed by photodischarge techniques.

4:20pm **OE+EM-MoA8 Localized Growth and Electrical Characterization of Polypyrrole on Temperature Programmed Microhotplates***, **C. Kendrick**, R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology

Arrays of microhotplates fabricated at CMOS foundries have been post-processed to realize suspended, heatable structures that have previously allowed localized deposition of SnO@sub 2@ by thermally activated CVD.@footnote 1@ This work presents an electrochemical, self-lithographic technique for the growth of polypyrrole on the micromachined platforms and a study of the effect of rapid heating/cooling cycles on film conductivity during gas exposure. Electropolymerization was performed in a sealed flow cell containing Ag-pseudoreference and Pt-counter electrodes mounted directly on the chip package and filled with a solution of acetonitrile, 0.1M LiClO@sub 4@, and 50mM pyrrole. Optical microscopy indicates that polypyrrole growth begins on the Au-plated microhotplate contacts and expands laterally, forming a continuous film. The effects of NO@sub x@, NH@sub 3@, CO, H@sub 2@, and methanol vapors on film resistance have been measured for different film dopings and temperature schedules. The highest sensitivities are found for the strongly oxidizing and reducing gases NO@sub x@ and NH@sub 3@, respectively, where resistance changes have been shown to be caused by changes in carrier concentration brought about by a weak charge transfer interaction between adsorbates and the film. We show that resistance changes (@DELTA@R/Ro) due to 100ppm NO@sub x@ exposure can be increased from ~15% at 25°C to ~30% when periodically pulsing the sensor to 150°C. A similar increase in sensitivity is observed for periodic heating during exposure to NH@sub 3@. Information on analyte adsorption rates and dynamics can also be extracted from the transient resistance characteristics observed between temperature pulses. @FootnoteText@ @footnote 1@S. Semancik, R. E. Cavicchi, K. G. Kreider, J. S. Suehle, and P. Chaparala, Sensors and Actuators B 34, 209 (1996).

Plasma Science and Technology Division
Room 314/315 - Session PS1-MoA

Environmental Issues and Emerging Technologies

Moderator: K.K. Gleason, Massachusetts Institute of Technology

2:00pm **PS1-MoA1 Scaling of PFC Abatement Using Plasma Burn-Boxes@footnote 1@***, **X. Xu**, M.J. Kushner,* University of Illinois, Urbana-Champaign

Perfluorinated compounds (PFCs), gases which have large global warming potentials, are widely used in plasma processing for etching and chamber cleaning. Due to underutilization of the feedstock gases or by-product generation, the effluent from plasma tools typically have large mole fractions of PFCs. The use of plasma "burn-boxes" located downstream of the plasma chamber is being considered as a remediation method for abating PFCs emissions. In the burn-box, typically located between the turbo- and roughing pumps, O@sub 2@ is injected into a high density plasma with the goal of converting PFCs into products such as CO, CO@sub 2@, and COF@sub 2@. Results from the 2-dimensional Hybrid Plasma Equipment Model (HPEM) have been used to investigate the scaling of plasma abatement of PFCs using burn-boxes with ICP reactors. The HPEM is used to model the etching chamber of the ICP reactor to determine the utilization of the feedstock gases and generation of by-products. The effluent from the etching chamber is then passed through the burn-box using O@sub 2@ injection and excited by a second inductively coupled source. Results will be discussed for Ar/CF@sub 4@/C@sub 2@F@sub 6@/O@sub 2@ mixtures. We found that reassociation of PFCs after dissociation in the burnbox, particularly problemmatic for CF@sub 4@, is an important by-product generation mechanism which can be controlled to some extent by controlling the gas temperature. The abatement of C@sub 2@F@sub 6@ is approximately 4 times more efficient that CF@sub 4@ due to both the cited reassociation and and larger dissociation cross sections for C@sub 2@F@sub 6@. Full oxidation of the PFCs is possible, though large mole fractions of O@sub 2@, typically on order of 50%, are required. The radius of the burn-box, skin depth of the inductively coupled field and residence time of gases in the burnbox must be optimally selected in order to minimize "pass-through" of the effluent which reduces the abatement efficiency. @FootnoteText@ @footnote 1@Work supported by NSF and SRC.

2:20pm **PS1-MoA2 Point-of-Use Plasma Abatement of PFCs in a High Density Inductively Coupled Plasma***, D.B. Graves,* ***E.J. Tonnis,*** University of California, Berkeley

A current major environmental concern in semiconductor manufacturing involves the use and emission of PFCs (perfluorinated compounds) and HFCs (hydrofluorinated compounds) during plasma etching of silicon dioxide and plasma-assisted chamber cleaning processes in dielectric film CVD systems.@footnote 1@ While significant progress has been made recently in reducing the emissions of PFCs and HFCs from CVD tools using alternate chemistries and process optimization, the stringent demands on oxide etch process recipes has limited emission reduction progress for etch. A promising alternate strategy for reducing or eliminating these emissions in etch processes is via point-of-use (POU) plasma abatement systems. In this approach, a high density plasma is ignited between the turbomolecular pump and the mechanical backing pumps downstream of a plasma process emitting HFCs and/or PFCs. A flow of O@sub 2@ is added upstream of the POU abatement plasma which dissociates the PFC/HFC and O@sub 2@ mixture causing the CF@sub x@ fragments to react with O atoms to form products that can be removed downstream through caustic water scrubbing processes. We present experimental results indicating that a high density, inductively coupled RF plasma can abate a variety of pure PFCs, including CF@sub 4@, C@sub 2@F@sub 6@, and CHF@sub 3@ in the presence of O@sub 2@ by between 90% and 99%. In addition, recent abatement experiments conducted on the effluent of an industrial high density oxide etcher indicate that these high levels of abatement can be realized even in the presence of complex mixtures of etch products found in actual tool exhausts. Issues that may limit POU plasma abatement implementation into an industrial environment such as process contamination, particulate formation, and transient control of the abatement plasma have also been examined. @FootnoteText@ @footnote 1@The National Technology Roadmap for Semiconductors, Semiconductor Industry Association, pp. 154-157, 1997.

2:40pm **PS1-MoA3 Plasma Etching Using PFC Replacement Chemicals***, T. Kure,* Hitachi Ltd., Japan*; T. Takaichi,* Showa Denko K.k., Japan*;* ***Y. Goto,*** Hitachi Ltd., Japan **INVITED**

PFC (Perfluorocompound) gases are widely used for plasma etching of thin film and for plasma cleaning of process chamber. However, unfortunately, PFCs have extremely long atmospheric lifetimes and absorb infrared radiation emitted by the earth that would otherwise be radiated into space. As a result, PFCs contribute to the greenhouse effect in the earth's atmosphere, thus helping to cause the phenomenon known as a global warming. To reduce the release of PFCs into the air, replacement chemicals and abatement devices for exhaust gases need to be developed. Recently, several kind s of abatement devices (combustion, plasma, thermal, and catalyst reaction) are being examined. In our research, we have focused on using iodofluorocarbons (IFCs) and unsaturated fluorocarbons (u-FCs) as replacement chemicals for PFCs. Since the binding energy of C-I bond and C=C bond are very weak compared with the C-F bond, the atmospheric lifetimes of IFCs and u-FCs are extremely short. Therefore, their impact on global warming should be small. For use in SiO@sub 2@ etching, we selected C@sub 2@F@sub 5@I and C@sub 3@F@sub 6@ because of its C/F ratio about 0.5, its boiling point less than room temperature, and nonflammability. We evaluated the SiO@sub 2@ and poly-Si etching rate in a microwave plasma with these gases comparing it with C@sub 4@ F@sub 8@ gas. We also evaluated XPS spectrum of deposited polymer on etched wafers. We found that both the etching performance and deposited material were similar among these gases. Therefore, we believe C@sub 2@F@sub 5@I and C@sub 3@F@sub 6@ can be used as replacement chemicals for PFCs in SiO@sub 2@ etching.

3:20pm **PS1-MoA5 Challenges in Plasma Etching and Patterning for Fabrication of New Systems and Devices***,* ***M. Engelhardt,*** Siemens AG, Germany **INVITED**

Among the most challenging tasks of plasma process technology today are, without doubt, plasma etching for fabrication of through-wafer interconnects in wafer stacks for vertical integration of chips (VIC) and plasma patterning of new materials used for electrodes and storage media in storage capacitors of Gbit scale DRAMs and FeRAMs. VIC realized by stacking and vertically interconnecting fully processed device wafers allows fabrication of both new systems with unique system qualities and systems with highly improved performance. 3D integration approaches are also driven by the interconnect crisis. Through wafer interconnects used for 3D chip integration require plasma etching of dielectrics, single cristal silicon, and interchip glue layers at aspect ratios exceeding 15 for vias through wafers thinned down to 15µm. Vertical profiles achieved with minimized RIE lags and high etch rates are the stringent requirements for all of these processes. Patterning of Pt electrodes is another challenging task. So far no volatile reaction products were obtained at usual process temperatures. Processes based on so-called reactive gases leading to a build-up of transient or removable sidewall films result in significant sidewall taper of the profiles and hence high CD gain whereas steep profile sidewalls have been obtained with processes based on inert gases with the tradeoff of build up of non-removable sidewall films. A new approach overcomes these tradeoffs by a combination of plasma patterning and CMP allowing fabrication of vertical Pt profiles with resist mask. The build-up of thin redepositions of Pt onto the sidewalls of the resist, obtained as a result of processing in pure Ar plasmas, is utilized to achieve a sidewall steepness of the patterned Pt film which is determined by the steepness of the pre-etch resist profile. After pattern transfer and resist stripping, the portion of the redepositions protruding above the fabricated storage node was completely removed by CMP.

4:00pm **PS1-MoA7 PECVD and Dry Etching on Large Glass Substrates for Flat Panel Displays***,* ***J.M. Perrin,*** Balzers Process Systems, France **INVITED**

Flat panel display manufacturing depends more and more on plasma processing. This is particularly the case in the fabrication of the thin film transistor (TFT) array for active matrix liquid crystal displays (AMLCD's). Besides PVD of metals or metallic compound films by magnetron sputtering, and PECVD of amorphous silicon (aSi) and silicon nitride or oxide, plasma dry etching is gradually taking over wet etching, still abundantly used in first and second generation fabrication lines. We will focus on process issues, reactor concepts, and architectures of processing tools for PECVD and plasma dry etching, both performed in RF-excited glow discharges. The evolution of process demand in PECVD goes towards i) a better control of film and interface quality to achieve thinner TFT's and improved aSi TFT mobilities, ii) the deposition of aSi films suitable for laser crystallization to produce polycrystalline Si TFT's, and iii) the deposition silicon oxide instead of nitride as gate insulator. For dry etching the general trends are i) the development of dry-etching of metal source and drain contacts which is very critical in the back-channel etch TFT technology, ii) the reduction of the number of masks trend by etching multilayers of metals, and iii) etching of the ITO pixels. The increasing size of glass substrates to (up to 1 m2) imposes severe constraints on the design of reactors, to insure process uniformity, deposited film quality, and control of etch profiles. The most widely used concept still remains the classical capacitively-coupled RF discharge configuration. But the scaling up of such sources involve problems such as the uniformity of RF power distribution and gas feed on the electrodes. Moreoverreactive ion etching faces the problem that the RF discharge become more and more symmetric as the ratio of RF-powered electrode and grounded electrode areas tends towards unity. To overcome this problem of scaling-up, and provide control of the ion energy on the substrate, we have developed a new triode configuration (Piano reactor) involving a periodic structure of isolated bars with independent RF impedances to ground. Then comes the production issue related to the best way to achieve a large throughput. The debate is between the development of high rate plasma sources or processes with fast substrate handling in a cluster type configuration, or keeping moderate deposition and etch rate in stacks of reactor with parallel processing. Eventually reactor maintenance issues such as dry-cleaning after PECVD are critical.

4:40pm **PS1-MoA9 Use of a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) to Kill a Broad Spectrum of Microorganisms@footnote 1@***,* ***K. Kelly-Wintenberg****, A. Hodge, T.C. Montie, L. Deleanu, J.R. Roth, D. Sherman,* University of Tennessee*; P. Tsai, L. Wadsworth,* Textile and Nonwovens Development Center (TANDEC)

The medical, industrial, and food processing industries are constantly in search of new technologies to improve existing sterilization and pasteurization methodologies. Available techniques must deal with and overcome such problems as thermal sensisitivity and destruction by heat, formation of toxic byproducts, cost, and inefficiency in performance. We report the results of a newly invented plasma source, a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) that is capable of operating at atmospheric pressure in air and providing antimicrobial active species at room temperature. OAUGDP exposures have reduced log numbers of bacteria (E. coli, S. aureus, Deinococcus radiodurans, and Bacillus subtilis), bacterial endospores (Bacillus subtilis and Bacillus pumilus), and various yeast and bacterial viruses on a variety of surfaces. These surfaces included polypropylene, filter paper, paper strips, solid culture media, and glass. Experimental results showed at least a @>=@ 5 log@sub 10@ CFU reduction in bacteria within a range of 15-90 sec of exposure, whether the samples were exposed in conventional sterilization bags or directly exposed to the plasma. An exception to these very short exposure times were experiments with solid culture media where 5 min of plasma exposure was necessary to produce @>=@ 5 log@sub 10@ CFU reduction in bacterial counts. The effects of plasma treatment on bacterial cell structures were investigated by exposing cells to plasma for various durations and examining them by Transmission Electron Microscopy. These experiments showed cell lysis had occurred with the release of cellular contents. These data were consistent with spectrophotometer data in which the release of cellular constituents was measured as a change in absorption at 210nm and 260nm. With all microorganisms tested, a bi-phasic killing curve (logarithmic number of survivors versus time) was generated in plots of doseresponse data. Differences in susceptibilities of microorganisms observed on various surfaces suggested that the degree of lethality was dependent upon the time of diffusion of active species and the makeup of the microbial cellular surface. @FootnoteText@ @footnote 1@This work was supported in part by the Air Force under a STTR with Environmental Elements, Inc. of Baltimore, MD; and by the UTK Textiles and Nonwovens Development Center (TANDEC).

5:00pm **PS1-MoA10 High Pressure Plasmas as an Anti-Terrorist Technology***, **G.S. Selwyn**, H.W. Herrmann, I. Henins,* Los Alamos National Laboratory

Plasmas have long been used for production of short-lived, reactive chemical species needed for etching or deposition of thin films. Plasmas are also widely used for dry ashing or stripping of organic films, such as photoresist, from wafers. We have recently developed a novel, atmospheric pressure, non-thermal plasma source with chemical and electrical characteristics closely resembling traditional low-pressure plasma discharges. However, unlike conventional low pressure plasmas, this source produces a fast-flow stream of chemically-reactive, metastable species capable of selective surface oxidation. One emerging application for this new technology is the use of plasmas for decontamination of civilian and/or military targets attacked by chemical or biological warfare agents. We have demonstrated rapid and effective decontamination of surfaces exposed to either anthrax-surrogate spores or a chemical agent used as a surrogate for mustard gas. Anthrax is an air-borne, persistent and highly toxic spore capable of causing mass casualties if spread in an urban area by terrorist. The atmospheric pressure plasma jet (APPJ) has been shown to produce a 7-log decrease in active spores after a 90 second exposure to the reactive effluent stream. Mustard gas is a chemical agent causing severe skin blistering, mass injuries and incapacitation capable of lasting several months. It can be used to reduce the effectiveness of military force and to interfere with military logistics as well as to render urban areas uninhabitable for prolonged periods. The APPJ source has been shown to detoxify a mustard gas simulant by 5 orders of magnitude in just 30 seconds of effluent exposure. Development of this new technology provides a potential means of defeating terrorist attacks using these agents, both in the US and overseas. By providing a means to effectively counter chemical and/or biological attacks, it is hoped the use of these weapons of mass destruction will also be deterred.

Plasma Science and Technology Division
Room 318/319/320 - Session PS2-MoA

Diagnostics I

Moderator: M.L. Brake, University of Michigan

2:00pm **PS2-MoA1 Density Measurements of Cf@sub x@ in a GEC Reference Cell by Infrared Absorption***, **I.C. Abraham**[1], R.C. Woods,* University of Wisconsin, Madison*; G.A. Hebner,* Sandia National Laboratories

Tunable diode laser absorption measurements in the region around 1250 cm@super -1@ were used to determine line integrated CF, CF@sub 2@, and CF@sub 3@ densities in a GEC reference cell, modified for inductively coupled plasma operation. A quartz ring was also installed around the source region to stabilize and confine the plasma and to make the plasma chemistry more like that in industrial etch tools. The experimental layout involved a two pass arrangement, with the path including both the plasma and the space outside the glow region, in a plane just above the wafer surface. Two gas chemistries, C@sub 2@F@sub 6@ and CHF@sub 3@, and two wafer surfaces, bare silicon and blanket photoresist, were investigated. A range of pressure and power conditions, from 5 to 20 mTorr and from 100 to 300 W, respectively, was employed. The concentration of undissociated C@sub 2@F@sub 6@ in the C@sub 2@F@sub 6@ plasma was also measured. An intense spectrum of COF@sub 2@ can be detected in an O@sub 2@ cleaning plasma. The time evolution of CF, CF@sub 2@, and CF@sub 3@ in a C@sub 2@F@sub 6@ plasma was monitored, starting from a clean chamber and continuing for much longer than an etch cycle. The data should provide important benchmarks for models of oxide etching in inductively coupled plasma tools. This project was funded by SEMATECH under contract no. 38010430.

2:20pm **PS2-MoA2 Un-Collided Beam Mass Spectrometric Measurements in C@sub 2@F@sub 6@ and CHF@sub 3@ Dielectric Etch Discharges***, **J. RaviPrakash**,* The Pennsylvania State University, U.S.A*; R.C. McGrath,* The Pennsylvania State University*; G.A. Hebner,* Sandia National Laboratories

Relative concentrations of reactive ions, neutral radicals and etch/resist products in dielectric etch chemistries have been measured using an uncollided beam mass spectrometer (Hiden EQP). Measurements were made in C@sub 2@F@sub 6@ and CHF@sub 3@ discharges produced in an inductively coupled research reactor operating with power densities, pressures, gas compositions and wafer materials typical of those found in etch processing tools. For C@sub 2@F@sub 6@ discharges we find that CF@sub 3@@super +@ is consistently the dominant fluorocarbon ion present, in agreement with published cross sections for dissociative ionization. Significant concentrations of CF@super +@, CF@sub 2@@super +@, and C@sub 2@F@sub 5@@super +@ are also observed. We will report on differences observed between our measurements of fractional yields for these reaction products and those expected from published dissociative ionization cross sections. Notable changes have been observed in concentrations of C@sub x@F@sub y@ species and of SiF@sub x@ etch products in the presence of photoresist. In CHF@sub 3@ discharges the dominant ion species are CF@sub 3@@super +@ and CHF@sub 2@@super +@. Smaller concentrations of CF@sub 2@@super +@, CF@super +@ and HF@super +@ are also observed. For each of the etch chemistries investigated, variation of species concentrations with changing power (100-400 W) and pressure (5-40 mTorr) were measured. We will report on discharge conditions which produce the maximum reactive ion species production within the processing reactor volume.

2:40pm **PS2-MoA3 Modeling High-Density Plasma Etching of Aluminum and Photoresist@footnote 1@***, P. Ho, **E. Meeks**, A. Ting, S.J. Choi,* Sandia National Laboratories

A plasma-etch mechanism has been developed to describe the high-density plasma etching of aluminum in BCl@sub 3@/Cl@sub 2@/Ar mixtures. Results of extensive validation comparisons with experimental data are shown for several different reactor models employing the aluminum-etch mechanism. Comparisons are made to diagnostic measurements of the gas-phase, including electron density, electron temperature, Cl@super -@ density, and relative radical densities, as well as to ion-flux and wafer-etch data from a commercial reactor. The reactor models employed include a well mixed reactor model and a 2-D axisymmetric plasma-flow model that can handle several, detailed surface-chemistry descriptions for different plasma-materials interfaces in the reactor. The gas-phase plasma chemistry mechanism includes dissociation, ionization, and excitation of etch products to accurately capture macroscopic loading effects. The gas-phase chemistry and aluminum-etch mechanisms provide very good quantitative agreement between the models and the wide collection of observations and measurements available in this study. Simulation results from the 2-D model predict well the measured radial uniformity for blanket-aluminum etching. In addition to the aluminum-etch mechanism, a simple description of photoresist etching is introduced, which reproduces most of the observed trends for blanket photoresist etching in the BCl@sub 3@/Cl@sub 2@/Ar plasmas. @FootnoteText@ @footnote 1@This work was supported by a Cooperative Research and Development Agreement between SEMATECH and Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

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

3:00pm **PS2-MoA4 Studies of Ion Bombardment in Plasma Cleaning and Etching Gases***, **J.K. Olthoff**, Y. Wang,* National Institute of Standards and Technology

Ion-energy distributions and relative ion fluxes have been measured in a variety of plasma etching and cleaning gases, and their mixtures, at the grounded electrode of a high density inductively-coupled plasma (ICP) reactor. The gases studied include pure CF@sub 4@ and C@sub 2@F@sub 6@, along with the following mixtures: CF@sub 4@ + Ar, CF@sub 4@ + Ar + O@sub 2@, C@sub 2@F@sub 6@ + O@sub 2@, and SF@sub 6@ + Ar. All ions exhibited fairly simple ion-energy distributions that were indicative of the plasma potential. For pure CF@sub 4@, the two dominant ions observed were CF@sub 3@@super +@ and CF@super +@, but 3 other ions exhibited intensitites that were within a factor of 3 of the dominant ions. Similar behavior was observed in CF@sub 4@ + Ar mixtures with the addition of a significant flux of Ar@super +@ ions. For CF@sub 4@ + Ar + O@sub 2@ mixtures, 9 different ions exhibited fluxes whose magnitudes were within a factor of 2 of each other, thus indicating the complexity of the plasma-surface interactions in multi-component gases. In pure C@sub 2@F@sub 6@, CF@sub 3@@super +@ was the dominant ion, with only minor contributions observed from other ions. In mixtures of C@sub 2@F@sub 6@ and O@sub 2@, a host of other ions are formed, but the dominant ions are either CF@sub 3@@super +@ or O@sub 2@@super +@, depending upon the mixture. In SF@sub 6@ + Ar mixtures, all of the SF@sub x@@super +@ ions are observed, with the lower mass ions exhibiting larger intensities.

3:20pm **PS2-MoA5 Diode Laser Measurements of CF@sub x@ and CO Radicals in an Inductively Coupled GEC Reference Cell***, G.P. Deering, **W.L. Perry**, H.M. Anderson,* University of New Mexico

Diode laser absorption measurements have been made on CF, CF@sub 2@ and CO radicals in an inductively coupled GEC reference cell. The GEC reference cell was modified with a quartz confinement ring around the source region to stabilize the plasma. Optical emission and Langmuir probe studies indicated this modification resulted in fluorocarbon discharges with a plasma chemistry similar to that found in commercial etch tools. The experiments in this study focused on radical concentrations found in the reactor under typical high density plasma etching conditions. At 300 W source power, 100 W bias power and 10 mTorr C@sub 2@F@sub 6@ pressure in the GEC cell, etching proceeded at about 5000 A/min. A range of source power and bias power conditions, from 100 to 400 W and from 0 to 130 W, respectively, was employed. The time evolution of CF, CF@sub 2@ and CO in a C@sub 2@F@sub 6@ plasma was monitored during an approximate 2 minute etch cycle. Chamber cleanliness and bias was found to exert a strong influence on radical densities. 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.

3:40pm **PS2-MoA6 Cavity Ring Down Spectroscopy on an expanding Ar/C@sub 2@H@sub 2@ Plasma***, A.H.M. Smets, K.G.Y. Letourneur, **M.G.H. Boogaarts**, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

In this contribution we present the first results obtained from a cavity ring down spectroscopy (CRDS) setup for the detection of low density species in a plasma reactor. In this reactor research is carried out on the use of an expanding plasma beam produced by a cascaded arc for the fast deposition of thin films. In the plasma beam acetylene is dissociated in several radicals which will react at the substrate to form hydrogenated amorphous carbon (a-C:H) films. At the moment the C@sub 2@H radical is considered to be responsible for the diamondlike quality of the a-C:H films. The aim of this project is to measure radical densities (C@sub 2@H, CH and H(n=2)) by using CRDS technique. CRDS is an absolute absorption technique based upon the measurement of the rate of absorption of the light pulse confined in an optical cavity. The absolute density of the n = 2 state of atomic hydrogen has been measured in an Ar/C@sub 2@H@sub 2@ expanding deposition plasma. From the measured H(n=2) densities it can be concluded that the C@sub 2@H radical is produced dominantly in an expanding Ar/C@sub2@H@sub2@ plasma. The results obtained by CRDS measurements on radicals will be used to develop a model for the growth of a-C:H films.

4:00pm **PS2-MoA7 VUV-Visible Emission Spectroscopy Investigation of Frequency Effects in Low Pressure Plasmas***, **A.C. Fozza**,* École Polytechnique, Canada*; M. Moisan,* Université de Montréal, Canada*; M.R. Wertheimer,* École Polytechnique, Canada

Low pressure (p@<=@10 Torr), high frequency (HF) plasmas have been used for many years in various processing steps in very-large scale integration (VLSI) manufacturing of integrated circuits, and are now increasingly used as an efficient method for surface modification of polymers. In order to optimize a particular plasma process, the operator can vary such "external" (operator-set) parameters as the HF power, pressure, feed gas composition, reactor geometry, excitation frequency, etc. In the present study, we focus on the effect of the excitation frequency, f, a parameter which has received relatively little attention in the literature over the years. The difficulties encountered in designing meaningful frequency - dependent experiments are the following: - varying f over a wide range requires that one change the reactor and/or the power-delivery system, which usually calls for a change of the plasma volume; - working at constant electron density, n@sub e@, or absorbed HF power density, P@sub a@, has frequently not been taken into consideration. These difficulties can be avoided by the use of surface wave discharges (SWD), which constitute the most thoroughly modeled type of HF plasmas. SWD plasma sources possess great flexibility: a very broad (continuous) range of excitation frequencies, wide ranges of operating pressures and plasma densities, and high coupling efficiency. In earlier experiments in these laboratories, we have examined f-dependence of plasma deposition and etching experiments.@footnote 1@ The present experiments have been designed to investigate f-dependence more "directly", by studying optical emission from pure gases or their mixtures, as recently reported for the case of 2.45 GHz excitation.@footnote 2@ The vacuum ultraviolet (VUV) to visible emission from SWD plasmas in pure hydrogen or 0.07 H@sub 2@/0.93 Ar mixture have been investigated over a broad range of excitation frequency (50@<=@ f @<=@ 200 MHz) using a spectrophotometer with a known (calibrated) transfer function. As in earlier experiments,@footnote 1@ we have been able to interpret the f-dependence of emission intensity (atomic lines and molecular bands) in terms of changes of the electron energy distribution function. @FootnoteText@ @Footnote 1@ M. Moisan, C. Barbeau, R. Claude, C.M. Ferreira, J. Margot, J. Paraszczak, A.B. Sá, G. Sauvé, and M.R. Wertheimer, J. Vac. Sci. Technol. B9, 8 (1991). @Footnote 2@ A.C. Fozza, A. Kruse, A. Holländer, A. Ricard, and M.R. Wertheimer, J. Vac. Sci. Technol. A16, 72 (1998).

4:20pm **PS2-MoA8 Plasma Sheath Electric Field Strengths Above a Grooved Electrode in a Parallel-Plate Radio Frequency Discharge***, **U. Czarnetzki**,* Universitaet GH Essen, Germany*; G.A. Hebner,* Sandia National Laboratories*; D. Luggenholscher, H.F. Dobele,* Universitaet GH Essen, Germany*; M.E. Riley,* Sandia National Laboratories

During plasma etching of microelectronic structures, the direction and energy of the ions that strike the surface has a major influence on the characteristics of the etch profile. In an ideal case, the sheath electric field vector will be perfectly perpendicular to the surface so that ions accelerated from the bulk plasma above the wafer will strike the wafer surface at normal incidence. In reality, the wafer surface is a multidimensional surface with several layers of subsurface dielectric that can significantly modify the electric field direction and ion trajectories. To examine the details of the spatial distribution of the electric field strength in the sheath region above an electrode with surface structure, and to provide data to validate recent advances in multidimensional sheath models, we have measured sheath electric fields above a structured electrode. The magnitude of the sheath electric field above a grooved electrode was measured using a novel, two color, laser induced fluorescence technique. Spatially resolved electric fields in the sheath region were determined by mapping the field induced Stark splitting of the n = 14 level in atomic hydrogen. Measured electric field values are in good agreement with calculated values. This work was performed at the University of Essen. GAH thanks the Deutsche Forschungsgemeinschaft for a travel grant in the frame of the SFB 191. GAH and MER were supported by the United States Department of Energy (DE-AC04-94AL85000). Expert technical support by Rainer Fuhrer is gratefully acknowledged.

4:40pm **PS2-MoA9 Ultrahigh Frequency vs. Inductively-Coupled Chlorine Plasmas: Comparisons of Cl and Cl@sub 2@ Concentrations and Electron Temperatures Measured by Trace Rare Gases Optical Emission Spectroscopy***, **V.M. Donnelly**, M.V. Malyshev*,* Bell Laboratories, Lucent Technologies*; S. Samukawa,* NEC Corporation, Japan

Using trace rare gas optical emission spectroscopy, Cl and Cl @sub 2@ number densities (n@sub Cl@ and n@sub Cl2@) and electron temperatures (T@sub e@) were measured for two source configurations of high-density chlorine plasmas. In one configuration, the reactor was outfitted with a spoke antenna, operated at a resonant ultrahigh frequency (UHF) of 500 MHz. Alternatively, the same reactor was configured with a single loop, inductively coupled plasma (ICP) source operated at a radio frequency of 13.56 MHz. Optical emission from trace amounts (1% each) of rare gases added to the main Cl@sub 2@ feed gas were recorded as a function of power and pressure, during slow etching of the SiO@sub 2@-coated Si wafer. Modeling was used to derive T@sub e@ from these data. Additional emission from Cl@sub 2@ (at 305.0 nm) and Cl (numerous lines between 700 and 900 nm), normalized to the appropriate emission from the rare gases (i.e. actinometry) was used to obtain n@sub Cl@ and n@sub Cl2@. In the ICP, T@sub e@ decreased monotonically from 5.5 to 1.2 eV as a function of increasing pressure between 1 and 20 mTorr. Conversely, with the UHF configuration, T@sub e@ was 3.3 eV, independent of pressure between 1 and 7 mTorr, and then decreased to 1.7 eV as pressure was increased to 27 mTorr. At the same input power (1000W), both sources resulted in electron densities of 1 x 10@super 11@cm@super -3@ at 3.5 mTorr, yet the UHF plasma was much less dissociated (30%) than the ICP (70%). This is attributed to differences in the electron energy distributions in the two plasmas, especially at low pressure, caused by differences in energy transfer from the E-field to the electrons, through collisions with the gas. @FootnoteText@ *Also at Princeton University

5:00pm **PS2-MoA10 Spectroscopic Measurements in an Inductively Coupled RF Discharge in Hydrogen@footnote 1@***, **M.L. Huebschman**, R.D. Bengtson, J.C. Wiley, J.G. Ekerdt,* University of Texas, Austin*; V. Bakshi,* International Sematech

Spatially resolved electron temperature profiles, T@sub e@(r,z), and plasma density profiles, n@sub e@(r, z) were measured with a multi-chord, multi-channel optical emission spectrometry in inductively coupled hydrogen plasmas over a range of RF power and pressure in a semiconductor growth and analysis chamber. The intensities from eighteen simultaneous chords viewing the plasma were measured for ten hydrogen Balmer lines. The calibrated intensities were Abel inverted to give local densities of the upperstate populations. Spatially resolved temperature profiles were obtained from the ratio of line intensities. Electron density profiles, n@sub e@(r,z) were determined from a collisional-radiative model@footnote 2@ using the electron temperature, pressure balance, and the populations of levels n = 3, 4, 5, and 6. Measurements were made with hydrogen pressures of 5 - 50 mTorr and with input powers from 50 - 200 W. Measured density and temperature profiles will be compared with fluid models. There are clear indications of capacitive coupling in the profiles. These experiments and models are motivated by the desire to develop physically accurate computational models of a simple chemical system -hydrogen on silicon- in a simple geometry which could be verified by measurements. @FootnoteText@ @footnote 1@Research supported in part by the Texas Advanced Research Program. @footnote 2@L. C. Johnson and E. Hinnov, J. Quant. Spectrosc. Radiat. Transfer. Vol. 13, 333 (1973).

Surface Science Division
Room 308 - Session SS1+NS-MoA
Novel Surface Probes

Moderator: J.T. Yates, Jr., University of Pittsburgh

2:00pm **SS1+NS-MoA1 Momentum Resolved ESDIAD, A New Technique, Probing the Low Frequency Motion of Adsorbed Molecules on Single Crystal Surfaces@footnote 1@***, **J.W. Ahner**, D. Mocuta, J.T. Yates, Jr.,* University of Pittsburgh

A new technique, Momentum Resolved ESDIAD (Electron Stimulated Desorption Ion Angular Distribution), provides a method for taking snapshots of the zero-point position and lateral momentum of particles adsorbed on crystalline surfaces. By employing state of the art electronics and computer technology it is possible to record for each desorbing particle the desorption direction together with the flight time. Highly momentum and directional resolved images are obtained, with time-of-flight resolution in the picosecond range and data acquisition rates up to 100 kHz. This enables us to deconvolute spatial and momentum contributions to the ESDIAD pattern and to map the low frequency motion of the adsorbed particles. These maps reflect the adsorbate interactions with the substrate and with neighboring species on the substrate. For selected examples we will present data 'movies' demonstrating how these unique maps of the dynamical behavior of adsorbed species are used in several ways to probe the lowest energy states, as well as to measure the momentum distribution when the particle gains thermal energy. One major opportunity involves dissimilar chemisorbed species which, when imaged together in momentum and real space, give new insights into the first stages of interaction between the species, leading ultimately to a chemical reaction. In addition we present lateral momentum distribution studies for an adsorbed molecule with a rotational symmetry axis showing the rotation of the molecule on its adsorption site about this axis. Such information can be used as a basis for thinking about anisotropies in lateral motion of particles on surfaces. @FootnoteText@ @footnote 1@work supported by DOE/BES.

2:20pm **SS1+NS-MoA2 UV Spectroscopy of CO and Benzene on Pt(110)***, N. Chen, I. Lee, **R. Masel**,* University of Illinois, Urbana

Recently there has been some controversy about the role of d-backbonding in the adsorption of gases on transition metals. People have suggested that the antibonding orbitals should shift, but without any direct measurements, the theory remains controversial. In this paper we use a standard HREELS spectrometer, with modified electronics to measure the equivalent of a UV spectrum for two different systems: CO on Pt(110) and benzene on Pt(110). In the CO case, the UV spectrum shows peaks at 5.41, 5.58 and 7.91 eV independent of coverage. By comparison, gas phase CO shows peaks at 6.04, 6.92, 7.58, and 7.94 eV. The large shifts are indicative of the antibonding orbitals being stabilized, as one would expect from the Blyholder model and recent calculations of Ilias et al, Surface Science 376, (1997) 279 but not with the calculations of Ohsishi and Watarri Phys Rev B 49(1994)14619. In the benzene case we observe two different spectra: a first monolayer spectrum with a broad peak center at 4.71 eV, and a multilayer spectrum with peaks at 3.78, 4.73, 6.11 and 6.82 eV. The multilayer spectrum matches the spectrum of condensed benzene, but the first monolayer spectrum is quite different. Again these results suggest that there is a substantial stabilization of the antibonding orbitals of adsorbed benzene. Together these results show that UV spectroscopy provides useful information about adsorbates on surfaces.

2:40pm **SS1+NS-MoA3 Calorimetric Measurements of Metal Adsorption and Adhesion Energies on Clean, Single-Crystalline Surfaces***, **C.T. Campbell**, J.T. Stuckless, D.J. Bald, D.E. Starr, J.E. Musgrove,* University of Washington **INVITED**

The adsorption and adhesion energies of metals on solids are important in many materials and chemistry applications including oxide-supported metal catalysts, bimetallic catalysts, epitaxial thin film growth, metal-ceramic interfaces in microelectronics, metalization of polymers, composite materials and metal adsorption on minerals in soils. The heats of adsorption of metals have been measured calorimetrically for the first time on clean, single-crystalline surfaces. A pulse of metal vapor from a chopped atomic beam adsorbs onto an ultrathin single crystal's surface in ultrahigh vacuum, causing a transient temperature rise. This heat input is detected by a pyroelectric polymer ribbon, which is gently touched to the back of the crystal during calorimetry. The sticking probability is measured by detecting the reflected fraction mass spectrometrically with a line-of-sight modification of the King and Well's method. The differential heat of adsorption is thus measured as a detailed function of coverage up through multilayer coverages. The integral heat of adsorption also provides the adhesion energy of the metal film, if the surface free energy of the clean metal surface is known. Adsorption and adhesion energies for metals (Pb or Cu) on the clean Mo(100) surface, on well-defined surface oxides of Mo(100) and W(100), and on clean and hydroxylated MgO(100) thin films will be reported. By comparing a variety of surfaces in Pb and Cu adsorption, an interesting correlation between the growth morphology of thin metal films and the initial heat of adsorption of the metal is revealed. The sticking probability also correlates with the heat of adsorption of the metal.

3:20pm **SS1+NS-MoA5 Multispectral Image Classifications of Si(001) Surface Electronic Structure***, **K.M. Horn**, B.S. Swartzentruber, G.C. Osbourn,* Sandia National Laboratories

We have imaged the electronic structure of Si(001) surfaces by applying multispectral image analysis techniques to multi-bias STM conductance data. Atomic surfaces are first characterized by recording conductance spectra, C(V), at each point in a 2D scan of the surface. The resulting 3D data set, (x, y, C(V)), is then converted into a series of bias-dependent conductance images. These images are analyzed to produce a single, color-coded, classed image that reflects the surface’s electronic structure. The image analysis is performed by a computed grouping algorithm that identifies pixels sharing common conductance characteristics. The resulting classed images distinguish features not clearly resolved in a topographic image, and reveal stark electronic differences between topographically similar features. We first demonstrate the reliability of this classification technique on simple Si(001) features. Classed surfaces are then presented for various surface defects and Si and Ge structures that have been deposited on the Si(001) surface. These electronic structure images reveal features that are not readily visible or distinguished in a constant-current topograph. Direct comparison of the conductance spectra from these features confirms the classification result. This computer-based data reduction technique may prove useful in defect detection, validating surface models, and in understanding more complicated systems in which atomistic models are derived from a limited number of single-bias topographic images. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S.DOE under contract DE-AC04-94AL85000.

3:40pm **SS1+NS-MoA6 A Simple Nulling Technique for Measuring Complex-Valued Nonlinear-Optical Susceptibilities of Interfaces***, **J.R. Dennis**, V. Vogel,* University of Washington

For studies of isotropic interfaces by nonlinear optics, a general technique is presented to measure the complete second-order surface susceptibility, up to an overall phase factor. The measurement and data analysis are simple and rapid, with no use of a variable reference phase, and the susceptibility is overdetermined, allowing consistency checks. The technique involves measuring the complete polarization state of the nonlinear-optical signal by nulling the signal, for several linear polarizations of the input beam. Mesurements of second harmonic generation from Langmuir monolayers of the liquid crystal 4'-n-octyl-4-cyano-biphenyl (8CB) have been made with this technique, giving results which agree with previous data, and also revealing a small phase shift between some susceptibility components. This phase shift may be explained by introducing a complex dielectric constant for the monolayer at the second harmonic frequency. Data for the free surface of isotropic 8CB have also been analyzed with this technique. The technique is particularly well-suited to testing or fitting different models of Fresnel factors and local-field factors.

4:00pm **SS1+NS-MoA7 Characterization of Near-Field Probes for Enhanced Raman Spectroscopy***, **C.E. Jordan**, L.J. Richter, R.R. Cavanagh, S.J. Stranick,* National Institute of Standards and Technology

Near-field Raman spectroscopy can potentially obtain chemical specificity with the subwavelength resolution of a near-field scanning optical microscope (NSOM). Signals from a single crystal diamond sample have been evaluated to assess the limits of this technique. Three different types of illumination mode fiber optic probes have been used in the near-field Raman experiments: an uncoated probe; a probe coated with a smooth layer of aluminum which has an aperture that is less than 100 nm in diameter; and a probe coated with a smooth layer of aluminum and then overcoated with a rough layer of silver. In order to discriminate between the enhanced contribution to the Raman signal observed in the near-field of the probe and bulk scattering, the Raman intensity from each type of probe is measured as a function of the probe sample separation. Very little change in the Raman intensity is observed as a function of probe sample separation when an uncoated fiber optic probe is used. For an optical probe coated with a smooth layer of aluminum the Raman intensity is about a factor of seven higher when the sample is in the near-field of the probe compared to the intensity measured when the sample is farther than 100 nm away from the probe. Probes that are coated with a rough silver film show a greater enhancement in the near-field Raman intensity than is observed for probes coated only with aluminum.

4:20pm **SS1+NS-MoA8 Element Specific Real-Space Imaging Surface Crystallography***, **L. Houssiau**, J.W. Rabalais,* University of Houston

Scattering and recoiling imaging spectrometry (SARIS) extends the technique of time-of-flight scattering and recoiling spectrometry (TOF-SARS) to include both spatial and time resolution of scattered and recoiled particles. SARIS uses a time-resolving, position sensitive, microchannel plate (MCP) detector, resistive anode encoder (RAE), time-to-digital converter (TDC), and a triple axis UHV goniometer to measure the velocity-resolved spatial distribution patterns of scattered and recoiled particles produced by a keV beam of pulsed ions from on a crystalline surface. The images combine the advantage of atomic scale microscopy and spatial averaging simultaneously since they are created from a macroscopic surface area but they are directly related to the short-range (< 10 Å) atomic arrangements in the surface. The non-planar scattering features in the images are not normally observed in conventional ion scattering experiments using small-area detectors. The technique is applied to carry out real space imaging of Ni(110) and oxygen chemisorbed Ni(110) with 4 keV He@super +@ ions. A mapping of the entire hemisphere where the ions are reflected was made possible by collecting several images at different angles and merging them together. These maps reveal the blocking cones of surface atoms, which gives a real space image of the crystal surface. After oxygen exposure, the images are modified and reveal the O chemisorption sites. The features of these images can be accurately reproduced by classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC).

4:40pm **SS1+NS-MoA9 An Axial Resonant Force Probe for Atomic Force Microscopy***, **J.A. Harley**, T.W. Kenny,* Stanford University

A resonant force probe has been constructed which exhibits high force sensitivity from a stiff transducer with a stationary tip. The resonant beam is mounted vertically relative to the surface, as in shear force microscopy, but a tether has been added near the tip. The tether forces the beam to oscillate in a pinned-pinned mode while the tip remains stationary, but does not interfere with axial forces. This configuration has several advantages over current force measurement techniques. First, since the beam is perpendicular to the surface, the probe is not susceptible to force gradient instabilities. Second, the stationary tip provides high spatial resolution in the force measurements. Typical oscillating cantilevers average forces over the oscillation amplitude. Third, since the oscillations can be large, the resonant detection method is not as demanding on the secondary detector, so the force sensitivity in a piezoresistive sensor could approach that of optical lever techniques. Finally, the oscillator could potentially be encapsulated, allowing a high Q resonator in a liquid environment. The beam was constructed out of single crystal silicon, and measures 0.2 x 3 x 200µm, with an implanted piezoresistor to detect the oscillations. The axial spring constant is over 200N/m. Resonant frequency shifts of 30kHz/µN are detected using a phase-lock loop circuit. In air, the oscillator is heavily damped (Q of 15) but still demonstrates 10nN force resolution in a 1kHz bandwidth. In a moderate vacuum the resonance quality improves to 1200, and10pN force resolution is expected. The design, analysis, and theoretical limitations of these sensors will be discussed.

5:00pm **SS1+NS-MoA10 Super Transmission and Resolution Energy Analyzer and Mass-Analyzer System (STREAMS)***, K. Siegbahn, R. Maripuu,* ESCA LASER Lab Institute for Materials Science, Sweden*; **N. Kholine**,* Russian Academy of Sciences, Russia*; U. Golikov,* State Technical University, Russia*; M. Larin,* Joint Stock Co. CRYOVACS, Russia

A new type of instrument for scientific and technological research is proposed. Its main peculiarity and advantage are the capability to separate charged particles in accordance with their energies and masses on high level of resolution and sensitivity. A basis of the spectrometer is electrostatic axially symmetrical field structure with matched radial and axial potential gradient. The electron optical system can function either in dispersion or time-of-flight mode of operation. The charge particles follow the same trajectories in this field independently of the mode of operation. Electron spectroscopy or mass-spectroscopy information from the same point of the analyzed sample can be received by switching over to the appropriate potentials of the power source and the detector system. So one and the same instrument can function as a high performance electron spectrometer or a mass-spectrometer. Relative energy resolution better than 0.05% in the energy range of 20-3000 eV and mass resolution more than 5000 in the mass range 1-500 a.e.m. are easily realized for acceptance solid angle of the spectrometer equals to at least 30% out of hemisphere. The diameter of the analyzer is 200 mm, its length is 600 mm. An ultra high vacuum is ensured in the spectrometer at the level 10@super-11@ mbar by oil free pumping system with highly economical cryo condensation-absorption pump cooled by liquid helium. Almost all the spectrometer is made of nonmagnetic materials and first of all from titanium. The surfaces faced into vacuum have special plating with very low absorption-desorption capacity. So ultra high vacuum is achieved without baking out the spectrometer.

Surface Science Division
Room 309 - Session SS2-MoA
Surface Chemistry on Model Catalysts

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

2:00pm **SS2-MoA1 Adsorption and Mass Transfer Processes on Stepped Metal Surfaces***, **J.E. Reutt-Robey**,* University of Maryland, College Park **INVITED**

We present experiments that explore the role of crystallographic steps in regulating the propagation of surface chemical processes. Using scanning tunneling microscopy as the primary structural probe, we track the evolution of step structures on clean metal surfaces, under chemical adsorption, and under reaction conditions. Substantial step motions are observed during these processes on vicinal Ag(110) and Al(111) substrates, even at room temperature, revealing these steps as efficient adatom sources and sinks. The interplay between these step motions and molecular events is further investigated. Atomically resolved STM measurements of adlayer structures, in conjunction with infrared spectroscopic characterization of the adsorbates, reveal the lateral distribution of adsorbates with respect to the step edge, and their chemical speciation. For the oxidation and hydrogenation reactions that we have investigated on these metallic substrates, steps serve two principal roles: They act as efficient adatom sources for the formation of adsorbate-substrate complexes. They introduce domain boundaries that facilitate mass flow in both adsorption and reaction.

2:40pm **SS2-MoA3 Visualization of Heterogeneously Catalytic Processes***, M. Bode,* ***M. Getzlaff****, R. Wiesendanger,* University of Hamburg, Germany

The goal of this study is to a get deeper insight into the understanding of heterogeneous catalysis by combining the special merits of scanning tunneling microscopy/spectroscopy (STM/STS) and ultra-violett photoemission spectroscopy (UPS). We report on the electronic structure and the development of the adsorption process of hydrogen covered Gadolinium films being exposed to carbon monoxide. Clean Gd(0001) films were epitaxially grown on W(110). These films were exposed to hydrogen which leads to a local quenching of the d@sub z@@super 2@-like surface state being characteristic for the clean Gd(0001) surface. Due to the high spatial resolution of STM and its sensitivity to the local density of states at close to the Fermi-level, the adsorption process can be visualized and directly be correlated to the electronic properties measured by from UPS. The adsorption process at room temperature consists of five steps. At the very beginning the total amount of CO causes a removal of hydrogen from the surface. In the next two steps the rest of the adsorbed hydrogen atoms is removed and carbon and oxygen remains at the surface. In the intermediate regime CO dissociates and carbon and oxygen is adsorbed at or near the surface. This information is corroborated by investigations of clean Gd(0001) being exposed to CO and oxygen, respectively. The last step demonstrates the oxidation to Gd@sub 2@O@sub 3@ acting as catalyst for the transformation of CO to CO@sub 2@ which creates stable carbonate species at the surface.

3:00pm **SS2-MoA4 Studies of Oxygen Species on a Heated Silver Membrane***,* ***R.J. Beuhler****, R.M. Rao, M.G. White,* Brookhaven National Laboratory

Oxidation reactions catalyzed by silver are a multi billion dollar enterprise worldwide. Such reactions have been investigated extensively by conventional surface science techniques, however, applications using state- or species-selective laser techniques are difficult to carry out for practical reasons specific to Ag surfaces. For example, the dissociative adsorption cross section of O@sub 2@ on Ag is on the order of 10@super -4@, which means that the high pressure of O@sub 2@ impinging on a silver surface makes state-selective detection of reaction products under collision free conditions nearly impossible. As a step towards understanding of the dynamics of oxidation reactions on Ag, we have undertaken a study of the oxygen species and reactions on the high vacuum side of a heated silver membrane. High surface coverages of O-atoms are produced by dissociative adsorption of molecular oxygen on the high-pressure side of a heated Ag-foil through which the O-atoms diffuse to the surface. Reactions at the high vacuum side can be studied under conditions that allow energy and spectroscopic analysis of the products. Preliminary results have been obtained for the recombination reaction O@sub (a)@ + O@sub (a)@ = O@sub 2(g)@ using (2+1) REMPI laser spectroscopy to probe state and energy distributions of the desorbing molecules. Initial measurements on the yield and temperature dependence of the oxidation reactions of CO and ethylene at intermediate pressures (10@super -5@-10@super -4@ Torr) have also been performed. These results and limitations in the foil experiment will be discussed.

3:20pm **SS2-MoA5 Promotion through Gas Phase Induced Surface Segregation: Methanol Synthesis from CO, CO@sub 2@ and H@sub 2@ over Ni/Cu(100)***,* ***I. Chorkendorff****, J. Nerlov,* Technical University of Denmark, Denmark

The synthesis rate of methanol formation over Cu(100) and Ni/Cu(100) from various gas mixtures of CO, CO@sub 2@ and H@sub 2@ have been studied. It was found that the presence of submonolayer quantities of Ni leads to a strong increase in the rate of methanol formation from mixtures containing all three components whereas Ni does not influence the rate from mixtures of CO@sub 2@/H@sub 2@ and CO/H@sub 2@, respectively. The influence of the partial pressures of CO and CO@sub 2@ on the rate indicates that the role of CO is strictly promoting. From temperature programmed desorption spectra it follows that the surface concentration of Ni depends strongly on the partial pressure of CO. In this way the increase in reactivity was interpreted as a CO-induced structural promotion introduced by the stronger bonding of CO to Ni as compared to Cu. It is suggested that this type of promotional behavior will be of general importance in existent catalysts and perhaps even more relevant in the development of new or improved bimetallic catalyst

3:40pm **SS2-MoA6 Carbon-Sulfur Bond Activation in Adsorbed Methylthiolate on Ni(100) with Gas Phase Atomic Hydrogen at 120 K***,* ***A.T. Capitano****, J.L. Gland,* University of Michigan

Low temperature carbon-sulfur bond activation has been observed during reaction with both gas phase atomic and subsurface hydrogen. These results show for the first time that hydrogen can directly induce C-S bond activation in an adsorbed species. This new surface reaction provides exciting new opportunities for examining fundamental mechanisms of hydrodesulfurization on surfaces under UHV conditions. Gas phase atomic hydrogen breaks the C-S bond in methylthiolate resulting in the formation of methane even at 120 K on the Ni(100) surface. These results indicate that the energy for C-S bond activation is furnished by the atomic hydrogen. In contrast, coadsorbed hydrogen causes no C-S bond activation in methylthiolate. For a constant flux of gas phase atomic hydrogen, the rate of methane formation is first order in methylthiolate coverage indicating a direct Eley-Rideal reaction. Some adsorbed methyl and methylthiolate can remain on the surface after reaction, depending on atomic hydrogen exposure. During subsequent TPD experiments, addition of hydrogen to these intermediates results in three methane formation processes. Subsurface hydrogen breaks the C-S bond in methylthiolate at 200 K. Methyl hydrogenation by coadsorbed hydrogen occurs at 250 K. Or, thermal activation of the C-S bond by the surface is observed at 320 K. Taken together, these results demonstrate that energetic forms of hydrogen can break C-S bonds by direct addition to adsorbed thiolates on metal surfaces. The new mechanistic information generated using this approach may have substantial implication in fields ranging from catalytic hydrodesulfurization to stability of microelectronic devices.

4:00pm **SS2-MoA7 Propylene Oxidation on the Pt (111) Surface over an Extended Range of Coverages***,* ***A.M. Gabelnick****, J.T. Sipowska, J.L. Gland,* University of Michigan

The reactions of propylene and oxygen coadsorbed on the Pt (111) surface have been characterized over an extended range of coverages using TPRS. Unexpected modification of the oxidation process is observed for high coadsorbed coverages. Initiation of propylene oxidation results in water formation at 200K which appears to involve abstraction of the acid methyl hydrogens. This low temperature reaction becomes increasingly important for high coadsorbed coverages suggesting that direct interaction between propylene and coadsorbed atomic oxygen may play an important role for high coadsorbed coverages. For the highest coadsorbed coverages and excess propylene we were surprised to observe acetone and acetic acid partial oxidation products. Large coverages of coadsorbed propylene also cause the formation of a new low temperature molecular oxygen peak at 140 K. For both coadsorbed molecular and atomic oxygen, the primary products observed are water, carbon dioxide, and carbon monoxide. Following initial water formation near 200 K, the dominant water peak appears at 300 K over the entire range of coverages. Further increase in temperature results in carbon dioxide formation at 350K. Oxidation of propylidyne has a larger activation energy and occurs in one step at 370K. At higher temperatures further propylidyne oxidation and decomposition resembles that of propylene. Large coadsorbed coverages result in low temperature reaction and modified reaction selectivities.

4:20pm **SS2-MoA8 The Catalytic Chemistry of Small Hydrocarbons on Palladium: Cyclization, and Hydrogenation***,* ***W.T. Tysoe****, H. Molero, M. Kaltchev,* University of Wisconsin, Milwaukee

The reaction pathways for acetylene trimerization catalyzed by palladium is investigated using a range of surface-sensitive techniques. It is found that benzene is formed from acetylene via the intervention of a metallocyclic C@sub4@subH@sub4@sub intermediate. This further reacts with a third acetylene to form benzene. However, the catalytic reaction proceeds in the presence of a carbonaceous layer. which consists of vinylidene species. At high pressures, acetylene is formed by reaction between acetylene adsorbed on the vinylidene-covered palladium surface and adsorbed vinylidene itself to form a C@sub4@subH@sub4@sub intermediate. It is shown that the hydrocarbon part of this layer can be removed by reaction in high pressures (several Torr) of hydrogen. The activation energy for this process on molybdenum surfaces is about 6 kcal/mol. Correspondingly, the rate of acetylene cyclotrimerization is found to be accelerated by the addition of hydrogen to the reaction mixture. The implication of these phenomena on alkene and alkyne hydrogenation reactions catalyzed by transition metals will also addressed and a model for hydrogenation reactions under high-pressure conditions is proposed that yield kinetic parameters in good agreement with those measured experimentally.

4:40pm **SS2-MoA9 Dehydrogenation of Ethylbenzene Studied on Single Crystalline Iron Oxide Model Catalyst Films***, **W. Weiss**, D. Zscherpel, M. Ritter, R. Schloegl,* Fritz-Haber-Institut der MPG, Germany

We study the dehydrogenation of ethylbenzene (EB) to styrene over single crystalline FeO(111), Fe@sub3@O@sub4@(111) and @alpha@-Fe@sub2@O@sub3@(0001) model catalyst films grown onto Pt(111) substrates. The epitaxial film growth and their atomic surface structures were studied by STM and LEED. 1-2 ML thick FeO(111) films form oxygen terminated surfaces structures. The Fe@sub3@O@sub4@(111) surface exposes iron atoms in the topmost layer, as determined by a dynamical LEED intensity analysis reveiling a Pendry r-factor of 0.2. The @alpha@-Fe@sub2@O@sub3@(0001) surface exposes two different terminations, iron and oxygen, depending on the ambient oxygen partial pressure. With TDS and UPS a stong chemisorption of EB is observed on the iron terminated Fe@sub3@O@sub4@ and @alpha@-Fe@sub2@O@sub3@ films, wheras only physisorption is observed on the oxygen terminated FeO(111) film. Surface defects on the films were imaged by atomic resolution STM measurements, and the role of the oxide stoichiometry and surface defect concentrations for the model catalyst activities was studied by combining batch reactor experiments at total gas pressures of 1 mbar with pre- and post reaction surface analysis in UHV. No styrene is formed over Fe@sub3@O@sub4@ films. Fe@sub2@O@sub3@ films are catalytically active, and the styrene formation rate increases with increasing surface defect concentration on these films. This reveals Fe@sub2@O@sub3@ as the active oxide phase and atomic surface defects as catalytically active sites thereon. These defects can be steps, vacancies or adatoms. The formation of carbonaceous surface deposits that deactivate the model catalyst films after about 30 min reaction time was monitored with a PEEM microscope. A pattern formation is observed which indicates that the catalyst deactivation is a site selective process, which presumably starts at extended surface defects.

5:00pm **SS2-MoA10 Chemisorption on and Modification of Molybdenum Carbide Surfaces***, **E. Zahidi**, C. Morin, H. Oudghiri-Hassani, P.H. McBreen,* Université Laval, Canada

Early transition metal carbides and nitrides are materials that combine a wealth of desired mechanical, electrical and chemical properties. Not the least of which is their catalytic activity and their resistance to poisoning by sulfur. RAIRS, XPS and TPD data will be presented for the interaction of simple molecules with bulk molybdenum carbides. The samples studied were prepared using the method typically used to synthesize high surface area carbide catalysts. Data for isotope labelled NO, CO and ethylene reveal how the carbide carbon may be either removed, replaced or deposited. RAIRS results for the cyclic molecules, cyclopropane, cyclohexane and cyclobutanone provide insight on the ability of molybdenum carbide to activate alkane molecules. The study also reveals methods for cleaning and preparing molybdenum carbide surfaces.

Thin Films Division

Room 310 - Session TF-MoA

Mechanical Properties of Thin Films

Moderator: F.K. Urban, Florida International University

2:00pm **TF-MoA1 Computer Simulation Modeling of Sculptured Thin Films***, **V.C. Venugopal**, R. Messier,* Pennsylvania State University

Sculptured Thin Films (STFs) are characterized by free standing columns whose shape can be engineered as desired. Films with S-shaped, C-shaped, helicoidal or chevronic columns have been grown. Low adatom mobility and self-shadowing effects are critical for the growth of such films. To aid characterization of STFs theoretically, the growth of STFs is simulated using a simple ballistic aggregation deposition model assuming a high sticking coefficient, negligible relaxations, and low substrate temperatures. Substrate manipulations and complex substrate topographies are investigated. Clustering is found at the 1-3 nm level and is related to the larger column sizes which result from competitive growth evolution. A 3-D model of a growing STF is built up. The model structures are directly correlated to our experimental results in the relations between the incoming vapor angle @chi@@sub v@, and the resulting morphology column angle @chi@@sub m@. The final simulated structure is being used to develop mechanical models of STFs. Mechanical strength and elastic moduli can be determined at several different continuum levels and verified experimentally to develop a reliable model. Residual stress fields and other mechanical characteristics can also be studied. Using acoustic wave propagation principles, the maximum theoretical strength of these films can be determined and verified experimentally. Initial results of such models developed are presented.

2:20pm **TF-MoA2 Characterization of TiN/CN@sub x@ Multilayers Deposited by DC Magnetron Sputtering***, **M.M. Lacerda**, Y.H. Chen,* Northwestern University*; W.C. Chan,* University of Hong Kong, China*; B. Zhou, Y.W. Chung,* Northwestern University

Titanium nitride (TiN) is commonly used in wear protection coatings due to its high hardness. However, it is well known that thick TiN films develop columnar structure and are subject to cohesive failure. In this work, we used CN@sub x@ thin films to interrupt the growing TiN before the columns could initiate. The samples have been deposited by DC unbalanced magnetron sputtering at low pressure (2.5 mTorr) using an argon-20% nitrogen mixture. We applied a substrate bias of -200 V to promote ion bombardment. The CN@sub x@ thickness was kept constant at 1.3 nm. X-ray diffraction (XRD) patterns obtained at low angles (2°@<=@2@theta@@<=@5°) showed good interface between layers. XRD patterns at higher angles showed strong TiN (111) texture. The mechanical properties of the multilayers have been studied as a function of the TiN/CN@sub x@ thickness ratio (t@sub r@). Nanoindentation of samples with t@sub r@ = 2.3 showed high hardness value as compared to TiN films deposited at the same conditions. The TiN/CN@sub x@ films are at least 2.5 times harder than TiN samples. Internal stress of the same samples was calculated by the substrate curvature. Results showed that multilayers have compressive stress up to 10 times lower than TiN films. Electron microscopy results of the microstructure of these multilayered coatings will be presented.

2:40pm **TF-MoA3 Characterization of Stress-Morphology Relationships in Sculptured Thin Films (STFs)***, **R.A. Knepper**, D.E. Fahnline, R. Messier,* Pennsylvania State University

Sculptured Thin Films (STFs) are a recent development in thin film technology wherein a substrate is rotated while a columnar thin film is deposited at varying oblique angles and orientations. The resulting microstructure can thus be engineered into a number of shapes, including non-normal matchsticks, zigzags, coils, and periodically bent nematics (S- and C-shapes). STFs are highly porous and can have properties that differ greatly from both the bulk material and isotropic films of the same material. However, the nature of the relationships between STF morphology and intrinsic deposition stress is not yet understood. In this work, a set of matchstick-shaped STFs has been prepared with varying vapor incidence angles, ranging from 15° 75° from the substrate surface. The deposition results in curvature changes along the two directions of the substrate surface that have been measured by a laser scanning method. These measurements are then used to calculate the biaxial stresses in the films. The measured stresses decrease with decreasing morphology angle, with an abrupt change at a vapor incidence of 45°, and are anisotropic with respect to direction. The stresses measured ranged from 60 MPa to 0.4 MPa. The implications of these results to the general sets of STFs will be discussed. The findings of this research may be used to evaluate future models of the origins of stress in STFs, as well as to control substrate curvature and avoid delaminations.

3:00pm **TF-MoA4 Mechanical Properties Measurements using Scanning Force Microscopy***, **W.N. Unertl**,* University of Maine **INVITED**

Considerable effort is aimed at using the Scanning Force Microscope (SFM) to measure the mechanical properties of surfaces with nanometer-scale resolution. The properties of interest include the Young and shear moduli, shear strength, and work of adhesion. The most widely used approach is to extract these properties from the SFM data by simply scaling the results of macroscopic continuum contact mechanics theory to the dimensions and forces of an SFM contact. This talk will focus on two aspects of this scaling problem@footnote 1@: (1) the mechanism for failure of a contact under shear and (2) the effect of creep on contacts to viscoelastic materials. In a contact subjected to a shear strain, contact mechanics predicts that a crack propagates at the interface and causes a non-linear increase in shear force until the interface ruptures and sliding begins. This behavior, called microslip, is observed for macroscopic contacts but not for SFM contacts, which suggests that the contact mechanics picture must be modified for nanometer-scale contacts. In contacts to viscoelastic materials, creep can significantly modify the formation and rupture of a contact compared to contacts to elastic materials. The most important effect is that the maximum contact area depends on the loading history and, unlike elastic materials, can reach its maximum value well after the maximum load is applied. The status of theoretical models for the analysis of contacts to linear viscoelastic solids including the effects of adhesion will be described. @FootnoteText@ @footnote 1@K.J. Wahl, S.V Stepnowski, W.N. Unertl, Tribology Lett. (in press 1998).

3:40pm **TF-MoA6 Meso-Scale Contact Hardness, Friction, and Wear of Aluminum Oxynitride Films*, S.D. Dvorak*,** *G.P. Bernhardt, O.D. Greenwood, R.J. Lad,* University of Maine

Aluminum oxynitride (AlO@sub x@N@sub y@) thin films attract interest as hard, wear resistant coatings for high temperature, oxidizing environments. We have used electron-cyclotron-resonance (ECR) plasma assisted electron beam evaporation of aluminum to grow aligned crystalline films on r-sapphire at 800 - 1100 K to nominal thicknesses of 100 nm at about 0.5 Å/s deposition rates. These AlO@sub x@N@sub y@ films were fabricated with compositions ranging from aluminum oxide to aluminum nitride, depending on the N@sub 2@/O@sub 2@ gas flow ratio in the ECR source. Film hardness as a function of depth was measured by nanoindentation, while friction and wear properties were determined during reciprocal sliding experiments using well characterized sapphire and diamond probe tips with applied loads in the micro-newton to milli-newton force range. Film topography examined with atomic force microscopy indicated rms roughness values ranging from 20 Å to 140 nm. Wear tracks examined by AFM consist of wear debris as well as microstructural features. We observe that friction is affected by the roughness of the surfaces in contact, and that these roughness effects are dependent on the hardness of the contacting asperities, as measured by a Hysitron Pico-Indentor. Inhanced surface diffusivity of oxygen and nitrogen species provided by the ECR source during film growth yields highly-oriented films with very high wear resistance.

4:00pm **TF-MoA7 Nanotribology of Single Crystal ZnO Surfaces: Relation of Atomic Level Friction to Macro Tribology of Thin Films*, J.J. Nainaparampil*,** *J.S. Zabinski, S.V. Prasad,* Air Force Research Laboratory

Atomic Force Microscopy (AFM) has been applied to the study of surface forces for more than a decade. Relatively recently, Lateral Force Microscopy (LFM) has evolved from AFM as a means to characterize surface forces in relation to friction, adhesion and surface topography. The significance of this approach is that it reveals insights into friction and wear at an atomic level. This work focuses on the nanotribology of single crystal ZnO surfaces after high temperature annealing treatments and in different gases. Annealing causes the formation of surface structures - etch pits on the 1010 surface and roughening or reconstruction on the 0001 surface. The pits and roughened areas provided lateral force contrast that could not be assigned to topography. Adhesion and relative contact stiffness were not significantly different among friction contrasting regions. The chemistry of these regions was analyzed using Scanning Electron Microscopy (SEM) and Scanning Auger Microscopy (SAM). The LFM and chemical analysis of the different single crystal surfaces will be presented. Insights into atomic level friction and wear processes will be related to the macroscopic tribology of ZnO nanocrystalline thin films.

4:20pm **TF-MoA8 Surface Stress in Silicon Oxide Layer made by Plasma Oxidation with Applying Sample Bias*,*** *A.N. Itakura,* National Research Institute for Metals, Japan*; T. Kurashina, T. Narushima,* University of Tsukuba, Japan*; **M. Kitajima,*** National Research Institute for Metals, Japan

We present the evolution of surface stress during plasma oxidation of Si(100) with applying bias voltage from -60V to +60V to the sample. The experiments were performed in a UHV condition. Oxide thickness was controlled from 0 to 3nm. The sample was a cantilever of Si(100) of dimensions 450µm x 50µm x 4µm. The bending of the lever due to stress was detected as a function of the oxidation time by a change in the reflection angle of laser beam from lever backside. Stress was calculated from the lever deflection using Stony's formula. The plasma was generated by RF discharge of oxygen gas at 13.56MHz. There has been observed three stages in the stress vs. time curve for the plasma oxidation of Si cantilever without applying sample bias. The first stage was rapidly building up of tensile stress and the second stage was the tensile stress decreasing slowly. In the last stage the stress changed to compressive. For the cases of oxidation with applying bias to the samples, stress curves showed different time dependence from that without bias. First, the stress curve showed a quick build-up of compressive stress, followed by a tensile stress formation, and the stress gradually changed to compressive one with further oxidation. The similar feature appeared in the curves with positive biases and negative biases. The stress values were not unique at same thickness but strongly depended on a bias voltage. We will discuss these stress changes in terms of the interface structure of silicon-oxide layer and silicon substrate.

4:40pm **TF-MoA9 Stress Alignment in SiO@sub 2@ Thin Films Deposited on Thin Chromium and Aluminum Film*, K.E. Coulter*,** *V. Raksha,* Flex Products, Inc.

SiO@sub2@ as a low index material in optical applications is often complicated by the intrinsic stress that induces film cracking, substrate deformation and delamination. 400 - 600nm thick SiO@sub2@ films were deposited by e-beam evaporation onto Cr (10nm) and Al (100nm) films. Using design of experiment methodology, we evaluated deposition process parameters such as rate, vacuum pressure, substrate type, coating material and storage conditions. The thin films were deposited on 50 and 175 µm thick PET substrates as well as fused silica witnesses. Analysis methods included interferometry, profilometry, microscopy, ellipsometry and an evaluation principle based on laser deflection off the free end of a coated PET strip. A correlation was established between absolute stress values measured by interferometry and the laser deflection method. Cr/ SiO@sub2@ and Al/ SiO@sub2@ films were deposited under vacuum conditions which produced tensile and compressive stress. S! tress in all SiO@sub2@ thin film stacks became more tensile with age (shelf life) regardless of the initial stress in the film. Dopants in the silica source material such as B@sub 2@O@sub 3@, Na@sub 2@O and Vycor produced films with similar correlations between stress and deposition conditions but at lower absolute stress magnitudes. In this presentation, the influence of the vacuum pressure, deposition rate, storage conditions and substrate properties will be discussed relative to the effect of stress on the thin film optical performance.

5:00pm **TF-MoA10 Investigation of Induced Recrystallization and Stress in Close-Spaced Sublimation CdTe Thin Films*, H.R. Moutinho,*** *R.G. Dhere, M.M. Al-Jassim, P. Sheldon,* National Renewable Energy Laboratory*; B.T. Mayo,* Southern University*; L.L. Kazmerski,* National Renewable Energy Laboratory

Close-spaced-sublimation (CSS) CdTe has produced the best CdS/CdTe thin-film solar cells reported to date. In all CdTe cell deposition options, a post-deposition treatment with CdCl@sub 2@/methanol solution at elevated temperature is a mandatory step for maximizing the device efficiency. We have previously reported that these large-grain CSS films do not recrystallize and that the initial in-plane stress is not completely relieved during the treatment, in contrast to films deposited by other methods (e.g. physical vapor deposition). In this work, we deposited CSS CdTe films at lower temperatures and higher deposition rates to force lower-grain-size layers, which are more susceptible to recrystallization. The objective was to induce recrystallization from the chemical/heat treatment to realize films with substantially less stress and, consequently, better device quality. The CdTe films were deposited on normal CdS/SnO@sub 2@/glass structures and chemically treated at various temperatures and times to optimize the recrystallization process. The topography and grain size of the films were determined by atomic-force microscopy, X-ray diffraction, and transmission electron microscopy, and the minority-carrier lifetime by time-resolved photoluminescence. The CdCl@sub 2@ treatment temperature was varied from 300 to 400° and the treatment time from 1 to 30 minutes. The stress in the films was investigated using X-ray techniques, and significant reduction in the stress was observed concurrent with the recrystallization/recovery process. We investigated the evolution of stress in the early stages of the treatment to establish the mechanisms through which recrystallization starts in these films. CdTe films deposited by physical vapor deposition were also analyzed, and the results were compared with the ones for the CSS films. Finally, the efficiencies of cells prepared from conventional CSS CdTe were compared to these lower stress thin-film devices.

Vacuum Metallurgy Division
Room 328 - Session VM-MoA

Plasma Assisted Surface Treatments and Coatings

Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **VM-MoA1 Low Temperature Growth of Protective Coatings in an ECR Plasma**, *C.-T. Lin, F. Li,* ***T.D. Mantei,*** University of Cincinnati

A high density microwave electron cyclotron resonance (ECR) discharge has been used to grow hard, colorless, and transparent silicon dioxide barrier coatings at deposition rates up to 0.7 µm/min and substrate temperatures from 80 to 120°C. The deposition precursors tested were tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO), and hexamethylcyclotrisiloxane (HMCTSO). Metal substrates were introduced into the process chamber through a vacuum loadlock and subjected to an in situ three minute argon plasma cleaning cycle. Oxygen was then metered into the chamber through ports located upstream just below the input microwave window, while the precursor reactant gas was introduced downstream. The total gas pressure prior to plasma ignition was 1 to 10 mTorr and the O@sub 2@/precursor flow ratios were varied from 2:1 to 8:1. The substrate temperature, measured with a clamped thermocouple, rose to 80-100°C within a few minutes and then rose slowly during the remainder of the deposition cycle to a final temperature less than 120°C. Final film thicknesses were 3 to 10 µm. Maximum deposition growth rates were 0.25 µm/min for TEOS, 0.65 µm/min for HMDSO, and 0.68 µm/min for HMCTSO, increasing with increasing precursor gas flow, increasing input power, and decreasing O@sub 2@/precursor flow ratio. Fourier transform infrared spectroscopy analysis showed mainly Si-O elemental bonding for all films, with small Si-CH@sub 3@ and SiOH components. Coating compositional analyses performed with X-ray photoelectron spectroscopy showed oxygen-to-silicon ratios of approximately 2:1, but with significant carbon percentages; e.g. the carbon fraction for TEOS films ranged from 29% with an O@sub 2@/precursor flow ratio of 2.5, down to 14% for an 8:1 flow ratio.

2:20pm **VM-MoA2 Low Temperature Polycrystalline Silicon Resistors on Glass Substrates**, ***A.T. Krishnan,*** *S.H. Bae, S.J. Fonash,* Pennsylvania State University

Polycrystalline silicon (poly-Si) thin film resistors have been processed on glass substrates at low temperatures (<300@degree@C) using a novel approach. This approach involves direct deposition of n+ polycrystalline silicon thin films using an electron cyclotron resonance (ECR) high density plasma (HDP) tool, with phosphine as the dopant source. These n+ poly-Si films have been deposited on both Corning 1737 glass and soda-lime glass substrates at 300@degree@C. The dependence of film quality on film thickness has been exploited to obtain devices with resistivities over a range of 1-10 ohm-cm. The range of resistivities that can be obtained can be further increased by altering the phosphine flow rate. The deposition rates are of the order of 100 Å per minute. The temperature coefficient of resistivity of these devices is less than 2000 ppm/@degree@C. Preliminary studies indicate that it is possible to obtain n+ poly-Si films at temperatures lower than 200@degree@C, which would allow the use of clear flexible plastic substrates. Thin film resistors processed at low temperatures find a wide range of applications, such as flat panel displays, multi-chip modules,@footnote 1@ anolog circuits, @footnote 2@ and high frequency applications.@footnote 3@ In CMOS technology, low temperature resistor fabrication would enable integration of resistors on fully processed Si chips. Conventional non silicon based resistor technology requires more than one material, such as a cermet for high resistivities and a metal for low resistivities, to achieve a wide resistivity range. Currently existing Si based resistor technologies, like LPCVD cannot be used for low temperature applications, because of the high deposition temperatures (600@degree@C, which is close to aluminum melting point) or higher temperatures needed for dopant activation (700-800@degree@C). The HDP technique allows the use of a single material (n doped poly-Si) to obtain a wide range of resistivities. Because it is Si based, it is compatible with current ULSI processing techniques. Its low deposition temperature and the fact that no annealing is required to activate dopants makes it ideally suited for low temperature applications listed above. @FootnoteText@ @footnote 1@Integration of passive components for microwave filters in MCM-D, Pieters, Philip; Brebels, Steven; Beyne, Eric, Proceedings of the 1997 6th International Conference and Exhibition on Multichip Modules 1997 Denver, CO, USA p 357-362. @footnote 2@BiCMOS analog front-end circuit for an FDM-based ADSL system Langford, D. Scott; Tesch, Bruce J.; Williams, Brian E.; Nelson, G. Rodney; Ross, Robert B.; Bechtel, Gerry R.; Lewis, Mike G, Proceedings of the 1997 Bipolar/BiCMOS Circuits and Technology p 180-182. @footnote 3@110 GHz slow-wave electrodes for velocity-matched distributed MSM photodetectors with integrated bias load, Pfitzenmaier, H.; Boettcher, E.H.; Droege, E.; Bimberg, D, Proceedings of the 1997 IEEE Lasers and Electro-Optics Society Annual Meeting, USA p 218-219

2:40pm **VM-MoA3 Closed Loop Control of Reactive Sputtering of Oxide Thin Films**, ***L. Lou,*** *M. Mai, G.W. McDonough, H.V. Walde, R. Scholl, G.A. Roche,* Advanced Energy

Rapid closed loop control of oxygen flow was used to prevent target poisoning and facilitate high growth rate during reactive sputtering. Low frequency AC reactive sputtering of Al@sub 2@ O@sub 3@ and SiO@sub 2@ was performed achieving stable film formation with high deposition rates. Thin film properties of rate, refractive index and stress are reported as a function of pressure and power. Results are compared to reactive sputtering of these films by other techniques.

3:00pm **VM-MoA4 Unbalanced Magnetron Sputtered Composite Metal-DLC Coatings**, ***X.T. Zeng,*** Gintic Institute of Manufacturing Technology, Singapore

Composite metal-diamond like carbon (DLC) coating is an approach to achieve a combination of high hardness and toughness, good adhesion, a low friction coefficient, and a low wear rate, which is ideal for various tribological applications. Previous studies often used hydrocarbon gases to produce amorphous a:C-H coating doped with metal (Ti, W, Cr) and/or their nitrides by magnetron sputtering from metallic targets. Relatively high hardness (15 ~ 20 GPa) could be obtained in these coatings by increasing the doping level at the expense of an increasing friction coefficient which results in high wear rates. This paper reports the preparations of composite metal-DLC coatings on high speed steel substrates using unbalanced magnetron sputtering of both metallic and graphite targets. W and Ti/Cr targets were used to deposit both the bond layer and transition ceramic layer to support the surface composite DLC coating. For comparison, amorphous CN@sub x@ surface coating was also prepared for sliding wear testing. Nanoindentation and scratch tests were used to characterize the mechanical properties and pin-on-disk wear tests, using @phi@9 mm alumina as the pin and 10 N normal load, were carried out to evaluate the tribological properties of the coatings. Friction coefficient of about 0.06 ~ 0.1, at an air humidity of 40% RH, hardness of 15 ~ 18 GPa, critical load of about 65 N in scratch tests, and normalized wear rate of about 5 x 10@super -8@ mm@super 3@.N@super -1@.m@super -1@ for wearing for 38000 to 76000 cycles (3400 m to 6800 m) were measured. This wear rate is substantially lower than those of the nitride coatings. The superior wear resistance coupled with good adhesion implies that composite metal-DLC coatings could be good candidates for sliding wear applications.

3:20pm **VM-MoA5 Overview of Plasma Source Ion Implantation**, ***J.R. Conrad,*** University of Wisconsin, Madison **INVITED**

Plasma Source Ion Implantation (PSII) represents a radical departure from conventional ion implantation technology. PSII circumvents the line of sight restriction inherent in conventional ion implantation. In PSII, targets to be implanted are placed directly in a plasma source and then pulse-biased to a high negative potential. A plasma ion matrix sheath forms around the target and ions bombard the entire target. Compared with conventional ion implantation, PSII minimizes the problems of shadowing and excessive sputtering of the target material, which can severely limit the retained dose of the implanted ion species. This talk will present: a historical overview of the development of PSII; a brief review of PSII physics and technology; a summary of world-wide PSII activities; a discussion of laboratory and industrial field test results in PSII; recent activities leading to scale-up and commercialization of PSII; recent extensions of PSII technology to semiconductor processing.

4:00pm **VM-MoA7 Improvement of Tribological Properties of Pure Aluminium by Isotropic ECR Ion Implantation**, ***D. Popovici,*** *B. Terreault, A. Sarkissian, B.L. Stansfield, R.W. Paynter, G.G. Ross,* INRS-Energie et Materiaux, Canada

There are serious limitations to using Al and its alloys for light-weight components: in the absence of lubrification they have relatively poor tribological properties such as high friction and wear rates in sliding contact. These characteristics are due to a low flow stress of the metal and the brittleness of the aluminum oxide. The improvement of the tribological characteristics of Al, by conventional and high energy(@>=@50keV)nitrogen and oxygen implantation has already been demonstrated. In the case of N@super +@ implantation the increase in hardness is due to the formation of an AlN film. Because relatively high substrate temperatures(400-500°C)are necessary when conventional plasma nitriding is used, the difference in the thermal expansion coefficients of Al and AlN leads to microcracks in the AlN coatings. In the case of O@super +@ implantation, the formation of a maetstable phase is followed by a thermal annealing, inducing the synthesis of nanoprecipitates of Al@sub 2@O@sub 3@ which are dense enough to pin all dislocations. In this study, we used a low temperature, low energy (30keV)isotropic PBII whith an ECR plasma source, to investigate and compare near-surface N@super +@ and O@super +@ implantation into high purity (99,99%) Al. The surface chemical composition and chemical bond formation of the implanted Al layer were investigated by AES, XPS and RBS. The surface tribological properties, structure and cristallinity were analysed by lateral force microscopy (LFM), nanoindentation and XRD. Implantation depth profiles were determined for several implantation times and sample-plasma geometries. The profiles were found to agree with TRIM simulations that supposed a monoenergetic ion source. The implantation of monoenergetic ions by our PBII technique, using a high frequency pulsed plasma and a steady high voltage for ion acceleration, allows for a precise tailoring of the implantation depth profile.

4:20pm **VM-MoA8 Molecular Dynamics Study of Al PVD Processes***, **U.P. Hansen**, P. Vogl,* Technical University Munich, Germany*; A. Kersch,* Siemens Ag, Germany

We present a computationally efficient classical many body potential that has been designed to model the Al-Al interaction in a wide range of bonding geometries ranging from bulk AL to Al surfaces and to the Al@sub 2@ dimer. It is shown that this potential yields Al elastic constants, Al surface diffusion barriers, surface formation energies and Al@sub 2@ properties in excellent agreement with experiment and/or previous ab-initio results. Detailed molecular dynamics simulations are performed that elucidate the different surface reactions taking place during Al physical vapor deposition. We find a high sticking probability for Al atoms impinging normal on Al surfaces and the sticking coefficient is decreasing with increasing incident angle to the surface normal. Detailed explanation for this prediction including atomistic surface reactions is presented. The energy dependence of the sticking probability calculated by our model deviates clearly from predictions of a simple hard sphere picture.

4:40pm **VM-MoA9 An XPS Study of the Effects of Chemical Pre-Cleaning of Aluminum Alloys on the Anti-Corrosion Properties of Plasma Deposited Films***, **C.E. Moffitt**, D.M. Wieliczka,* University of Missouri, Kansas City*; H.K. Yasuda,* University of Missouri, Columbia

DC-plasma deposited films are showing great promise as an alternative to chromate conversion for enhanced coating adhesion and corrosion protection of the aircraft alloys AA2024 and AA7075. The oxide structure of these alloys is usually modified by chemical treatments prior to application of corrosion resistant coatings. The effects of cleaning with certain chemistries employed in industry were investigated with XPS sputter depth profiling. This study of the remaining oxide layer indicates that the cleaning process leaves some undesirable deposits on the surface, which affect the stability of the coating/alloy interface region during corrosive attack. The XPS depth profiles reveal the extent of the changes in alloy surface composition after cleaning. Depth profiles of plasma film coatings on alloy surfaces treated with specific chemistries are also presented. This work was supported under Air Force contract AF F33615-96-C-5055.

Applied Surface Science Division
Room Hall A - Session AS-MoP
Aspects of Applied Surface Science Poster Session

AS-MoP1 Auger Depth Profile Analysis of Ba@sub x@Sr@sub 1-x@TiO@sub 3@ Thin Films*, M.L. Kottke,* Motorola, Inc.

High dielectric constant sputtered thin films of Ba@sub x@Sr@sub 1-x@TiO@sub 3@ are being developed for use in the storage capacitors of high density microelectronic memory circuits. The correlation of the electrical characteristics of such capacitors with the compositional and structural properties of the Ba@sub x@Sr@sub 1-x@TiO@sub 3@ films is key to optimizing device and circuit performance. This paper gives a detailed description of the methodology developed to provide quantitative Auger depth profiles with high resolution and high precision. Data will be shown giving the optimum angles of incidence for best depth resolution when sputtering with both Ar and Xe ions. Sputter rates versus angle of incidence will be provided for both Ar and Xe at 1.0 keV. Variations in sputter rate and Auger sensitivity factors with variations in composition between x=0 and x=0.7 will be presented. The Auger analysis provides insight into the accuracy of BST thin film stoichiometry measurements made by x-ray fluorescence and Rutherford backscattering techniques, and a discussion of the issues involved will be provided.

AS-MoP2 Characterization of Shallow Implants with SIMS using Electron Beam Oxidation*, M. Puga-Lambers,* *P.H. Holloway,* University of Florida, Gainesville

Secondary ion mass spectrometry (SIMS) depth profiles of boron shallow implants in silicon have been measured with a quadrupole Perkin-Elmer 6600 PHI SIMS system. Oxygen backfill from the base pressure (10@super -10@ Torr) to 10@super -6@ Torr was applied in conjunction with oxygen bombardment. Silicon wafers implanted with 8 keV As and 5 keV and 0.5 keV B to doses of 3, 5 and 1 x10@super 15@ cm@super -2@, respectively were analyzed. Maximum peak concentrations were about 2.5x10@super 21@ cm@super -3@ for As, and 1.5x10@super 21@ cm@super -3@ and 1.0x10@super 21@ cm@super -3@ for B, respectively. The peak maxima were located at 10 nm, 22 nm and 3 nm for As at 8KeV and B at 5 KeV and 0.5 keV, respectively. Oxygen backfill improved the depth resolution but degraded the dynamic range of 0.5 keV B implants by about half an order of magnitude. Simultaneous electron bombardment during oxygen backfill and during depth profiling further improved the depth resolution while maintaining the dynamic range of the SIMS analysis as measured both by the surface transients in the Si@super +@ and SiO@super +@ substrate as well as the B@super +@ signal. In addition, analysis of both the Si@super +@ and SiO@super +@ transients demonstrated that the extent of surface oxidation during oxygen backfill was accelerated by simultaneous electron bombardment. The prospects for further improvement in this technique for shallow implant profiles will be discussed.

AS-MoP3 Total Sputtering Yield of Ag/Cu Alloys Versus Composition and Temperature for 260 eV Ar+*, K.W. Pierson,* *C.D. Hawes, M.S. Vogel, N.C. Harris, P.J. Gustafson, G.C. Falkenberg,* University of Wisconsin, Eau Claire

The results of recent sputtering yield experiments have important implications concerning depth profiling of the Ag/Cu alloy system. The total sputtering yield of a range of Ag/Cu alloy compositions for various target temperatures has been measured for normally incident 260 eV Ar+ and a dose of 5.4x10@super 19@ ions/cm@super 2@. At temperatures between -50 C and +40 C the yield of all compositions between 20/80 (% atomic Ag/Cu) and 80/20 is approximately equal to pure Cu. For targets with an increased Ag percentage above 80/20 the yield climbs toward the value of pure Ag. At temperatures above 40 C, micron size cones develop on the target surface and the yield decreases dramatically in an unpredictable manner due to redeposition of ejected material. We hypothesize that the relatively sharp transition to cone development is due to the exponential nature of surface diffusion, which is believed to be necessary for cone develoopment. The low transition temperature to cone development and unpredictable yields is important for depth profiling, as these temperatures are easily attainable for improperly heat-sinked targets, high ion energy, or high ion beam flux. The fact that yield of a large range of compositions becomes approximately equal to pure Cu at low temperatures for properly heat-sinked targets is important for predicting depth scales.

AS-MoP4 Study on Reaction Mechanism of Aluminum Chemical Vapor Deposition with In-situ XPS and TOF-SIMS Measurements*, K. Tanaka,* *H. Yanashima,* Sumitomo Chemical Co., Ltd., Japan*; T. Yako,* Sumika Chemical Analysis Service Ltd., Japan*; K. Kamio,* Sumitomo Chemical Co., Ltd., Japan*; K. Sugai, S. Kishida,* NEC Corporation, Japan

Chemical vapor deposition (CVD) of Al is one of the most promising methods for multilevel metallization of ultra-large-scale integration (ULSI) circuits as it can fill via holes that have sub-half-micron diameters and high aspect ratios with superior step coverage. However, the surface morphology of CVD Al films deposited on oxidized Si surfaces is generally unsatisfactory. The CVD Al films deposited on TiN barrier layers, on the other hand, show much smoother surfaces due to higher Al island density in the early stage of growth.@footnote 1@ In the present work, the reactions of dimethylaluminum hydride (DMAH; (CH@sub 3@)@sub 2@AlH) with slightly oxidized TiN and Si surfaces were investigated in situ with x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Si substrates with/without TiN surface layer were introduced into a UHV chamber. After evacuation H@sub 2@ gas was introduced at a pressure of 1x10@super -3@ Pa and the substrates were heated to 200°C, following the introduction of DMAH vapor at partial pressures of 1x10@super -6@ to 1x10@super -4@ Pa. After CVD reaction, the chamber was evacuated to UHV again and the specimens were transfered to XPS and TOF-SIMS spectrometers in vacuum. It was observed that the native oxide layer formed on TiN surface was reduced when exposed to DMAH vapor and a clean TiN surface became to appear. The reduction of oxide and deposition of Al on TiN surface were enhanced with increase of DMAH exposure. In contrast with the TiN surface, no reduction of native oxide layer by DMAH was observed on Si surface except the uppermost surface analyzed by TOF-SIMS. The amount of Al deposited on Si surface was also decreased and substantially equal independent of DMAH exposure. The reduction of oxide and appearance of clean TiN surface must be important to account for the nucleation mechanisms of Al film growth on TiN during CVD. The difference of chemical states of adsorbed DMAH molecules on TiN and Si surfaces will also be discussed. @FootnoteText@ @footnote 1@K. Sugai, H. Okabayashi, T. Shinzawa, S. Kishida, T. Kobayashi, N. Hosokawa, T. Yako, H. Kadokura, M. Isemura, and K. Kamio, Proceedings of the 10th International IEEE VLSI Multilevel Interconnection Conference, 1993 (IEEE, New York, 1993), p. 463.

AS-MoP5 The Orientational Relationship in Epitaxial Rocksalt(001)/Rocksalt(001) and Rocksalt(001)/Perovskite(001)*, G. Chern,* National Chung-Cheng University, Taiwan*; C. Cheng,* National Cheng Kung University, Taiwan

We have grown several different oxide thin films, including MgO, SrO, NiO, and Fe@sub 3@O@sub 4@ on single crystalline MgO(001) and SrTiO@sub 3@(001) substrates by molecular beam epitaxy. These oxides have either rocksalt or perovskite structure which are two of the most standard crystalline structures in ionic crystals. By using high energy electron diffraction (RHEED) we observed some specific orientation relations between these two structures. The interface of a rocksalt/rocksalt only shows a direct matching configuration. However, the interface of rocksalt(001)/perovskite(001) shows at least two different matching configurations, direct on and 45-degree rotation of the film relative to the substrate. These results imply:(1) SrTiO@sub 3@ (or other perovskite substrate) is a "better" substrate candidate for a hetero-epitaxial thin film growth. The grown material may or may not need to be closely lattice matched to the substrate because there are two stable interface matching possibilities for an epitaxial growth. (2) Since the matching configurations are originated from the interfacial energy, a simple "electrostatic matching" instead of "geometrical matching" may be constructed for the ionic systems with different structures.

AS-MoP7 Optical and Structural Characterization of Copper-based Colloidal Particles in SiO@sub 2@ Coatings*, R. Bernal,* CICESE, Mexico*; F.J. Garcia-Rodriguez,* Univ. Autonoma de Queretaro, Mexico*; J.F. Perez-Robles,* ***F.J. Espinoza-Beltran,*** CINVESTAV-IPN, Mexico*; R. Ramirez-Bon,* Univ. de Sonora, Mexico*; Y.V. Vorobiev, J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

By using the sol-gel method were produced coatings having colloidal copper-based particles embedded in a SiO@sub 2@ matrix. The particle composition in each sample depended on the amount of copper added to the stating solutions, the atmosphere in which the samples were annealed and the annealing temperature. The optical properties of the colloidal system were determined by transmission and photoacoustic spectroscopies. X-ray diffraction, Raman scattering, and infrared measurements were used to characterize the structure of the composite glass. The model proposed by Mie was used with effective values for the optical constants of the colloidal particles to determine characteristic parameters of the colloidal system and the particle composition.

AS-MoP8 Role of Surface Chemistry on the Nature of Passive Oxide Film Growth on Fe-Cr (Low & High) Alloys at High Temperatures*, S. Seal,* ***R. Nardelli***[1]*, A. Kale, K. Casey, V. Desai,* University of Central Florida

High temperature material degradation or protection of Fe-Cr alloys are often related to the nature of their oxide scale formation. Breakdown of passive oxide films leads to localized corrosion. Many a times, various alloying elements are incorporated in these alloys to prevent high temperature degradation. Addition of selected alloying elements is cumbersome and not always cost effective. In this paper, we investigate the role of rare earth oxide coatings on high temperature corrosion prevention of both low and high Cr steel at various temperatures. An in-situ high temperature oxidation set up has been built to study the oxidation kinetics of both coated and uncoated alloys under ambient pressure and dry air. Reduction in reaction rate constants is observed in the presence of coating. While SEM and XRD are employed to study the structure and morphology of the films, XPS, AES are used to study the surface chemistry of the oxide layer. This paper relates some of these data to explain the linear, para-linear and parabolic growth kinetics observed in both low and high Cr steels.

AS-MoP9 Surface Microchemistry of Roman and Etruscan Bronzes of the Vatican Museums*,* ***E. Paparazzo****, L. Moretto,* Consiglio Nazionale delle Ricerche, Italy*; M. Sannibale,* Vatican Museums, Vatican City

The main objective of this work is to find out how a given burial site affects the surface chemistry of archaeomaterials lying in it. To accomplish this task we have explored the surface chemical composition of Roman and Etruscan bronzes of the Vatican Museums using x ray photoemission spectroscopy (XPS) and scanning Auger microscopy (SAM). The Roman bronze, a statue of the 1st century AD found in seawater, contains copper sulfides as the main corrosion products, along with minor amounts of copper chlorides. We relate the former to both the presence of sulfide ions formed in seawater via bacteria-assisted chemical reduction of sulfates and to the solubility products of copper sulfides being much lower than those of copper chlorides. Conversely, the Etruscan bronze, a helmet of the 6th century BC found in the soil, contains a mixture of copper chlorides and copper oxides which we explain as being due to corrosive attack of sodium chloride from the soil. We find that the tin, always entirely present as SnO@sub 2@, plays a beneficial role in limiting the corrosion of copper, since it is about twice as abundant, as is metallic copper, in the Etruscan bronze than in the Roman one. This beneficial role of tin is directly shown by way of SAM imaging at the surface of the two objects. Indeed, the regions that are rich in this element are virtually free of either sulfides (Roman bronze) or chlorides (Etruscan bronze), and these lateral inhomogeneities are highlighted with a spatial resolution ~ 200 nm. Our results are compared with the findings of other studies on "modern" Cu-Sn systems, as well as with the reports of historical sources.

AS-MoP10 Surface Analysis Studies of Bidri Archaeomaterials from the Collection of the British Museum*,* ***M. Anderle****, M. Bersani, M. Fedrizzi,* ITC-IRST, Italy*; L. Moretto, E. Paparazzo,* Consiglio Nazionale delle Ricerche, Italy

Bidri ware is a class of inlaid Indian archaeological metalwork, made froma Zn-Cu alloy, and characterized by a black patina which contrasts strikingly with the shiny metallic inlays. While the chemical composition of the patina is well known, the reason for its black color is not, knowledge of such a reason being an essential pre-requisite for devising appropriate schemes for both restorative and conservative purposes. In order to ascertain whether the surface microchemistry of the patina is responsible for the black color, we undertook a thorough study of Bidri samples (courtesy of the British Museum) using XPS, scanning Auger microscopy, SIMS, and EDS as a means of analysis. We find that the patina, about 0.5 micrometers thick, contains Zn, Cu, O, Cl, and C along with trace amounts of Pb and Sn. The Zn/Cu atomic ratio is about 7 in the patina and increases considerably in the alloy, whereas the interface is high in Cl and poor in Cu. Both the copper and zinc are entirely oxidized at the patina, and laterally separated from each other to a few microns, whereas Cl lateral segregation is lower than 0.5 microns. The SIMS analyses has been performed using a magnetic sector mass spectrometrer (CAMECA 4f) in depth profile and immaging mode to obtain elemental maps. SEM/EDS were also cairred out to obtain morfological and elemental information from the surface samples and from the bottom of the SIMS craters. We propose a model which explains the black color of the patina as originating from a highly-dispersed ZnO-like phase which features a broad range of light absorption coefficients.

AS-MoP11 X-ray Photoelectron Spectroscopy of Ru@sub 3@(CO)@sub 9@(MeCN)@sub 3@ Modified Platinum Surfaces*,* ***C.R. Cabrera****, E.R. Fachini,* University of Puerto Rico

The ability to tailor surfaces is important in electrocatalysis. Furthermore, the interest in obtaining clean energetic systems has driven an additional effort on developing novel catalysts for fuel cells. An extensive study is being made with bimetallic Pt/Ru catalyst for methanol oxidation. This is because it combines the ability of platinum to oxidize methanol and the capacity of ruthenium to decrease the CO poisoning of the electrode surface. Different methods have been proposed to achieve the most economical way to prepare bimetallic catalyst. In the present work, we present a way to modify Pt surfaces with a Ru cluster by using surface organometallic coordination. The cluster used in our experiment is Ru@sub 3@(CO)@sub 9@(MeCN)@sub 3@ (1 mmol in CH@sub 2@C@sub l2@) (I). This cluster was used to modify a platinum foil (99.9%). The cluster (I) was sinthetized from Ru@sub 3@(CO)@sub 12@ (II) following a procedure presented by Aime et al..@footnote 1@ The purity and characterization of the product was confirmed by IR. The modified cluster (I) adsorbs on Pt surface, however, the original cluster, Ru@sub 3@(CO)@sub 12@, was unable to coordinate. The amount of platinum oxides on the surface did not seem change the amount of adsorption of the clusters, even when the platinum surface had a complete oxide layer. The platinum oxide was obtained by electrochemical procedures@footnote 2@ and the amount of oxides was quantified by XPS. Despite of this, a very clean surface (certified by hydrogen adsorption on a CV of H@sub 2@SO@sub 4@ (0.5M)) was required to obtain good reproducibility on the adsorption of (I). After this, a reductive treatment was made by exposing the modified surface a H2 atmosphere: 400@super o@C at 15 min. was enough for the total reduction of the cluster to metallic Ru , either on a platinum surface or in crystalline form (this finding was confirmed by absence of CO and CN stretches in IR measurements). The presence of ruthenium at the platinum surface and its chemical environment was monitored very carefully by XPS analysis. This is necessary because Ru 3d peak overlaps with C 1s transition and is the unique signal for Ru chemical analysis by XPS.@footnote 3@ The binding energy of Ru were 281.7 ± 0.1 eV (cluster on Pt surface) and 280.3 ± 0.2 eV (Ru peak after H@sub 2@ reduction and corresponds to metallic Ru). No peak for Ru oxides was observed. The platinum presented peaks at 71.1 ± 0.2 eV (metallic Pt without Pt oxides), 71.9 ± 0.3 eV (metallic Pt when Pt oxides were present) and a single peak for Pt oxide at 74.7 eV. Just one peak for metallic platinum appeared after the reduction with H@sub 2@. The migration of the Ru atoms into Pt substrate was minimum or inexcistant because with a slight sputtering with Ar was able to eliminate the Ru XPS peak. @FootnoteText@ @footnote 1@ S. Aime, W. Dastr, R. Gobetto, J. Krause, L. Violano, Inorg. Chim. Acta, 235, 357 (1995). @footnote 2@ J.S. Hammond, N. Winograd, J. Electroanal. Chem. 78, 55 (1977). @footnote 3@ J.R. Felthouse, P.B. Framdorf, R.M. Friedman, C.L. Schoesser, J. Catal. 157, 421 (1991).

AS-MoP12 New SERS-Active Substrates Based on Thin Films of Noble Metals*,* ***L. He***[2]*, S.P. Mulvaney, S.K. St. Angelo, M.J. Natan,* Pennsylvania State University

A new approach to fabricating SERS substrates in which coats of Ag (or Au) are evaporated on Ag-coated Au colloid monolayers is described. The newly developed substrate circumvents the problems faced in previously reported techniques that use commercial plating solutions to chemically reduce Ag@super +@ onto Au colloid monolayers. The optical properties of the resulting new substrates depend critically upon particle size and interparticle spacing in the initial monolayer as well as on the amounts of chemically deposited Ag and evaporated metal. Under certain condition, extremely large enhancement factors can be realized with excellent spot-to-spot and sample-to-sample reproducibility. This presentation will describe characterization of these novel substrates by AFM, field emission SEM, and other techniques, and will provide a rationale for the observed SERS behavior.

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[1] **Best ASSD Student Paper Competitors**

[2] **Best ASSD Student Paper Competitors**

Monday Evening Poster Sessions, November 2, 1998

Biomaterial Interfaces Group
Room Hall A - Session BI-MoP

Biomaterial Interfaces Poster Session

BI-MoP1 Molecular Structure of Protein-Resistant Plasma-Deposited Oligoglyme, Dioxane, and Crown Ether Films, ***E.E. Johnston***, *B.D. Ratner,* University of Washington

Poly(ethylene oxide)-like (PEO-like) films are of interest as biomaterials for their ability to resist protein adsorption and cellular attachment.@footnote 1,2@ Here we compare the chemistry and molecular structure of PEO-like films that were plasma deposited from linear and cyclic ether rich precursors. The plasma precursors consist of a series of four linear oligo ethylene glycol dimethyl ethers (oligoglymes) (CH@sub 3@-O-(CH@sub 2@CH@sub 2@O)@sub n@-CH@sub 3@, n = 1-4) and a corresponding series of cyclic oligomers -(CH@sub 2@CH@sub 2@O)@sub m@-: dioxane, (m=2); 12-crown-4 ether, (m=4); and 15-crown-5 ether (m=5). Analysis by x-ray photoelectron spectroscopy (XPS), and time of flight SIMS (TOF-SIMS) will be reported. The view emerging from the analysis is that oligoglyme plasma deposited films consist of a carpet of randomly branched, methyl-terminated chains of -(CH@sub 2@CH@sub 2@O)- repeat units. The films are generally free of hydroxyl groups and hydrocarbonaceous domains. Films from larger molecular weight precursors contain longer fragments of intact monomer suggesting that the films are more loosely crosslinked. Proposed models of the oligoglyme PDF surface structure can account for many aspects of the high mass TOF-SIMS spectra. Interpretation of the crown ether PDF spectra was more difficult than that of the oligoglyme films. On the basis of the (45/43+45) positive ion ratio analysis and adventitious binding of sodium and potassium cations it is concluded that the outermost surface of crown ether films consist predominantly of intact cyclic fragments. TOF-SIMS analysis of dioxane films suggests the presence of hydroxyl groups pendant to an unsaturated hydrocarbonaceous matrix and the presence of ether-carbon bearing precursor fragments. @FootnoteText@ @footnote 1@ L@aa o@pez, G. P.; Ratner, B. D.; Tidwell, C. D.; Haycox, C. L.; Rapoza, R. J.; Horbett, T. A. J. Biomed. Mater. Res. 1991, 26, 415-436. @footnote 2@ Johnston, E. E., PhD dissertation, University of Washington, 1997.

BI-MoP2 Curvature-Induced Domain Formation in Lipid Bilayer Membranes, ***C.D. Keating***, *T.G. D'Onofrio, M.J. Natan, P.S. Weiss,* Pennsylvania State University

A number of studies have suggested the importance of domain formation in biological membranes. We describe recent results concerning the effect of lipid bilayer lateral heterogeneity on model membrane function in single unilamellar vesicles. Initial work has focused on preparation and imaging of lipid membranes of various curvatures, and manipulation of these membranes in flowing solution by optical trapping. Several methods have been applied to alter liposome morphology, from encapsulation of materials (both biological and nonbiological) to stretching vesicles using multiple optical traps. Fluorescence microscopic data on lateral domains as a function of membrane curvature will be discussed.

BI-MoP3 In Situ AFM Study of Myoglobin Monolayers on Bare and Modified Graphite, *M.J. Giz,* IQSC/University of Sao Paulo, Brazil*;* ***S. Boussaad***, *N.J. Tao,* Florida International University

We have examined with the atomic force microscopy (AFM) technique the structure of myoglobin (Mb) monolayers on graphite. This protein adsorbs weakly and slowly on bare graphite. The formation of a Mb monolayer can take up to 80 minutes. Furthermore, the molecules of Mb form a rod like assemblies randomly distributed on the surface of graphite. The length and the width of a single rod are 50 and 8 nm, respectively. The value of the width is similar to the dimension of a single protein. However, on graphite modified with a monolayer of Didodecyldimethylammonium bromide (DDAB) or Lauric acid (LA), the Mb is well ordered. The AFM images show that the protein preserves the rod-like assembly. In the case of DDAB, the Mb rods are aligned and almost parallel to each other, whereas on LA the rods are arranged into a V-type structure. In addition, the rods formed on modified graphite (70-80 nm) are much longer then their counter part on bare graphite. The Mb rods can be viewed as chains of 5-10 molecules and their formation can be attributed to an interaction between the proteins.

BI-MoP4 Nanofabricated Structures for Laser Induced Fluorescence, ***M.E. Foquet***, *A. Lopez, S.W. Turner, H.G. Craighead,* Cornell University

Fabrication techniques of microfluidic systems are being developed for use in laser induced fluorescence studies of macromolecules. Devices with submicrometer size capillaries have been fabricated on glass substrates for the study of electrophoretic motion of biopolymers. The motion of individual DNA molecules can be observed and their speed estimated. Other devices integrating both optical waveguides and capillaries have been fabricated. The waveguides are included to perform fluorescence using lasers as light source, allowing for the excitation of very small volume combined with a very high intensity and a perfect alignment to the capillary. Gratings defined by electron-beam lithography are used for the coupling of light into the waveguide. The same fabrication process can readily be used to fabricate capillaries with dimensions down to 0.1 µm. Light has been coupled into the waveguide and the patterns of scattered light have been recorded. Excitation of fluorescent solution in the capillaries can be observed. We are now characterizing the efficiency and the optical properties of these structures.

BI-MoP5 Effects of Surface Finish on the Corrosion of NiTi Shape Memory Alloy, ***S. Trigwell***, VG Scientific*; G. Selvaduray,* San Jose State University

NiTi (nitinol) alloys have become very attractive to biomedical applications because of their unique shape memory and superelastic properties. Due to the high Ni content of the alloy (up to 55%), concern has been expressed as to its biocompatibility. Nickel is known to cause toxic reactions in the body and be a possible carcinogen in cases of long term exposure, such as in implants. In this study, coupons of an equiatomic alloy were prepared by four methods (mechanically polishing, electropolishing, chemically etching, and plasma etching) to produce various levels of roughness and surface chemistry, as examined by AFM, SEM, XPS, and AES. The corrosion current (rate) for each finish was determined in Hank's Balanced Salt Solution at 37°C. The correlation between surface finish and corrosion susceptibility was determined that may be important in the preparation of NiTi for biomedical applications.

BI-MoP6 Second-Harmonic Generation in Thin Films of Bacteriorhodopsin: Sensor for Organic Electronic Devices, ***N.V. Didenko***, *A.A. Fedyanin, T.V. Murzina, E.P. Lukashev, O.A. Aktsipetrov,* Moscow State University, Russia

The nonlinear-optical method of second-harmonic generation (SHG) that has been shown to be a sensitive probe for studying surfaces, interfaces and thin films is suggested as a new non-destructive pH-sensor for biological display elements and readout of information for photochromic optical storage. The pH-induced changes of quadratic susceptibility of oriented micron-thick bacteriorhodopsin D85N films obtained for basic titrations (pH range 5-11.5) have led to drastic (more than an order of magnitude) variations in the SHG response. The photo- and electroinduced effects in SHG and Hyper-Rayleigh Scattering (HRS) in solid films of native bacteriorhodopsin are shown to be quite sufficient to distinguish by means of SHG and HRS quazistable states of bacteriorhodopsin molecule which can be used as functional states of memory storage elements. The output of a Q - switched YAG laser at the wavelength of 1064 nm that has been used as a fundamental radiation is shown not to cause the destruction of the samples and switching the memory element as well.

BI-MoP7 Observation of Infected Lymphocyte Cells by Atomic Force Microscopy, ***A. Cricenti***, *R. Generosi, M. Girasole,* Consiglio Nazionale delle Ricerche, Italy*; C. Colizzi, S. Bach,* Universita' di Roma Tor Vergata, Italy*; P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy

The interaction between lymphocyte cells and HIV virus have been studied at the membrane level by Atomic Force Microscopy in the repulsive regime of contact mode. Morphological characteristics of non infected lymphoid cells and HIV infected cells were easily imaged in fixed and dried cell preparations. After HIV exposure we observed a decrease in surface protrusions (loss of microvilli) and the creation of many dips. Some particles, presumably of viral origin (120 - 130 nm size), were also observed in proximity of the cell surface. Similar changes have been observed by AFM on cells exposed to intense electromagnetic field thus indicating that such cells undergo modifications of their morphology upon suffering from an external agent.

BI-MoP8 Enhancing the Sensitivity and Selectivity of the Solid-Phase Immunoassay Using Water Soluble Polymer Coatings, ***M. Natesan***, *S. Metzger,* Geocenters, Inc.*; R.J. Colton, G.U. Lee,* Naval Research Laboratory

Immunoassays have gained acceptance as both a bioanalytical technique and diagnostic tool due to the availability of antibodies from a variety of species against a wide range of analytes. These assays are often conducted on a solid surface to facilitate separation of the enzymes or radioisotopes that are typically used to amplify the antibody-analyte reaction. The antibody is usually immobilized on a hydrophobic surface by spontaneous adsorption, which is a process driven by molecule-surface interactions and/or conformational changes. The complex nature of this spontaneously adsorbed film can lead to erroneous signal due to the unwanted adsorption of assay constituents or antibody conformational changes. In this presentation we will describe two new schemes for directly immobilizing antibodies at a surface using a monolayer of water-soluble polymer that resists adhesion of proteins and cells. One technique uses direct covalent immobilization of the antibody to the polymer film while the other uses a molecular recognition interaction for assembly. We will describe the physical properties of the polymer films and compare the activity of the polymer immobilized antibodies to spontaneously adsorbed antibodies.

**BI-MoP9 Time-of-Flight Cluster Static SIMS, XPS and XRD Studies of Calcium Phosphate Phases*, C.C. Chusuei,* *D.R. Justes, M.J. VanStipdonk, E.A. Schweikert, D.W. Goodman,* Texas A&M University

Calcium phosphate phase identification is of interest in the modeling of bone growth on metal oxide surfaces. Ostwaltd's step rule suggests that various phases of calcium phosphate will form first prior to that of the principal phase found in bone, hydroxyapatite (HAP). XRD has been shown to be effective in distinguishing between brushite, octacalcium phosphate, amorphous calcium phosphate, alpha-tricalcium phosphate, beta-tricalcium phosphate and HAP. However, this technique is not sensitive to microscopic amounts of material. The effectiveness of ToF cluster SSIMS and XPS methods in the qualitative analysis of standard calcium phosphate powders are compared with XRD. In addition, results of SIMS and XPS studies the solid-liquid uptake of calcium phosphate on UHV prepared metal oxide are presented.

BI-MoP10 Surface Analysis of Anodic Behavior of 316L SS in SRB-Containing Seawater*, G. Chen,* Constellation Technology Corporation, US*; D.C. White, R.J. Palmer,* University of Tennessee/Oak Ridge National Laboratory*; S.S. Cristy,* Lockheed Martin Energy Systems

Type 316L stainless steel concentric electrodes were exposed to pure cultures of Desulfovibrio desulfuricans, of Vibrio harveyi and the coculture of these bacteria. A 1 microA/cm@super 2@ current was applied for 3 days while the chemostats were closed systems. Subsequently, aerated fresh medium was added. Impedance spectroscopy detected pitting of the coculture-exposed electrodes after addition of fresh medium. X-ray photoelectron spectroscopic analysis after current application and at the end of the experiment revealed that oxygen reduction induced pitting by: (a) formation of a SO@sub 4@@super 2-@, S@sub 2@O@sub 3@@super 2-@ and SO@sub 3@@super 2-@ mixture, (b) oxidation of relatively stable compounds such as Cr(OH)@sub 3@ and, (c) causing sulfides to penetrate the passive film.

Organic Electronic Materials Topical Conference
Room Hall A - Session OE-MoP

Organic Electronic Materials Poster Session

OE-MoP1 Photoelectron Spectroscopic Studies of Interfaces Between Metals and CBP*, I.G. Hill,* *A. Kahn,* Princeton University

A mixture of Mg and Ag is traditionally used as a low work function electron injecting contact in small molecule organic light emitting devices (OLEDs). Thin cathode interface layers of aromatic diamines, such as 4,4'-N,N'-dicarbazolyl-biphenyl (CBP), have recently been shown to increase the electron injection efficiency of Ag cathodes.@footnote 1@ The resulting devices are more stable than traditional structures utilizing reactive MgAg cathodes, and have comparable efficiencies. The role of the aromatic diamine interface layer is unclear. We have investigated the interfaces between CBP and Mg, Ag and Au using ultraviolet photoemission spectroscopy. Each interface was studied by depositing the organic on the metal, and by depositing the metal on the organic. The two methods produced inequivalent interfaces, except in the case of Au/CBP. We have measured the Fermi level/HOMO offset, and estimated the electron injecting barriers at each of these interfaces. The electron injection barrier was 0.5 eV for Mg, 0.6 eV for Ag and 1.2 eV for Au. This variation with the metal work function is quite strong, when compared to PTCDA and Alq@sub 3@.@footnote 2@ The discontinuity of the vacuum level at the interface, caused by the formation of an interface dipole layer, was also measured. The barriers to electron injection from Mg and Ag are comparable in magnitude, and surprisingly large, considering the performance of devices using these contacts. The evolution of the UPS spectral shape with overlayer thickness indicates a rough morphology in the cases of Ag and Mg on CBP. This qualitatively supports the suggestion that a rough interface may lower the barrier to electron injection and improve contact efficiencies.@footnote 3@ @FootnoteText@ @footnote 1@H. Kanai, S. Ichinosawa and Y. Sato, Synthetic Metals, 91, (1997) 195. @footnote 2@I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Submitted to Appl. Phys. Lett. @footnote 3@Y. Yang, E. Westerweele, E. Zhang, P. Smith and A. J. Heeger, J. Appl. Phys., 77, (1995) 694.

OE-MoP2 Ultraviolet and X-ray Photoemission Spectroscopy Characterization of Base and Acid Treated Indium Tin Oxide for Organic Device Applications*, F.A. Nüesch,* *E.W. Forsythe, Y. Gao,* University of Rochester

Because of its transparency and high conductivity, indium tin oxide (ITO) electrodes are ideal for optoelectronic device applications. Its ability to inject charges into organic solids, however, depends strongly on the interface properties. The effective ITO workfunction can be modified by a surface treatment such as plasma cleaning and chemical treatments. Here, we report the ultraviolet and X-ray photoemission spectroscopy (UPS, XPS) of chemically modified ITO using acids and bases. The UPS results confirm the presence of a dipole layer at the base treated ITO surface, with a vacuum level decrease of more than 1 eV. Current-voltage characteristics of tris-(8-hydroxyqinoline) aluminum (Alq) films sandwiched between the treated oxide electrode and a metallic counter electrode are in agreement with the workfunction shifts obtained by the UPS measurements. From XPS results, we will report the surface composition of the ITO films. In addition to base treatments, we will report UPS and XPS results for acid treated ITO and correlate these results with device transport measurements. The construction of thin dipole layers on the ITO substrate is a promising technique to modify the effective work function of ITO and improve the overall organic LED performance.

OE-MoP3 Investigation of the Growth Mode of Phenyldiamine (NPB) on Indium Tin Oxide*, F.M. Avendano,* *E.W. Forsythe, Y. Gao,* University of Rochester*; C.W. Tang,* Eastman Kodak Company

Since the first report on Organic Light Emitting Devices (OLED)@footnote 1@ there has been much interest for their potential applications as flat panel displays. In these devices charge carriers are injected into the organic layers across the interfaces and the electrode/organic interface characteristics have a strong effect on the device efficiency. Among these characteristics, the morphology of the anode(Indium Tin Oxide) strongly affects the device stability@footnote 2@ as revealed by the presence of microshorts in I-V curves. We study the growth mode of N,N-bis-(1-naphthyl)-N,N-diphenyl-1,1-biphenyl-4,4-diamine (NPB) on Indium Tin Oxide (ITO)/Glass substrates using Atomic Force Microscopy (AFM) and Lateral Force Microscopy (LFM). The addition of LFM to AFM allows us to clearly distinguish the features due to NPB or ITO. The study was performed as a function of the ITO morphology and NPB thickness. In order to modify the ITO surface morphology a series of processing steps were applied reducing the roughness more than three times as compared to the as received ITO. Next, NPB was deposited with thickness of 5, 15, 30 and 150Å onto the flat and as received ITO. At 5Å of NPB on the flat ITO, AFM/LFM pictures reveal the formation of NPB islands. These islands start to coalesce at a thickness of 15Å. At 30Å of NPB on flat ITO the film exhibits some pinholes which are no longer present at 150Å of NPB on flat ITO. The NPB films grown onto as received ITO show ITO features at the thickness of 5, 15,and 30 Å of NPB and the roughness of the NPB film is an order of magnitude bigger as compared to the NPB grown onto flat ITO. These ITO features present in the NPB film grown onto as received ITO may have detrimental effects on device performance as a consequence of microshorts. @FootnoteText@ @footnote 1@C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. 51, 913 (1987) @footnote 2@F. M. Avendano, E. W. Forsythe and Yongli Gao. The American Physical Society, March 1998.

OE-MoP4 Second-Harmonic-Generation Spectroscopy and Hyper-Rayleigh Scattering in Langmuir Films of C60 and its Derivatives*, E.D. Mishina,* *T.V. Misuryaev, A.A. Nikulin,* Moscow State University, Russia*; V.R. Novak,* Institute of Physical Problems, Russia*; Th. Rasing,* University of Nijmegen, The Netherlands*; O.A. Aktsipetrov,* Moscow State University, Russia

We report here the results of experimental studies by second-harmonic-generation (SHG) spectroscopy and hyper-Rayleigh scattering (HRS) of thin Langmuir films of C60 and C60-derivatives: C60-tetracyanoethylene oxide derivative (C60[CN]) and C60-indopane derivative (C60[-ind]). Langmuir technique allows to fabricate thin films with controlled thickness with monolayer resolution and ordering the molecules within the layer, while the SHG probe provides a reliable diagnostic tool for such films. For the SHG measurements the output of a Ti:Sapphire laser in the range of the fundamental wavelength of 710-800 nm is used. SHG spectroscopic studies showed that, depending on the nature of organic group, the modification of C60 molecules can either increase (for C60[CN]) or decrease (for C60[-ind]) the SHG intensity in thin fullerene films, while the general character of the spectra remains unchanged. The obtained results can be interpreted as due to the following two mechanisms: nonuniform broadening of resonances due to fluctuations, that is also revealed in absorbtion spectra; breaking of the inversion symmetry of C60 molecules by the organic "grafts" resulting in appearence of dipole hyperpolarizability and its interference with the quadrupole hyperpolarizability of C60 "cage". Hyper-Rayleigh scattering allowed us to get information about the structural and statistical properties of these systems. In particular, the modification of C60 molecules with the [CN] "graft" does not noticeably change the structure of the Langmuir films: for both C60 and C60[CN] monolayer samples have a disordered island-like structure, whereas the multilayer C60 and C60[CN] samples indicate their more regular structure. The modification of C60 molecules with the [ind]-"graft" significantly increases homogeneity of the monolayer samples. In all films the characteristic spatial scale of in-plane fluctuations of the HRS sources has been estimated.

OE-MoP5 Structure and Properties of the System of Nanometer-scale Quantum Wells Fabricated by the Incorporation of Organic Molecules in Sol-gel SiO@sub 2@ Glass*, J. Perez-Bueno,* Univ. Autonoma de Queretaro, Mexico*; L.L. Diaz-Flores,* Inst. Tecnologico de Saltillo, Mexico*; F.J. Espinoza-Beltran,* CINVESTAV-IPN, Mexico*; R. Ramirez-Bon,* Universidad de Sonora, Mexico*; **Y.V. Vorobiev**, J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

Organic molecules of the colorants (like Fast Green, Brilliant Black, Tartrazine, etc.)were encapsulated in SiO@sub 2@ glass derived by the solution-gelatinization process. The doping organic material in a power form was added to the initial solution, and after its solidification and annealing the colored glass was obtained containing the molecules of the colorants within the vitreous matrix. The optical and photoacoustic absorption as well as the photoluminescence excitation and emission spectra reveal the existence of sets of the discrete energy levels in these systems. The levels separation were determined by the structure of the colorant's molecule and the percentage of doping. The quantum mechanical description of the system is given considering the organic molecules as the two-dimensional or circular potential wells, depending on the molecular structure. The finite depth of the wells is taken into account by introduction of the periodic boundary conditions, which essentially influences the calculated energy spectra. The dependence of the spectra upon the colorant concentration is explained on the basis of the perturbation theory and, in itself, confirms the importance of the account of the finite depth of the potential wells. The theory was a reasonable agreement with the experiment. The results obtained demonstrate that the sol-gel technology gives a simple and cheap method of fabrication of a system of the nanometer-scale potential wells with a set of the energy levels which could be regulated by the structure of the doping molecules and their concentration.

OE-MoP6 Structures and Growth of Monolayers of 4-methyl-4'-mercaptobiphenyl on Au(111): The Role of the Molecular Backbone*, **T.Y.B. Leung**,* Princeton University*; P. Eisenberger,* Columbia Earth Institute*; F. Schreiber,* Max-Planck-Institut für Metallforschung, Germany*; P. Schwartz,* Princeton University*; A. Ulman,* Polytechnic University*; G. Scoles,* Princeton University

We present the results of a comprehensive diffraction study of monolayers of 4-methyl-4'-mercaptobiphenyl assembled on Au(111) [abbreviated as mbp]. Two phases of different density are observed. The diffraction patterns suggest that a low-density phase can be comprised of molecules assembling in rows with their molecular axes parallel to the surface. A second, high-density phase is thought to be composed of a hexagonal arrangement of molecules, which are aligned along the surface normal. We denote the low-density phase as the "striped" phase and the high-density phase as the "hexagonal" phase. Although the striped phase and the hexagonal phase are also observed in monolayers of n-alkanethiol on Au(111) [abbreviated Cn], interesting differences have been found. Apart from the structural differences, annealing experiments show that both phases of mbp are more thermally stable than the phases of Cn. In addition, the growth behaviour of mbp is investigated and different growth protocols have been attempted. Unlike the case of Cn where the hexagonal phase can be grown reliably and reproducibly, the hexagonal phase of mbp has only been observed a few times. We will address the role of the molecular backbone in the self-assembly process process of thiol on gold, based on the disparities in the structures, the thermal behaviour, and the growth behaviour between mbp and Cn.

Plasma Science and Technology Division
Room Hall A - Session PS-MoP

Plasma Science and Technology Poster Session

PS-MoP1 Plasma-CVD with a Pulsed DC Glow-Discharge: A Time Resolved Experimental Investigation@footnote 1@*, **T.A. Beer**, J. Laimer, H. Störi,* Technische Universität Wien, Austria

Pulsed direct-current (d.c.) glow discharges are commonly used in systems for plasma-assisted chemical vapour deposition (PACVD). In the present work we investigate the development of plasmas relevant for the production of TiN coatings. A videocamera with gateable image-intensifier is used to study the spatial and temporal evolution of the development of the plasma. Additionally, we use a single electrostatic probe to determine a time resolved charged particle distribution. Measurements are performed on a commercially available Plasma-CVD. Different steel-cylinders have been used as substrates. The typical shutter-speed used in our experiments is 100 ns. The pictures taken were used to generate MPEGmovies@footnote 3@ showing the plasma developement. Our investigations reveal large differences between plasmas with and without TiCl@sub 4@. In the absence of TiCl@sub 4@, the plasma ignites within the first 500 ns. In the presence of TiCl@sub 4@, the formation of the plasma along the substrates occurs with a certain delay, which has also been reported by Mogensen@footnote 2@. Our experiments show that the plasma ignites at the beginning of each pulse at one spot, where a positive column is observed, and spreads from there across the substrate surface. The pattern of the spatialtemporal evolution is quite complex and the evolution of the negative glow depends on various parameter, including geometry. The observed delays in the plasma formation are in the range of 10 us to 130 us. Detailed investigations of the time-dependent density of electrons and negative ions with our Langmuirprobe-setup are still in progress, first measurements show a high concentration of negative ions in the afterglow. @FootnoteText@ @footnote 1@ Supported by the Austrian Science Foundation FWF under Project No. P10794 @footnote 2@ K Mogensen, C Mathiasen, S Eskildsen, H Stöori, Surf. Coat. Technol.(in press) @footnote 3@ http://www.iap.tuwien.ac.at/www/plasma/mp_plasma/

PS-MoP2 Comparison of Feature Profile Evolution for Halogen Plasma Etching of Silicon (100)*, K.H.A. Bogart, **F.P. Klemens**,* Bell Laboratories, Lucent Technologies*; J. Lane,* Massachusetts Institute of Technology*; M.V. Malyshev,* Bell Laboratories, Lucent Technologies and Princeton Univ.*; V.M. Donnelly, A. Kornblit, J.T.C. Lee,* Bell Laboratories, Lucent Technologies

Feature profile evolution during halogen plasma etching of silicon-based materials is affected by several contributions to the etch mechanism. These aspects, including isotropic chemical etching, broad ion angle distributions, ion scattering within a feature, and redeposition of etching products, can cause deviations from anisotropic etching such as bowed or undercut sidewalls and mictrotrench formation in trench bottoms. Different halogen source gases produce various feature profiles and likely affect changes in the mechanistic components of silicon (Si) etching. Crystalline silicon (100) wafers (p-type, 150 mm) and poly-crystalline silicon (poly-Si) deposited onto silicon dioxide (SiO@sub 2@) were etched in a transformer coupled plasma reactor at two applied rf powers (250, 500 W, bias = 150 W) with Cl@sub 2@, HBr and HCl plasmas. Both Si (100) and poly-Si were patterned with nested and isolated lines and trenches using a SiO@sub 2@ mask. Scanning electron microscopy (SEM) was used to identify feature morphology and make comparisons between different halogen sources. Cross sectional SEM micrographs showed that HBr plasmas produced features with vertical sidewalls and little or no microtrenching. Deviations from anisotropically etched profiles (bowed sidewalls and deep microtrenches) were most severe for wafers etched in Cl@sub 2@ plasmas. Line and trench features for wafers etched in HCl plasmas evolved hybrid profiles; microtrenching and sidewall bowing occurred, but to a lesser degree than for Cl@sub 2@ plasmas. These data indicate that the presence of hydrogen or the type of halogen species in the plasma plays a significant role in feature profile evolution.

PS-MoP3 Plasma Damage in Metal Etch Processes Using an Oxide Hardmask*, **J.I. Colonell**, N.A. Ciampa,* Bell Laboratories, Lucent Technologies, US*; M.V. Malyshev,* Princeton University*; V.M. Donnelly, J.T.C. Lee,* Bell Laboratories, Lucent Technologies*; C.P. Chang, K.P. Cheung, W.Y.C. Lai, C.T. Liu, C.S. Pai, H.M. Vaidya,* Bell Laboratories, Lucent Technologies, US

Plasma damage in metal etch remains a serious problem in ULSI fabrication, and is expected to become more severe as gate oxide thickness is scaled. One proposed solution is to use an oxide hardmask, rather than a photoresist mask, to pattern the metal. Metal to oxide etch selectivities of 8:1 are achievable, so the mask thickness can be reduced from 1 µm to 1500 Å, thus reducing the aspect ratio for 0.4 µm spaces from ~4 to ~2 or lower. This change should reduce damage by reducing electron shading and aspect ratio dependent etching. However, metal etch processes using hardmask generally require low pressure conditions (2 to 5 mTorr, compared to 10 to 20 mTorr for a typical photoresist process) which lead to higher plasma densities and electron temperatures. We have measured plasma damage due to metal etch in a commercial, high density, inductively coupled reactor on 0.25 µm technology CMOS capacitor and transistor testers, with oxide thicknesses from 50 Å down to 25 Å. The effect of source power (from 300 W to 600W) and process pressure (3 mTorr to 7 mTorr) on the damage will also be discussed.

PS-MoP4 2DINESE - Topography Simulation Software for Process Modeling and Optimization*, I.V. Katardjiev,* Uppsala University, Sweden*; G. Carter,* Salford University, United Kingdom, U.K.*; S. Berg,* Uppsala University, Sweden

2DINESE@footnote 1@ is a powerful two-dimensional topography simulation program designed specifically for process simulation in IC R&D and manufacturing. It can simulate virtually all erosion and deposition processes currently employed in IC manufacturing - Reactive Ion Etching, Ion Beam Etching, Plasma etching, wet chemical etching, various PVD and CVD methods, multilevel metalization, to name a few. 2DINESE is built on a robust numerical implementation of the Theory of Surface Evolution, based on the generalized Huygens Principle of Wavefront propagation in anisotropic media. The basic points of this theory will be presented and its numerical implementation briefly discussed. Ample simulation examples will also be presented as well as a demonstration of the program will be given. @FootnoteText@ @footnote 1@ 2DINESE is freely available for academic use.

PS-MoP5 A Comparison of Oxide Damage in MOS Capacitors in Plasma Cleaning Applications*, X.M. Tang,* College of William and Mary*;* ***Q. Wang,*** Keithley Instruments*; D.M. Manos,* College of William and Mary

This paper reports a study of a comparison of damage produced by three different sources for photoresist dry-cleaning and removal. The sources include a CW 1kW, 13.6 MHz TCP plasma source, a pulsed TCP source capable of operation at variable frequency and duty cycle, and a source creating a directed stream of energetic (1-10 eV) neutral oxygen atoms. By judicious choice of conditions among these three sources, it is possible to identify the relative contributions to gate oxide damage from ions, electrons, neutrals, and photons. Damage from contamination by deposition of wall materials or other impurities were also included in these studies. Test structures included MOS capacitors consisting of (Al/100 Angstoms of SiO2/Si). Source parameters were varied including pressure, RF power, gas composition, pulse length, and, in the case of neutral stream cleaning, reflected neutral energy and flux. Ion fluxes were estimated from measured plasma parameters and by calorimeter probe methods. Pre-exposure and post-exposure damage levels, under these variations of conditions, were measured using simulataneous high frequency and low frequency C-V and i-V techniques.Results are compared to damage assessments and to models which have previously been reported. Results showed less gate oxide damage in the neutral stream cleaning source. Residue removal and correlative surface damage from impurity effects are assessed by studies using XPS, STM, and Auger spectroscopy. Simulation models are used to correlate the process damage to the plasma discharge parameters.

PS-MoP6 Etching and Cleaning using a Pulsed ICP Plasma*, D.M. Manos,* *X.M. Tang,* College of William and Mary

In this paper, we report studies of a pulsed ICP plasma using mixtures of argon, oxygen, water, hydrogen, and CF4 for removal of photoresist and cleaning and etching of SiO2. This paper reports measurements of the spatial and time-resolved electron temperature, plasma density, and measurements of the relative density of reactive species using optical emission spectrometry. Relative contributions of particle fluxes arising from ion vs. neutral species are estimated from measurement using heat flux and momentum sensors. The rf antenna power was monitored with current and voltage probes for 2 kW operation into dummy loads and into etching plasmas. Etching and cleaning rates were measured as a function of rf power, pulse frequency, duty cycle, gas composition, using SEM, AFM and a quartz microbalance. The modulation frequency and duty cycle were varied to optimize cleaning and etching efficiency. Experimental results are compared to a globally averaged model published by Ashida et. al.@footnote 1@ and to particle-in-cell simulations performed in this work, using MAGIC.@footnote 2@ @FootnoteText@ @footnote 1@S. Ashida, et. al., J. Vac. Sci. Techol., A13, 2498, (1995) @footnote 2@B. Goplen, et. al., "Magic Users Manual", MRC/WDC-R-409, August 1997

PS-MoP7 Increase of Etch Resistance of Deep UV Photoresist by Implantation*, K.K. Ong,* Nanyang Technological University, Singapore*; C.P. Soo,* National University of Singapore, Singapore*; M.H. Fan,* Chartered Semiconductor Manufacturing Ltd., Singapore*; A.J. Bourdillon,* National University of Singapore, Singapore*; M.H. Liang,* Nanyang Technological University, Singapore*; L.H. Chan,* Chartered Semiconductor Manufacturing Ltd, Singapore, Republic of Singapore

As device dimension shrinks, there is a need to use deep UV lithography to define sub-quarter micron features. However, most of the novel photoresists used in deep UV lithography generally face a problem: low etch resistance. In this study, implantation of various kinds of dopant into the resist layer was the approach to increase etch resistance. The first approach was that implantation of dopant into the resist formed a carbonized layer at the surface. The carbonized layer formed at the surface could be clearly observed on the cross SEM micrographs. This might increase the etch resistance by the assumption that the etch resistance is proportional to the C/H ratio of the resist (made by Wilson et al.). The etch rate of the treated resist was extracted from detailed experiment. Generally for both B and P implantation, the carbonized layer was thicker with increase implantation voltage. The thickness could reach to the range of around 0.5 µm. This enables a thinner resist (probably at 0.6-0.7 µm) used in the lithography, which enhance the resolution and the depth of focus. Secondly, implantation of Si into the resist might form the silylated resist which normally bears a higher etch resistance. Besides that, implantation of B or P into the oxide substrate increased the oxide etch rate greatly with respect to the above resist layer. The greater difference in the etch rate of the resist and oxide substrate gave a better etch selectivity.

PS-MoP8 An Integrated Surface Kinetics-Plasma Equipment Model for Etching and Deposition: Effects of Bias on Wall Reactions@footnote 1@*,* ***D. Zhang****, M.J. Kushner,* University of Illinois, Urbana-Champaign

In high plasma density, low pressure etching tools, heavy particle reactions which occur at the walls are equally, if not more important, than heavy particle reactions which occur in the gas phase. To self consistently address these reactions, as well as to address reactions mechanisms occuring on the wafer, a Surface Kinetics Module (SKM) has been developed for the Hybrid Plasma Equipment Model (HPEM). The SKM is a surface site balance model which is employed at every mesh-point at the border between the plasma and surfaces. During each iteration of the HPEM, the fluxes and energies of species from the plasma to selected surfaces are used as input to a set of differential equations encompassing the surface reaction mechanism. The SKM then solves for the steady state values of surface coverages, processing rate (etching or deposition), and the species/fluxes leaving the the surface to the plasma. These values are then used to update the flux-in/flux-out boundary conditions which are used in the plasma portion of the HPEM. The SKM has been employed to investigate reaction mechanisms in Inductively Coupled Plasma (ICP) etching (oxide and poly-Si) systems with an rf biased substrate. With increasing rf biasing, the sheath voltage at surfaces other than the wafer also increase, thereby increasing the rate of sputtering of passivating species. These species return to the plasma, thereby increasing their flux to the wafer. The goal of the investigation is to determine whether the variation of these wall sputtering processes with rf bias amplitude is sufficient to significantly perturb the etching rate on the wafer. @FootnoteText@ @footnote 1@Work supported by SRC and NSF.

PS-MoP9 Investigations of Oxide Etching Using Validated Plasma Models*,* ***J.E. Johannes,*** *T.J. Bartel, M. Gallis, E. Meeks,* Sandia National Laboratories

Future technology, 0.25 micron and below, will require continued use of high density plasma (HDP) etch reactors to perform dielectric etch of fine-line, high aspect ratio features using fluorocarbon gases. Applying plasma models to better understand and design this process is difficult due to the lack of chemical information. By coupling fundemental chemical data, diagnostic data, and reactor scale models a validated plasma mechanism and model can be developed for predictive HDP simulations. A three step process will be defined for developing predictive HDP models. This study will focus specifically on a C@sub 2@F@sub 6@ plasma for oxide etch, although the strategy can be applied to other lasma systems. First, a preliminary mechanism is developed using existing cross sections and beam studies from the literature. A sensitivity analysis is then used to reduce the number of reactions and species in a preliminary C@sub

2@F@sub 6@ mechanism to generate a 'manangable' chemistry set for 2-D/3-D simulations. Phase two of this process is mechanism and model validation; this step is required to have confidence in the model. O-D and 2-D simulations are compared to available C2F6 plasma data, from both experimental and commercial reactors, to suggest improvements in the chemistry models and to validate the plasma models. A wide range of data comparisons used for mechanism development and validation will be presented for this study including: spatially resolved langmuir probe data, laser induced fluoresence (LIF) data, diode laser absorption data, Hiden probe data and oxide etch rates. A suite of four different codes will be used: 1.) Aurora, a well stirred reactor model, 2.) MPRES, a 2-D finite element plasma model , 3.) Icarus, a 2-D Direct Simulation Monte Carlo (DSMC) plasma code and 4.) Pegasus, a 3-D version of Icarus. The final step in the process is to apply the validated mechanism to investigate commercial processes. The validated mechanism will be applied in the DSMC codes to study the effects of etch rate and uniformity as a function of gas injection and flow rate in a commercial HDP. In addition, Icarus/Pegasus simulations will be performed to investigate 300 mm scale-up issues.

PS-MoP10 Model for Etch Depth of Contact Hole*, B. Abraham-Shrauner,* Washington University

A linear relation between the etch depth and the inverse diameter of a contact hole is derived approximately. The linear relation was found experimentally for contact holes etched in silicon dioxide and several models for it were computed.@super 1@ This linear relation can also be reexpressd as a function of time for which there is also data.@super 2@ The new feature is the application of Langmuir kinetics with synergistic etching of neutrals and the ions. The neutrals are modeled for molecular flow in a pipe with a sticking coefficient equal to one.@super 2@ This assumption is supported by a recent finding that the etching (nondepositive) neutrals are not adsorbed appreciably on top of the same neutrals on the passivated walls of contact holes etched in silicon dioxide.@super 3@ The ions are modeled simply by a vertical beam since the directed ion energy fluxes at the center of the contact hole fall off slowly with depth. The effect of the depositive neutrals on the etch depth relation is estimated. Etch rates for the neutrals and ions are computed from data.@super 1@ @FootnoteText@ @footnote 1@ 1. S. C. McNevin, M. Cerullo and J.T.C. Lee, Bull. Am. Phys. Soc. 42 1707 (1997). @footnote 2@ H. H@um u@bner and M. Engelhardt, J. Electrochem. Soc. 141, 2453 (1994). @footnote 3@ A. Misaka and K. Harafuji, IEEE Trans. Elect. Dev. 44, 751 (1997).

PS-MoP11 Oxide Etch Characteristics of Inductively Coupled Plasmas Using Multipole Magnets for the Fabrication of Optical Waveguides*, K.J. An,* *D.H. Lee, G.B. Yoo,* SungKyunKwan University, Korea*; J.H. Joo,* Kunsan National University, Korea, South Korea*; G.Y. Yeom,* SungKyunKwan University, Korea

Dry etching of silicon oxide is one of the key steps not only in the silicon integrated circuit fabrication but also in other applications such as the fabrication of optical waveguides. In case of the fabrication of optical waveguides, dry etching characteristics of anisotropic etch profile, low sidewall roughness to reduce scattering loss, and high SiO@sub 2@ etch rates with high etch selectivities over mask materials easily to etch the films over 10µm thick are required In this study, glass etch characteristics of inductively coupled plasmas using multipole magnets were investigated. Various fluorocarbon gases and their combinations were used as etch gases. The10µm thick glass layer on silicon wafers used in this experiment was grown by plasma enhanced chemical vapor deposition. As the etch mask material, 3000Å thick Cr patterned using an Ar ion beam etching technique was used. To investigate the effects of multipole magnets on the characteristics of the plasmas and etch properties, ion density and F radical intensity were measured with and without the magnets along with etch rates, etch selectivities, and etch profiles. Also, we have analyzed the etched glass surface by x-ray photoelectron spectroscopy(XPS) to investigate the change of stoichiometry and binding states of the surface materials. When the glass was etched, the significant increase of etch rate, the increase of etch uniformity, and changes in the surface composition were obtained with the magnets together with the increase of ion densities and radicals. Using CF@sub 4@, 1000watts of inductive power, 5mTorr of operation pressure, -100Volts of dc-self bias voltage, and with the magnets glass etch selectivity over Cr higher than 30 and glass etch rate over 4500Å/min with anisotropic etch profiles and smooth sidewalls of 10µm thick etched glass waveguides could be obtained.

PS-MoP12 Consequences of Photon Injection in an Inductively Coupled Plasma@footnote 1@*, E.R. Keiter,* *M.J. Kushner,* University of Illinois, Urbana-Champaign

The plasma chemistry used for PECVD and etching are usually complex and consist of many different neutral and ionic species, only a subset of which may be desirable. Due to the nonselective excitation and dissociation typically obtained in plasmas, it can often often be difficult to simultaneously optimize all process variables. For example, a plasma with optimally high ion flux may have other plasma parameters that are detrimental to the process, such as a larger density of a polymerizing radical. By using an auxiliary source of excitation, such as a photon beam for photolysis or photoionization, it may be possible to simultaneously optimize multiple plasma parameters. In this paper we present results from a numerical study of an Inductively Coupled Plasma (ICP) system which includes an auxilliary photon source. The Hybrid Plasma Equipment Model (HPEM) has been modified to include a Monte Carlo Photon Beam (MCPB) module and is the simulation tool used in the study. Photons in the MCPB are represented as numerical particles, and photon absorption is described by using a variable particle weighting method. Photon reactions are specified in the same manner as other chemical processes. Source rates for charged and neutral species which result from photon absorption are generated by the MCPB and used by the fluid module of the HPEM. We will present the results from a parametric study of the effects of an external photon source on species densities and plasma parameters for a Cl@sub 2@ etching system and Ar/SiH@sub 4@ deposition system. @FootnoteText@ @footnote 1@Work supported by Applied Materials, SRC and NSF.

PS-MoP14 Low-Temperature Helicon Assisted Reactive Evaporation of Sn-doped and Ge-doped Silica Films for Planar Waveguide Photonics*, K.W. Gaff,* *A. Durandet, R.W. Boswell,* The Australian National University, Australia

Photosensitive silica films are a key technology in the development of silica based integrated optic devices. While the photosensitivity of silica glass doped with a variety of elements has been investigated for fibres, the development of photosensitive films for planar waveguides is still nascent. Previous research has concentrated on germanium doped silica films, often hydrogenated, and fabricated primarily by flame hydrolysis or PECVD, although ion-implantation techniques are also being researched. Fibre preform fabrication and flame hydrolysis silica film deposition normally involve temperatures around 1000°C, while temperatures during PECVD fabrication of silica films are typically 300-400°C. In the present work, we employ a unique process - helicon assisted reactive evaporation (HARE) - which combines three-crucible, electron-beam evaporation with a helicon source to generate a high density reactive plasma for thin oxide film deposition. The process enables deposition of hydrogen free, multi-component doped silica films at relatively low temperatures, typically between 100-150°C. Using this process, we were able to deposit tin-doped silica films. We compare the optical properties of the tin-doped films with those of germanium-doped films deposited using the same process and with germanium-doped films fabricated by the higher temperature processes.

PS-MoP15 In-situ Cleaning of GaAs and Al@sub x@Ga@sub 1-x@As Surfaces and Production of Ohmic Contacts Using an Atomic Hydrogen Source Based on a Reflected Arc Discharge*, V.A. Kagadei,* Research Institute of Semiconductor Devices, Russia*; D.I. Proskurovsky,* Institute of High Current Electronics, Russia

The existence of a thin-metal-film - semiconductor interface containing no contaminant is a necessary condition for the formation of high-quality ohmic contacts. Chemical treatment of the surface of a semiconductor is insufficient to provide an interface free from oxide. This is most pronounced for semiconductors showing high rates of oxidation of the surface, e.g., for Al@sub x@Ga@sub 1-x@As. A technology for production of ohmic contacts with n-type GaAs and n-type and p-type Al@sub x@Ga@sub 1-x@As has been proposed, such that the surface cleaning in a flow of atomic hydrogen (AH) and the deposition of a metal film are accomplished in a unified vacuum cycle. A feature of this technology is that the processes are conducted in a vacuum deposition system with a residual pressure of 3 10@super -6@ Torr for GaAs and (3-7) 10@super -7@ Torr for AlxGa1-xAs. The AH flow was produced by a reflected-arc-discharge-based source with a hollow cathode and a self-heating element. In the course of cleaning, the hydrogen pressure was 10@super -4@ Torr. The specimen temperature and the treatment time were varied in the range as follows: T = 100 - 400 C and t = 0.5 - 90 min. AuGe/GaAs interfaces have been produced with the contaminant content being below the sensitivity threshold of the method of Auger electron spectroscopy (AES). With some technological procedures having been executed, an AuGe/Al@sub 0.6@Ga@sub 0.4@As interface has been produced with the oxygen content less than 1% and the contents of other impurities below the AES sensitivity threshold. A comparative examination has been carried out for ohmic contacts produced using the technology proposed and the conventional technology based on "wet" chemical cleaning. The contacts produced by the proposed technology show a better morphology of the surface and of the contact area edge, high adhesion, and a low contact resistant; the process of their production features good reproducibility. Performance data of devices made using the new technology are reported. The technology developed is promising for production of shallow-lying contacts with GaAs and contacts with AlxGa1-xAs having a high Al content.

Surface Science Division

Room Hall A - Session SS-MoP

Surface Science Division Poster Session

SS-MoP2 Adsorption Dynamics of Monoenergetic Oxygen on Al(111)*, **A.J. Komrowski**, Y. Liu, 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. An intriguing scanning tunneling microscope (STM) study observed that dissociated O atoms on Al(111) at low coverages are separated by >80 Å when the surface is dosed with thermal O@sub 2@ molecules@footnote 1@. More recently, a detailed energy-resolved sticking probability experiment using supersonic molecular beams reported a strong O@sub 2@ translational energy dependence of the sticking coefficient on Al(111), demonstrating an activated process with no indication of precursor-mediated adsorption@footnote 2@. Further, the sticking measurements suggested that high incident energy O@sub 2@ may access regions of the multipotential energy surface unavailable to thermal O@sub 2@ and therefore chemisorb by a different mechanism. We will present results of the adsorption of monoenergetic O@sub 2@ molecules on the Al(111) surface over a range of incident energies using supersonic molecular beam techniques and STM. We will show how the chemisorption site distribution changes with incident translational energy. @FootnoteText@ @footnote 1@ Brune, H. et. al. J. Chem. Phys. v99, 2128 (1993). @footnote 2@ Österlund, L. et. al. Phys. Rev. B v55, 15452 (1997).

SS-MoP3 Gas Phase Oxidation of Uranium-Niobium Alloys by O@sub 2@ and H@sub 2@O, ***W.L. Manner**, M.T. Paffett, R.J. Hanrahan,* Los Alamos National Laboratory

Secondary concentrations of certain transition metals (e.g. niobium, titanium, and chromium) alloyed with uranium are known to improve numerous physical and mechanical properties. One such property is the enhancement of corrosion resistance exhibited by the uranium alloy with six weight percent niobium (denoted as U6Nb) relative to the unalloyed uranium. Despite a tremendous knowledge base concerning the bulk metallurgical properties of this material, very little is known concerning the surface chemistry of U6Nb toward corrosion by O@sub 2@ or H@sub 2@O. Specifically, we seek to understand the role of niobium toward oxidation resistance of this alloy. We have initiated a series of studies using surface-sensitive techniques that include X-ray photoelectron spectroscopy (XPS), thermal desorption-mass spectroscopy (TDMS), and secondary-ion mass spectroscopy (SIMS) in order to better understand the chemistry between this alloy and O@sub 2@ or H@sub 2@O. XPS studies of the oxidation of clean U6Nb by O@sub 2@ at 300 K produces a thin oxide overlayer of stoichiometric UO@sub 2.0@ intermixed with Nb@sub 2@O@sub 5@. While the same stoichiometry is exhibited for uranium when the oxide is prepared at 500 K with O@sub 2@, niobium is much less oxidized showing a mixture of NbO and Nb. Depth profiling studies reveal that oxidation by O@sub 2@ is much greater than that exhibited by H@sub 2@O. Only the first layer or two is oxidized using H@sub 2@O as an oxidant at 300 K (the oxidation by O@sub 2@ is approximately an order of magnitude higher). Formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to be responsible for the enhanced corrosion resistance by preventing diffusion of O@super -@ (O@super 2-@) or OH@super -@ into the oxide/metal interface region.

SS-MoP4 Vibrational Spectra and Structure of Hydrogen Adsorbed on Ni(111)*, **M. Gostein**, Q.Y. Yang, S.T. Ceyer,* Massachusetts Institute of Technology

The structure and adsorption site of hydrogen on Ni(111) were investigated using high-resolution electron energy loss spectroscopy. At 0.5 ML coverage where the adsorbed hydrogen forms a (2x2)2H unit cell, the vibrational spectra show a pair of fundamentals at 733 and 791 cm@super -1@ and a pair at 1077 and 1109 cm@super -1@, as well as three overtones at 1260, 1396, and 2180 cm@super -1@. The pair of fundamentals at the lower frequency and the two lower frequency overtones are assigned to H-Ni modes parallel to the surface, while the higher frequency pair and highest frequency overtone are assigned to modes perpendicular to the surface. These assignments are based on the expected anharmonicity of the modes and on the angular distributions of the loss features. The features in each fundamental pair, which are closely-spaced in frequency, are resolved by exploiting their different electron impact energy dependence. Preliminary results indicate that the fundamentals are split into pairs because of different potential energy surfaces at the hcp versus fcc three-fold hollow binding sites of hydrogen in a structure previously proposed from the observation of a (2x2)2H unit cell.

SS-MoP5 C-C Bond Breaking in Cyclopropane on the Ni(411) Surface*, **A.J. Guikema**, J.L. Gland,* University of Michigan

Thermal C-C bond breaking in cyclopropane has been observed on the stepped Ni(411) surface indicating that (111) step sites on a (100) terrace can break C-C bonds both in the presence and absence of coadsorbed hydrogen. Propane resulting from C-C bond activation in the presence of hydrogen is observed near 220 K. With increasing coverages of coadsorbed hydrogen and cyclopropane the yield of propane at 220 K increases. Above half saturation coverages of hydrogen and cyclopropane the yield of propane decreases with increasing coadsorbed coverages. The maximum propane yield corresponds to approximately 25% of cyclopropane saturation coverage. Experiments with coadsorbed deuterium clearly indicate that coadsorbed deuterium participates in propane formation. These observations support a Langmuir-Hinshelwood mechanism for propane formation associated with active sites in the step or near-step region. In the absence of coadsorbed hydrogen, cyclopropane dehydrogenation on the step sites dominates. A small amount of methane and ethane are observed around 120 K indicating multiple bond breaking during disproportionation. No deuterium incorporation is observed for methane and ethane in the presence of coadsorbed deuterium indicating that intermolecular hydrogen transfer dominates during disproportionation. These results indicate that the most reactive disproportionation sites responsible for multiple bond breaking react first and result in formation of about 5% of a monolayer of methane and ethane below 150 K.

SS-MoP6 LEED and STM Measurement of NO/Pt(111) at Low Temperature*, **M. Matsumoto**,* Institute of Molecular Science, Japan*; T. Yamada,* University of Tsukuba, and CREST, Japan*; N. Tatsumi, T. Itoyama,* University of Tokyo, Japan*; K. Miyake, K. Hata, H. Shigekawa,* University of Tsukuba, and CREST, Japan*; K. Fukutani, T. Okano,* University of Tokyo, Japan

The chemisorption of nitric oxide on Pt(111) at low temperature has been studied by electron energy loss spectroscopy (EELS), infrared absorption spectroscopy (IRAS) and low energy electron diffraction(LEED). The vibrational spectroscopy showed that N-O stretching frequency is 1490 cm@super-1@ at low coverage(0.5L).@footnote 1@ At high coverage, 2X2 LEED pattern was observed and its structure was attributed to the fcc hollow site by LEED dynamic theory.@footnote 2@ But there is no reasonable account for the difference of the N-O stretching frequency between low and high coverage regions and the structure is controversial yet. We measured the LEED I-V curves and STM images of NO/Pt(111) surface at several temperature and coverage conditions . At 175K, diffuse 2X2 LEED pattern could be seen even at low dosage(0.05L) and the I-V curve was the same as that at high dosage(1L). This indicates that (2X2)-NO islands grow with coverage increase but the local structure does not change at this temperature region. @FootnoteText@ @footnote 1@M.-B.Song, M.Suguri, K.Fukutani, F.Komori, and Y.Murata : Appl.Surf.Sci. 79/80 (1994) 25. @footnote 2@N.Materer, A.Barbieri, D.Gardin, J.D.Batteas, M.A.VanHove, and G.A.Somorjai: Surf.Sci. 303 (1994) 319.

SS-MoP7 Chemical Contrast by Funtionalized Tips and Movement of Highly Excited "Hot" Adsorbates: LT-STM Experiments with CO on Cu(111)*, **L. Bartels**,* Paul-Drude-Institut, Germany*; G. Meyer, K.-H. Rieder,* Freie Universität Berlin, Germany

Chemical Contrast between species looking otherwise very similar in STM images (like CO and oxygen on Cu(111), both of which image as circular indentations) can be achieved by controlled in-situ functionalization of the STM tip apex with a single molecule: Electrons tunneling from a STM-tip to a CO molecule on Cu(111) at a sample bias exceeding 2.4V@footnote 1@

can lead to the excitation of the addressed molecule resulting in its hopping either to the tip apex or to a nearby site on the substrate with approx. 1:3 probability. Thus, tips bearing a CO molecule on their apex can be produced. As putting down the CO molecule from the tip apex is easily accomplished using inverted bias, this technique can be used for a whole range of new manipulation (transfer) experiments. Additionally, imaging with a CO tip the apparent shape of CO molecules is inverted to a protrusion, while the shape of oxygen (and several other molecules) remains unchanged, thus allowing for easy discrimination between them@footnote 2@. It could be shown that the transfer of the CO molecule is achieved by single electron attachment to the CO 2@pi@* level, leading after electronic deexcitation to highly vibrational excited CO molecules. Thus, events, in which the CO molecule does not jump onto the STM tip but ends up on the substrate surface, can be used to study the diffusion of highly excited ("hot") adsorbates. We found, that their diffusion is limited in 2/3 of the cases to one adsite distance. In case of longer diffusion distance, scattered movement dominates. A Monte-Carlo simulation of the measured distribution of diffusion paths, however, allows to estimate that in 1/3 of the cases an adsite is transgressed, it is transgresses without scattering the movement of the "hot" molecule.@footnote 3@ @FootnoteText@ @footnote 1@ L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Phys. Rev. Lett. 80, 2004 (1998) @footnote 2@ L. Bartels, G. Meyer, K.-H. Rieder, Appl. Phys. Lett. 71, 213 (1997) @footnote 3@ L. Bartels, M. Wolf, G. Meyer, K.-H. Rieder, submitted to Chem. Phys. Lett. (1998)

SS-MoP8 Phenyl Containing Radicals on Cu[111]*, G.S. McCarty,* Pennsylvania State University*; M.K. Kamna,* Intel*; P.S. Weiss,* Pennsylvania State University

Surface features such as step edges, impurities, and adsorbates cause modification of the local electronic properties of a surface. We are taking advantage of this phenomenon to produce active sites for surface reactions. We explore the atomic scale electronic effects on reactions of phenyl containing species to understand the catalytic properties of copper. Copper catalyzes reactions of phenyl containing species through the Ullmann coupling reaction. A low temperature UHV STM was used to study Cu[111] dosed with iodobenzene, di-iodobenzene, and biphenyl. The dissociation of iodobenzene into iodine and phenyl was observed. The reaction can be driven to produce biphenyl. We observed the intermediate complex pairs responsible for the exquisite specificity of this reaction.

SS-MoP9 Adsorbate Azimuthal Orientation from Reflectance Anisotropy Spectroscopy*, B.G. Frederick,* University of Maine, U.K.*; J.R. Power, R.J. Cole, C.C. Perry, Q. Chen, S. Haq, T. Bertrams,* University of Liverpool, United Kingdom*; N.V. Richardson,* University of St. Andrews, Scotland, U.K.*; P. Weightman,* University of Liverpool, United Kingdom

We have determined the azimuthal orientation of an adsorbate on a metal surface from an intramolecular-transition-derived feature in reflectance anisotropy spectroscopy (RAS). Adsorption of 9-anthracene carboxylic acid onto p(2x1)O/Cu(110) led to an ordered structure with a strong (2%), derivative-like feature at 4.5 eV. Fresnel theory predicts the measured intensity, functional behavior, and sense of the RAS signal for the molecule aligned along [110]. IR measurements confirm that the molecular plane is perpendicular to the surface and STM measurements support the azimuthal orientation.

SS-MoP10 Nickelocene Adsorption on Single Crystal Surfaces*, D.L. Pugmire,* *M.A. Langell,* University of Nebraska, Lincoln

The adsorption and decomposition of nickelocene on Ag(100), Ni(100), and NiO(100) has been studied by high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Nickelocene adsorbs molecularly on less reactive surfaces such as Ag(100) at 140K, and desorbs molecularly at approximately 212K. In contrast to this, more reactive surfaces such as Ni(100) dissociatively adsorb nickelocene at 140K and desorb a variety of metallocene fragments. The orientation of molecularly adsorbed nickelocene as a function of surface coverage and the identification of decomposition products will be presented.

SS-MoP11 Analysis of Desorption Behavior of Sulfur from Pd by Temperature Programmed XPS*, K. Dohmae,* TOYOTA Central R&D Labs, Inc., Japan

Desorption of sulfur in oxygen gas from polycrystalline palladium plate was investigated by temperature programmed X-ray photoelectron spectroscopy (TP-XPS). The temperature programmed experiments in a range from room temperature to 773K were performed in an ambience of O@sub 2@ gas at 1x10@super -6@ Pa under a base pressure of 2x10@super -8@ Pa. As the initial coverage of sulfur on Pd increases in the range below 0.5 ML, the temperature that the quantity of sulfur on Pd decrease to half of its initial value becomes higher. Over 0.5 ML of the initial coverage of sulfur, the coverage of sulfur on Pd remained more than 0.5 ML at 773K, though the adsorbed sulfur decreases slightly as the temperature went up. The results were compared with calculations of Langmuir-Hinshelwood model with an assumption that the adsorbed sulfur react with the adsorbed oxygen on Pd and desorbe as sulfur dioxide molecule from Pd. The desorption behavior of sulfur in the experiments was well explained by the calculation model. The adsorption and desorption behavior of oxygen did not much agree with the calculations. Though the calculations suggest that the quantity of adsorbed oxygen on Pd decreased when the sulfur desorbe from Pd, the quantity of adsorbed oxygen did not decrease at the time in the experiments. Furthermore, total quantity of adsorbed sulfur and oxygen on Pd became over 1 ML at higher initial coverage of sulfur than 0.5 ML. They suggest that adsorbed sulfur on Pd affects the ability of adsorption of oxygen onto Pd.

SS-MoP12 Atom Probe Analysis of Dissociation of CO and N@sub 2@ Gas on a W(110) Oriented Tip*, T. Shimizu,* *A. Ohi, H. Tokumoto,* JRCAT, Japan

An atom probe (AP) is an attractive mass spectrometer of single-ion sensitivity. But the application of the AP technique to gas-surface phenomena is less advanced than the corresponding study of metallurgical processes. Because the high electric field for desorption induces the dissociation of gases, which hinders us from investigating the gas-surface catalytic phenomena themselves. We measured the dissociative and non-dissociative ions and estimated the temperature dependence of the dissociation probability. Here we introduced 10@super -7@ Torr x 10 s of CO and N@sub 2@ gas and investigated the dissociation on a W(110) oriented tip by using voltage-pulsed AP without a probe hole. The temperature of introduced gas was kept at RT and the tip temperature was changed from 50 K to RT. The count of gas ions increased with lowering temperature. Further AP at 50 K could detect two different states by the desorption field strength. A state desorbing at low field strength is related to the physisorption at low temperature, which was not observed at higher temperature. A state desorbing at high field strength is related to the trapping state following the dissociation. The dissociation probability decreased with lowering temperature. But below 100 K, the dissociation probability became almost constant (41% (CO), 45% (N@sub 2@)), which is caused by the field induced dissociation of chemisorbed gas. We postulated the ratio of field induced dissociation is almost constant up to RT and estimated the energy barrier from the trapped to the dissociation state as 30 meV (CO) and 22 meV (N@sub 2@).

SS-MoP13 The Kinetics of Methanol Synthesis by Hydrogenation of CO@sub 2@ Over a Zn-deposited Cu(111) Surface*, I. Nakamura,* *H Nakano,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; T. Uchijima, J. Nakamura,* University of Tsukuba, Japan

We have found that Zn deposited on a Cu(111) surface promotes methanol synthesis by the hydrogenation of CO@sub 2@. In this study, we examined the kinetics of methanol synthesis over the Zn-deposited Cu(111) surface by measuring the rates of elementary steps such as formation, decomposition and hydrogenation of formate species to clarify the promotional effect of Zn. The experiments were carried out in an infrared reflection absorption spectroscopy (IRAS) apparatus with a closed-reactor. The formate synthesis was performed using a gas mixture of CO@sub 2@/H@sub 2@=1 at a total pressure of 760 Torr and reaction temperatures of 323-353 K. The formate decomposition was carried out at a constant temperature of 373-403 K under vacuum. The initial formation rate of formate species on a clean Cu(111) surface was obtained by the initial slope of the formate coverage estimated from the peak intensity of the symmetric OCO stretching bands of formate species versus exposure to the CO@sub 2@/H@sub 2@ gas mixture. For example, at 353 K the initial formation rate was estimated to be 8.2 x 10@super -4@ formate molecules/site/sec, which agreed with that measured by the previous XPS experiment under the same reaction conditions. From the arrhenius plot of the initial formation rates, the activation energy for the formate synthesis on the clean Cu(111) surface was found to be 56.7 kJ/mol. The rates of formate decomposition was found to be first-order for the formate coverage and the activation energy was 100.7 kJ/mol. Furthermore, the equilibrium coverage of formate species was calculated by the kinetic data of formation and decomposition, which was in good agreement with experimentally measured coverage.

SS-MoP14 Characterization of CO Oxidation over Au/TiO@sub 2@(110) by Scanning Tunneling Microscopy*, **X. Lai,*** Texas A&M University, USA*; M. Valden, D.W. Goodman,* Texas A&M University

Au clusters of 1-6 nm in diamteter were vapor deposited onto a TiO@sub 2@(110)-(1x1) single crystal under ultrahigh vacuum (UHV) condition, monitored by Auger Electron Spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Fresh Au clusters on TiO@sub 2@(110) were transferred in situ into a high pressure cell, then exposed in separate experiments to 10 torr CO:O@sub 2@ (2:1), CO and O@sub 2@. STM observed the morphology change of Au clusters induced by reaction mixtures at 300 K, indicating the chemisorption of O@sub 2@ on Au clusters and TiO@sub 2@ substrate even at room temperature. The maximum activity for the oxidation of CO on Au/TiO@sub 2@ is obtained with Au clusters less than 3.5 nm in diameter and 1.0 nm in height (~300 atoms/cluster) exhibiting an electronic structure characterized by a band gap in the range of 0.2 V - 0.6 V as measured by STM and scanning tunneling spectroscopy (STM/STS), which suggests that CO oxidation over Au/TiO@sub 2@ is structure sensitive.

SS-MoP15 Selective Chemical Reaction of HBO@sub 2@ Molecules on the Si(111)-7x 7 Surface Studied by Scanning Tunneling Microscopy*, **K. Miyake**, K. Hata,* University of Tsukuba, and CREST, Japan*; R. Morita, M. Yamashita,* Hokkaido University, and CREST, Japan*; H. Shigekawa,* University of Tsukuba, and CREST, Japan

The formation process of boron (B) induced @sr@3x@sr@3 structure by HBO@sub 2@ irradiation was studied by scanning tunneling microscopy (STM). In the chemical reaction of HBO@sub 2@ molecules with Si(111)-7x7 surface, change in the charge density on the adatoms of the 7x7 units during the process play an exceedingly important role, which was analyzed by the bias dependence of STM images, i.e., the adatoms with less charge density become darker in the filled state STM image.@footnote 1,2@ The molecules preferentially reacted with the center adatoms in the unfaulted half units first. This result indicates that HBO@sub 2@ molecules tend to react with the adatoms in less charge density. The center adatoms surrounding the reacted center adatoms became darker compared to those in the normal 7x7 units in the filled state STM images, which indicates some charge redistribution occurred by the reacted center adatoms. Such charge redistribution is supposed to increase the chemical reactivity of the modified center adatoms because HBO@sub 2@ molecules prefer to react with adatoms in less charge density. In fact, center adatoms in the faulted half units, which were adjacent to the firstly reacted center adatoms, reacted subsequently with the HBO@sub 2@ molecules. According to this process, chain structures were formed by the reacted center adatoms. With further irradiation, B atoms were found to form an 1-dimensional network with the same @sr@3x@sr@3 phase, resulting in the formation of an ordered @sr@3x@sr@3 surface. Small off-phase @sr@3x@sr@3 domains remained only in the areas occupied by Si atoms. The remaining Si adatoms were replaced by B atoms with further deposition of HBO@sub 2@ molecules, and a completely ordered @sr@3x@sr@3 surface was formed. @FootnoteText@ @footnote 1@K. Miyake et al., Appl. Phys. Lett. 66, 3468 (1995). @footnote 2@K. Miyake et al., Surf. Sci. 357-358, 464 (1996).

SS-MoP16 Electron-Stimulated Desorption of Na from SiO@sub 2@ Films*, **B.V. Yakshinskiy**, T.E. Madey,* Rutgers University

As part of a program to probe the mechanisms by which Na atoms are produced in tenuous planetary atmospheres (e.g., Mercury, The Moon, etc.) we have studied the electron-stimulated desorption (ESD) of sodium ions and neutral atoms from ultrathin amorphous stoichiometric silica films (~100Å thick) grown on a Re(0001) surface. The desorbing neutral Na flux is detected by using a novel surface ionization detector, which also permits measurements of energy distributions of neutral atoms by means of a time-of-flight method. Sodium ions, desorbing from the surface under electron bombardment, are analyzed by a guadrupole mass spectrometer. Approximately the same appearance threshold (~25eV) is found for both Na@super+@ and Na@super0@ desorption, corresponding to O2s core level excitation. A Coulomb pair O@super+@- Na@super+@ forms as a result of intraatomic Auger decay in the oxygen atom, leading to Na@super+@ desorption. The sodium neutral atom desorbs due to Pauli repulsion between Na and the neutralized oxygen ion. The total ESD cross section for Na is ~3x10@super-19@cm@super2@ at an electron energy of 300eV. The yield of Na atoms grows linearly with increasing sodium concentration in the monolayer, whereas the yield of Na@super+@ ions passes through a maximum at ~0.5ML. Velocity and energy distributions of desorbing sodium neutrals demonstrate evidence for the ESD of "hot" atoms, with most probable kinetic energies of ~0.5eV. The results are compared with recent photon stimulated data from oxides, and with observations of Na in planetary atmospheres.

SS-MoP17 Reaction of Atomic Hydrogen and Activated Methane with Si(111) as Precursor for Diamond Nucleation Studied with High Temperature STM*, **F. Schaefer**, H. Bethge, A. Bianco, U.K. Koehler,* Ruhr-Universitaet Bochum, Germany

An STM has been designed especially for studies under the extreme conditions of hot-filament-CVD diamond growth. As a first step the etch-attack of atomic hydrogen and the reaction of activated methane with Si(111) has been investigated by in-situ, time resolved STM in the temperature range between 500°C and 800°C. Gas activation was done by the iongetter pump of the UHV system or by hot filaments. The etch-attack of atomic hydrogen on Si(111) starts at step edges and preferential etching along crystallographic directions is found. The etch-rate has been investigated in dependence on hydrogen flux and substrate temperature. Etching is found to be an activated process with an acitvation energy (E=0.8eV) close to the diffusion energy of Si-atoms on Si(111). Activated methane does not react with Si(111) at temperatures below 500°C. At higher temperatures a layer-by-layer consumption of substrate material and the formation of disordered clusters up to 60 Å height can be seen. Two different contributions to the consumption of Si are discussed: formation of SiC and etching due to the hydrogen supplied by the activated methane. The ratio of consumed substrate material to Si incorporated in the clusters is about 1:1, indicating a consumption of Si due to the formation of amorphous SiC clusters. A quantitative analysis of the nucleation behavior has been carried out. Although the clusters are amorphous their density evolution with growth-rate and temperature can be described according to classical rate equation theories. Different activation energies for nucleation for the two activation methods are found and can be assigned to different species responsible for the growth. As a further step to real hot-filament-CVD diamond growth conditions the reaction of activated methane diluted with hydrogen (1%CH@sub 4@/H@sub 2@) has been investigated for pressures up to 1 mbar.

SS-MoP18 Molecular State Identification of the Adsorbate Present on the Si(111)-(7x7) Surface Reacted with Oxygen. A Cs@super +@ Reactive Scattering Study*, K.-Y. Kim, T.-H. Shin, **H. Kang**,* Pohang University of Science and Technology, South Korea

While the interaction of molecular oxygen with a Si(111)-(7x7) surface has been one of the most actively studied surface reactions, the nature of the surface adsorbate, or the precursor state produced during initial oxidation of the Si surface, is still an open question. Interpretation of the experimental results on this system varies from molecular oxygen, either in the peroxide or superoxide form, to atomic oxygen bonded to various sites of the surface. To this surface we have applied a recently developed technique of Cs@super +@ reactive scattering.@footnote 1,2@ From this investigation we have found that oxygen exists on the surface only in the oxide form, and that the molecular oxygen bonded to a surface does not exist. The present finding allows explanation for many of the controversial issues regarding the initial oxidation mechanism of the Si surface. @FootnoteText@ @footnote 1@ M. C. Yang, C. H. Hwang, and H. Kang, J. Chem. Phys., 107, 2611 (1997). @footnote 2@ H. Kang, K. D. Kim, and K. Y. Kim, J. Am. Chem. Soc., 119, 12002 (1997).

SS-MoP19 Reactivity of Hydrogen with Fluorinated LaNi@sub5@*, **A.R. Layson**, C.J. Jenks,* Iowa State University

Much interest has been shown in hydrogen storage alloys as possible replacements for cadmium-based rechargeable batteries. Recent work under atmospheric conditions has shown that fluorination of the hydrogen storage material LaNi@sub 5@ substantially improves its ability to adsorb and subsequently desorb hydrogen. We report on studies aimed at understanding the effects of fluorination of LaNi@sub 5@. These are conducted in an ultrahigh vacuum environment using a single crystal of LaNi@sub 5@. Despite LaNi@sub 5@ being notoriously difficult to clean we have developed a method of cleaning which leaves less than 2% impurities at the surface. We follow surface compositional changes with Auger electron spectroscopy and hydrogen release with thermal desorption spectroscopy; these studies are the first such studies on LaNi@sub 5@. We compare results for D@sub 2@ adsorption/desorption on the clean surface to that of an oxidized surface and a surface that has been fluorinated after oxidation. We find that fluorination of the oxidized surface results in a low temperature channel for D@sub 2@ evolution not present on the surface that has only been oxidized. In addition the fluorinated surface enhances the amount of D@sub 2@ dissociation possible.

SS-MoP20 The Study on Activated Chemisorption on Surface of La Thin Film*, **S.M. Shao**, W. Qian, J.P. Song, S.L. Li, Z.Q. Zhuo, G.K. Xi,* Nankai University, China

The surface characteristics of evaporated rare-earth metal La thin film were studied by ex-situ and in-situ AES and molecular beam techniques. In case 1, the La thin film was prepared in the vacuum system, then taken out of the system exposing under atmospheric condition and finally put into the UHV chamber to be studied. In case 2, the La thin film was prepared and in-situ studied in the UHV chamber. The surface composition by ex-situ AES studies corresponds to mainly La(OH)@sub 3@ which can be attributed to a surface modification by O@sub 2@ and water vapor from the ambient atmosphere. The in-situ AES studies reveals the surface composition of La. The activated chemisorption of CH@sub 4@ on La thin film was studied in both cases using molecular beam technique.@footnote 1,2@ After surface cleaning treatment of samples, chemisorption probability was measured as a function of translational kinetic energy. The initial sticking probability was found to depend strongly on the incident kinetic energy E,scaling E@sub n@=Ecos@super 2@@theta@@sub i@. The initial sticking probability increases linearly with the translational kinetic energy of the incident molecular beam, but the threshold value and the activated energy were not changed when the surface temperature was increased from 500 K to 700 K.} @FootnoteText@ @Footnote 1@ G. Xi et al., J. Vac. Sci. Technol., A9(3),1688(1991) @Footnote 2@ S. Shao et. al., Chinese Vac.Sci. Technol.,12(2/3),263(1992)

SS-MoP21 Electron Induced Reactions of Ammonia and Nitric Oxide Adsorbed on Si(100)*, **C. Bater**, J.H. Craig, J.H. Campbell,* University of Texas, El Paso

Electron beam enhanced nitridation of Si(100) by ammonia and nitric oxide was studied using XPS, TPD, ESD and HREELS. At low coverages, both ammonia and nitric oxide dissociatively adsorbed on Si(100) at 120 K while molecularly adsorbed ammonia and nitric oxide were detected by TPD and HREELS at higher exposures. Ammonia condenses on the surface at 110 K. During electron beam irradiation, adsorbed hydrogen atoms were effectively removed from the surface so that the site poisoning effect of adsorbed hydrogen was reduced. The electron stimulated dissociation of the adsorbed NH@sub x@ species enhanced the nitridation process. Enhanced nitride formation occurred when weakly physisorbed and condensed ammonia were present on Si(100) during electron beam irradiation at 110 K. H@super +@ ESD KEDs were used to deduce the surface reaction occurring during electron beam irradiation, and HREELS following electron beam irradiation was used to confirm and enhance the conclusions drawn from the ESD study. The formation of nitride and oxynitride was observed using the peak shifts of the N 1s and Si 2p X-ray photoelectron peaks. From the O@super +@ ESD KED signals, we distinguished O@super +@ originating from NO(a) and O(a), which we used to monitor the surface reaction occurring during electron beam irradiation. Changes in surface chemistry due to different levels of surface nitridation were also studied extensively. From the H@super +@ and O@super +@ ESD decay curves, the ESD cross sections for different surface conditions were obtained.

SS-MoP22 The Interactions of XeF@sub 2@ and F@sub 2@ with Si(100)*, **M.R. Tate**, M.F. Bertino, S.C. Eckman, J.R. Holt, S.T. Ceyer,* Massachusetts Institute of Technology

The interactions of molecular fluorine (F@sub 2@) and xenon difluoride (XeF@sub 2@) with Si(100) are model semiconductor etching systems. Despite the similar energetics and chemical nature of these two etchant molecules, XeF@sub 2@ is a much better etchant of Si than F@sub 2@. This comparative study probes the dynamics of the interactions of these two gas-surface systems and seeks to understand the molecular origins of this disparity in reactivity. Using gas-surface scattering techniques, three reaction channels are identified for both etchants including a novel gas-surface mechanism, atom abstraction, in which the surface abstracts a fluorine atom from the incident molecule and ejects the remaining particle into the gas phase. The fluorinated silicon surfaces resulting from exposure to F@sub 2@ and XeF@sub 2@ are nearly indistinguishable until the silicon dangling bonds are saturated - that is, only a small fraction of Si-Si lattice bonds are broken until the fluorination of the dangling bonds is complete. Beyond one monolayer of fluorine, however, only XeF@sub 2@ is able to attack the Si-Si lattice bonds, and SiF@sub 4@, an etch product, is observed to desorb. A detailed analysis of the energetics of the scattered products yields insight into the disparate reactivities of F@sub 2@ and XeF@sub 2@ with Si.

SS-MoP23 Atomic Hydrogen Reactions with Si(100) Surfaces*, **S.K. Jo**, J.H. Kang,* Kyung Won University, South Korea*; B. Gong, D.E. Brown, J.M. White, J.G. Ekerdt,* University of Texas, Austin

Chemical reactions of hydrogen atoms with Si(100)2x1 have been investigated over a wide range of substrate temperatures (T@sub s@ = 110 - 635 K) by using temperature-programmed desorption (TPD) and low-energy electron diffraction (LEED) techniques. Thermal-energy hydrogen atoms generated from a hot tungsten filament were found to react with Si(100) surfaces over the entire temperature regime, resulting in silicon etching, amorphization, and hydrogen penetration into the crystalline substrate. Extensive silicon etching occurred at all substrate temperatures investigated. A large hydrogen uptake of more than 4 monolayers (1 ML = 6.8 x 10@super 14@ H atoms/cm@super 2@) and destruction of 2x1 LEED patterns upon H exposure at T@sub s@ = 415 K and 635 K indicate that the etching continues at substrate temperatures where tri- and di-hydride species are not stable. Moreover, in addition to the H@sub 2@ desorption peak at T@sub s@ = 780 K, a new desorption peak at T@sub s@ = 850 K grew in with increasing hydrogen exposure for T@sub s@ @>=@ 415 K. Deuterium exchange experiments suggest that the 850-K peak is due to H@sub 2@ evolution from the crystalline silicon bulk. At T@sub s@ @<=@ 300 K, amorphization as well as etching of Si(100) occurred readily. The observed opposing T@sub s@ effects on the rates of hydrogenation [Si(s) + xH(g) -> SiH@sub x@(a)] and etching [SiH@sub x@(a) + (4-x)H(g) -> SiH@sub 4@(g)] reactions have been elucidated. Terrace etching and step etching have been invoked to explain the observed etching at low (@<=@ 415 K) and high (@>=@ 635 K) substrate temperatures, respectively. Implications for damage-free, dry etching of crystalline silicon surfaces by thermal-energy hydrogen atom beams are discussed.

SS-MoP24 Hydrogen Diffusion and Desorption from the Si(100)-2x1 Surface*, **E.J. Buehler**, J.J. Boland,* University of North Carolina, Chapel Hill

The mechanisms of hydrogen diffusion on the Si(100) surface and desorption from the 2x1 monohydride surface are being studied using high temperature scanning tunneling microscopy. Several desorption mechanisms have been proposed in the literature to explain the observed first-order kinetics, large energy barrier to adsorption, and similarity between hydrogen molecules desorbing from the decomposition of the mono- and dihydride phases. The possible role of surface defects has also been discussed. Using high temperature imaging conditions at which the tip does not induce desorption, we have observed pairs of vacant dangling bond (DB) sites on the surface following desorption. The spatial distribution of DB's on the surface shows no correlation with the locations of steps and defects. A particular surface feature has been identified, however, which may be a stable intermediate formed during the hydrogen desorption process. The structure and stability of this intermediate are discussed, as is the possible role of this feature in hydrogen desorption.

SS-MoP25 Adsorption and Reaction of H@sub 2@O on GaAs(100)*, **X.M. Wei**, Q.P. Liu, Y.T. Wong, H.H. Huang, G.Q. Xu,* National University of Singapore, Singapore

The adsorption and reaction of H@sub 2@O on Ga-rich GaAs(100) surface have been investigated using TDS and HREELS. During the H@sub 2@O dosage at 100 K, we believe the adsorption proceeds as follows: initially, molecular H@sub 2@O is adsorbed, probably onto Ga. For a higher exposure at about 0.28 L, a 2-D H@sub 2@O monolayer is built. A subsequent dose increase leads to phase transition from a 2-D monolayer to a 3-D H@sub 2@O multilayer. During heating to 500 K, the desorption follows the reverse scheme. The H@sub 2@O multilayer is first desorbed at about 170 K, as detected by TDS, which makes the surface resemble that prepared by exposure at 0.28 L. On heating to a higher temperature, the remaining H@sub 2@O molecules are desorbed by 250 K. On the other hand, the first monolayer H@sub 2@O dissociates to give hydroxyls and hydrides. Hydroxyls are bound to Ga sites while hydrides tend to occupy As sites. More hydrides are formed from the further dissociation of Ga-bound hydroxyl. These hydrides adsorb onto Ga sites which are left vacant after the recombinative desorption of Ga-bound hydroxyl. At ~500 K, H@sub 2@ gas is also liberated.

SS-MoP26 Sites for Arsine Adsorption on GaAs(001)-(4x2)*, **Q. Fu**, L. Li, M.J. Begarney,* University of California, Los Angeles*; B.-K. Han,* University of California, Los Angeles, US*; R.F. Hicks,* University of California, Los Angeles

Arsine adsorption on GaAs(001)-c(8x2) at 298K-693K has been studied by internal-reflectance infrared spectroscopy and x-ray photoelectron spectroscopy. At 298K, AsH@sub 3@ dissociatively adsorbs on terminal Ga sites on step edges and transfers hydrogen to terminal As sites. No gallium hydride was observed during the dosing of AsH@sub 3@ at room temperature. c(8x2) reconstruction was well maintained when GaAs(001) surface was under extended exposure of AsH@sub 3@ between 298K and 573K. Upon dosing AsH@sub 3@ with a dosage of 9600L at 650K, surface reconstruction was converted from c(8x2) to a mixture of c(6x4) and (4x2) domains as illustrated by LEED. XPS also revealed a small increase of As/Ga area ratio after dosing at 650K. Further adsorption of arsine at 650K transformed surface to As rich (2x4) reconstruction. We found that it is necessary to have enough adsorption sites(terminal As) to accomodate hydrogen from arsine in order to incorporate As efficiently during epitaxy growth.

SS-MoP27 A New GaCl Molecular Beam Cell for Surface Dynamic Studies*,* ***M. Ohashi****, M. Ozeki,* JRCAT-ATP, Japan

An understanding of the surface reaction dynamics between source molecules and solid surface is required for the development of an advanced technological base for III-V semiconductor growth. Gallium chloride (GaCl) is one of the most important sources for III-V epitaxial growth. GaCl has an advantage of controlled chemical reaction, because it easily dissociates with H@sub 2@ on GaAs surface in spite of its strong bonding. However it is necessary to produce GaCl in-situ in the production cell, because GaCl preferably exists at higher temperature above 870 K. In order to study the surface reaction dynamics between GaCl molecule and GaAs surface, high purity GaCl molecular beam is necessary. We developed a new GaCl molecular beam cell, where high purity GaCl molecular beam was produced by direct reaction between Ga metal and Cl@sub 2@ gas. We optimized the gas flow rate of Cl@sub2@ gas for the production of GaCl molecular beam and the cell temperature from 920 to 1230 K. The byproduct of GaCl@sub 3@, which is stable and form large particles at low temperature, was observed under excess supply of Cl@sub 2@ gas. Under the optimized condition, which is the gas flow rate of Cl@sub 2@ at .25 ccm, the only GaCl was produced and no Cl@sub 2@ was observed. The Flux density at the sample surface, which is 40 cm away from the nozzle of this cell, was estimated 1.1x10@super 13@ molecules cm@super -2@ s@super -1@. The newly developed GaCl molecular beam cell would be useful for the study of the surface reaction dynamics between GaCl source and GaAs surface. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

SS-MoP29 Electronic Promotion of Graphite Oxidation in the Presence of Cs Trapped between the Basal Planes*, J.R. Hahn,* ***K.-Y. Kim****, H. Kang,* Pohang University of Science and Technology, South Korea

Oxidation of graphite is investigated by using scanning tunneling microscopy (STM) in the presence of Cs atom trapped between the carbon basal planes. Low energy (< 150 eV) bombardment of Cs@super +@ ions onto a graphite surface produces Cs interstitial defects (Cs-ID), where a Cs atom is trapped between the first and the second graphite layers. Oxygen adsorption onto the defected surface and the subsequent heating at 560 °C inside vacuum leads to formation of the pits with a depth of monolayer and a diameter of several nm. The pit formation starts from the Cs-ID's, indicating its promotion effect on the reaction with oxygen. The average diameter of the pit increases with the amount of supplied oxygen molecule. The experimental results suggest that a Cs-ID donates electron density to the neighboring carbon atoms, making the upper-layer carbons to be reactive with the oxygen molecule. The electron transfer from Cs-ID is the prevailing mechanism for the promoted oxidation, which is different from the direct mechanism proceeding via complex formation between the adsorbed Cs and the oxygen molecule, proposed from the previous studies of the oxidation of graphite covered with Cs.

SS-MoP30 The Penetration Range of Low Energy (50-500 eV) Ar@super +@ and Kr@super +@ Ions Impinging onto a Graphite Surface Studied by the Oxidative Etching Method and STM*,* ***J.R. Hahn****, H. Kang,* Pohang University of Science and Technology, South Korea

Penetration of low energy (50-500 eV) Ar@super +@ or Kr@super +@ ions into a graphite surface results in the formation of surface vacancy defect (VD), formed by knock-out of carbon atoms, and interstitial defect (ID) where the incident atom is trapped between the carbon layers@footnote 1@, @footnote 2@, @footnote 3@. Thermal oxidation of the defected graphite surface etches away the carbon atoms surrounding a defect, leading to the formation of a pit of a large diameter and nearly circular shape. The etching process, when occurs from a defect of multi-layer depth, removes the carbons at and above the defect-containing layers simultaneously. Such phenomena enable us to locate the spatial position of the ion-generated defects by measuring the STM topography of the etched pits. The yield for production of multi-layer defect increases with ion collision energy. The depth distribution of the defect obtained by this method agrees well the result of theoretical trajectory calculation@footnote 1@. Lateral displacement of the incident ion inside the basal planes, upon penetration into the first carbon layer, is measured by STM from the distance between the VD and the ID formed in a pair. The average distance of the lateral travel varies with the incidence angle and the mass of ion. @FootnoteText@ @footnote 1@ W. Choi, C. Kim, and H. Kang, Surf. Sci., 281, 323 (1993). @footnote 2@ D. Marton, K. J. Boyd, T. Lytle, and J. W. Rabalais, Phys. Rev. B 48, 6757 (1993). @footnote 3@ J. R. Hahn, H. Kang, S. Song, and I. C. Jeon, Phys. Rev. B 53, R1725 (1996).

SS-MoP31 Scanning Tunneling Microscopy Studies of the Growth of Copper, Silver and Gold Overlayers on TiO@sub2@(110) in Ultrahigh Vacuum*,* ***D.A. Chen****, K.F. McCarty, R.Q. Hwang,* Sandia National Laboratories

The growth of metal films on oxide surfaces has become an area of increasing technological importance for applications involving electronic devices, sensors, catalysis and ceramic joining. We are investigating the growth of copper, silver and gold overlayers on a TiO@sub2@(110) surface in ultrahigh vacuum in order to develop a fundamental understanding of metal-oxide interactions. After annealing at 1000 K in vacuum, the titania substrate is reduced and becomes sufficiently conductive for scanning tunneling microscopy experiments. The resulting (1x1) TiO@sub2@ surface is characterized by low energy electron diffraction, Auger electron spectroscopy as well as STM. Previous work by Diebold and Madey et al. have shown that many transition metals, including copper, grow by three-dimensional island formation on titania. Scanning tunneling microscopy is used to study the nucleation, growth and size distributions of the metal islands as a function of annealing temperature and coverage. Furthermore, by comparing the characteristics of copper, silver and gold overlayers deposited on titania, we will investigate how varying the interaction strength between oxygen at the surface and the admetal affects film growth and morphology. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBESDivision of Materials Sciences.

Thin Films Division

Room Hall A - Session TF-MoP

Thin Films Poster Session

TF-MoP1 Studies on Anti-Glare, Anti-Static and Transparent Conductive Film on Display Tubes*,* ***G.K. Xi****, G.H. Zhang, S.L. Li, S.M. Shao, W. Guo, X.J. He,* Nankai University, China

Anti-glare,anti-static thin film and transparent conductive film are widely used in many fields of production, science and technology, such as solar cell,TV image display panel, instrument panel and transparent electrode. Anti-glare and anti-static double-layered coating on ordinary glass prepared by a sol-gel technique is introduced. The outer layer of low refractive index is coated on high refractive index inner layer. The main composition of outer layer is SiO@sub 2@. Some SnCl@sub 4@ added into this film increases the conductivity of this film. The latter can be replaced by other hygroscopic metal salts,such as Al(NO@sub 3@) @sub 3@,AlCl@sub 3@,ZnCl@sub 2@, etc.. The inner layer is composed of TiO@sub 2@ and SiO@sub 2@. The glass panel with the double-layered coating shows the resistivity of 10@super 9@ @OMEGA@/square and reflectance of 1.6 % which is reduced to one-fourth of that without coating. A transparent film with high conductivity on ordinary glass panel prepared by a sol-gel technique is also introduced. This Sb-doped SnO@sub 2@ film is made from alkoxide which was previously prepared in our lab. This ATO film has a polycrystall structure. The resistivity of the ATO film has minimum value of 10@super 3@ @OMEGA@/square while the doping level of the solution is about 7%. Finally,factors such as enviromental temperature and humidity,coating technology,effecting the characteristics of these films are discussed.

TF-MoP2 Humidity Sensing Properties of Plasma Polymerized Organic Thin Films*,* ***G.B. Park****,* Yuhan College, Korea*; J.T. Kim, D.C. Lee,* Inha University, Korea*; C. Kim,* Korea Electronic Technology Institute

In order to fabricate humidity sensitive films, the mono-layer polymer thin films from various monomers were deposited on a comb-shaped electrode using a capacitive-coupled gas flow type plasma polymerization apparatus with rf power. The humidity sensing characteristics of these thin films were measured by means of changes in electrostatic capacitance within the frequency and humidity range of 60Hz - 100 kHz and 20% RH - 90% RH, respectively. The capacitances of these thin films were increased with increasing relative humidity. And the increments of the capacitance grew larger with a lower discharging power and a shorter polymerization time. The linearity and increment of the capacitance change became apparent with the lower frequency of input power to thin films during the capacitance measurements. The copolymerized thin films, vinylacetate and methylmethacrylate, were fabricated using the conditions of low discharging power and short discharging time. The capacitances of this films were remarkably changed showing the linear behaviors, and these changes were continued from 20% RH to 90% RH.

TF-MoP3 Rotating-Compensator Spectroscopic Ellipsometry: Applications of Four-Parameter Stokes Vector Spectroscopy to Real Time Characterization of Non-Ideal Thin Films*, **R.W. Collins**, P.I. Rovira, J.C. Lee,* Pennsylvania State University

We have developed a multichannel ellipsometer in the rotating-compensator optical configuration, i.e., (fixed polarizer)-(sample)-(rotating compensator)-(fixed analyzer). This instrument has the advantage of providing the spectrum in the degree of polarization p of the light beam reflected from the sample, in addition to the spectra in the ellipsometric angles (@psi@, @DELTA@). In a recent advance, we have extended the instrument capabilities to a simultaneous measurement of the spectral reflectance R of the sample. As a result, the new instrument can collect four-parameter spectra [(@psi@, @DELTA@), p, R] that characterize the unnormalized Stokes vector of the reflected light beam. The minimum measurement time is 32 ms for all four spectra from 1.5 to 4.0 eV. In this paper, instrumentation and calibration issues specific to the simultaneous reflectance measurement will be described. Applications of the rotating-compensator instrument to date include (i) optical anisotropy in nanoscale sculptured thin films of MgF@sub 2@, (ii) nucleation and growth of nanocrystalline and polycrystalline diamond films, and (iii) optical properties, structure and stability of specular and textured transparent conducting oxide thin films. We review these applications and highlight the unique capabilities developed so far. These include the use of p along with (@psi@, @DELTA@) to characterize the evolution of thickness non-uniformity during the growth of diamond films, and the use of R along with (@psi@, @DELTA@) to characterize the effect of annealing and H@sub 2@-plasma exposure on the optical properties and surface roughness on micro/macroscopic scales for textured SnO@sub 2@:F used in photovoltaics applications.

TF-MoP4 Characterization of Thin Metal Films Processed at Different Temperatures*, **L. He**, J.E. Siewenie,* Northern Illinois University

Thin metal films are of considerable interest for electronic device fabrication. Not only do these films provide electrical interconnection between circuit elements, they can also be an integral part of a circuit element, as in the case of Schottky diodes and metal semiconductor field-effect transistors(MESFETs) and metal-semiconductor-metal photodetectors (MSM PDs). It is well known that the electrical conduction in metals is due to electrons, while electrical resistivity, defined as the reciprocal of the conductivity, is the result of electron collisions. The high resistivity of thin metal films result in drawback of their applications in afore mentioned devices. Recent studies have been conducted in thin metal films obtained by low temperature (LT = 77K) deposition. Comparing to the same film formed at room temperature, the LT film resistivity could be 4 to 5 orders lower in magnitude. In another hand, metal/semiconductor Schottky barrier heights are significantly increased in materials including InP, GaAs, and InGaAs. This work extensively studied the electrical and micro-structural properties of several often used metal films including Au, Ag, Al, Pt, Pd, and Ni formed at LT and RT. Atomic force microscopy (AFM), transmission electron microscopy (TEM), and in-situ resistivity measurements were conducted. In AFM surface scanning, surface morphology consistently showed the LT and RT films difference in the grain sizes. The larger grain size in LT thin film explains the lower resistivity. TEM electron diffraction pattern showed very different degree of crystallization of the LT and RT thin films. The LT film diffraction pattern suggests that LT films develop a less regular structure which may be responsible for the Schottky barrier enhancement. LT deposition prevents both adatom diffusion and re-evaporation, leading to the earlier conducting than the same RT films.

TF-MoP5 Optical Properties of the Ge:Sb:Te System*, E. Garcia-Garcia,* Univ. Autonoma de Queretaro, Mexico*; A. Mendoza, G. Martinez-Montes,* Univ. Autonoma de Puebla, Mexico*; Y.V. Vorobiev, **J. Gonzalez-Hernandez**,* CINVESTAV-IPN, Mexico*; B.S. Chao,* Energy Conversion Devices

Stoichiometric compositions of the Ge:Sb:Te system are commercially used for optical data storage. In this work, we have measured using ellipsometry, the optical constants (n, k) in the range of 1.4 to 6 eV in all the stoichiometric composition in the Ge:Sb:Te system. It is known that the amorphous phase of these compositions undergoes an amorphous-to-crystalline transition at temperatures in the range from 140-160 °C depending on Sb concentration. The crystalline structure of this phase is the fcc. Heat treatments at temperatures above the mentioned range produce a new crystalline-to-crystalline transition from the fcc to the hexagonal phase. The n values for the amorphous and crystalline fcc phase are not so different and both decrease from a value of about 5 to 1.4 eV to a value of 1 at 6 eV. In general, this phase transition produces an increase in the values of k in the whole energy range. The observed changes in n and k in the hexagonal phase are more complex due to the increase in the free charge density and will be discussed in the extended presentation.

TF-MoP6 Influence of Annealing Temperature on the Formation and Characteristics of Sol-gel Prepared ZnO Films*, R. Castanedo-Pérez, O. Jiménez-Sandoval, S.J. Jiménez-Sandoval, A. Maldonado-Alvarez, J. Márquez-Marín, **G. Torres-Delgado**,* Cinvestav-IPN, Mexico

ZnO films have been obtained by the sol-gel method, from a Zn(OOCCH@sub 3@) precursor, on silica glass and silicon wafer substrates. The films, obtained by a single dipping procedure, were characterized by FT-IR and UV-VIS spectroscopy, atomic force microscopy, X-ray diffraction and ellipsometry measurements. Untreated and single-step, annealed (100-450°C) films were studied, in order to analyze the influence of temperature on the formation and properties of the ZnO coatings. Remarkably, these results indicate that ZnO forms at considerably lower temperatures than 450°C, which is usually considered in literature as a reference temperature for the formation of ZnO. Thus, a sharp absorption edge of ZnO at ca. 380 nm, can be neatly observed in the UV-VIS spectra of films annealed at 200 and 300°C, and accordingly, IR data indicate the absence of organic groups at these temperatures. Somewhat surprisingly, at 400 and 450 °C, the ZnO optical absorption edge is not as sharp as is at lower temperatures. Atomic Force Microscopy results show larger grain sizes as the annealing temperature is increased. The X-ray diffraction patterns show that the films are polycrystalline and also evidence the formation of ZnO at temperatures as low as 200°C.

TF-MoP7 Structural Characterization of SrBi@sub 2@Ta@sub 2@O@sub 9@ Ferroelectric Thin Films Grown by PLD on Pt and RuO@sub 2@ Bottom Electrodes*, **J.M. Siqueiros**,* UNAM, Mexico*; M.P. Cruz,* CICESE, Mexico*; J. Portelles,* Universidad de la Habana, Cuba*; R. Machorro, G. Hirata, S. Wang,* UNAM, Mexico

To study the effect of the bottom electrode on the properties of the ferroelectric layer, thin SBT (SrBi@sub 2@Ta@sub 2@O@sub 9@) films were deposited by PLD on Pt/Ti/Si, Pt/TiO@sub 2@/Si and RuO@sub 2@/Si grown by DC sputtering. Due to the previously reported experience that the Ti in the adherence promoter layer diffuses to the Pt surface, a study of the SBT/electrode interface using AES and TEM is performed. XRD, SEM, STM and ellipsometry measurements were performed on the SBT films and compared with the corresponding measurements on the ceramic used as target for the deposit, which showed a layered perovskite structure.

TF-MoP8 Characteristics of CuInSe@sub 2@ Thin Films Prepared in Different Selenization Pressures*, **S.D. Kim**, C.H. Chung,* Seoul National University, Korea*; K.H. Yoon, J.S. Song,* Korea Institute of Energy Research, Korea*; H.J. Kim,* Seoul National University, Korea

CuInSe@sub 2@ based solar cell has great interest because CuInSe@sub 2@ has high absorption coefficient, suitable bandgap energy, good thermal stability, and good lattice match with window layers such as CdS, Cd(Zn)S. Its conversion efficiency has been reached above 15%. The selenization method has been known as an excellent technique to acquire low cost and high efficiency CuInSe@sub 2@ thin films. The effects of chamber pressure during selenization of Cu-In alloy layers on the optical, electrical and structural properties of CuInSe@sub 2@ films were investigated. The uniform Cu-In alloy layers could be reproducibly deposited on the glass substrate by dc co-sputtering method. The two atmospheres, Ar atmosphere at 1 atm and in vacuum of 10 mTorr, were chosen for the selenization of Cu-In layers. The properties of all films were analyzed by XRD, SEM, EDX, four point probe, Raman spectroscopy and photoluminescence. Cu-In precursors consisted of two phases, CuIn@sub 2@ and Cu@sub 11@In@sub 9@, and the amount of Cu@sub 11@In@sub 9@ phase increased with varying the composition from In-rich to Cu-rich. Less compounds of Cu-Se and In-Se were observed during the early stage of selenization and also CuInSe@sub 2@ single phase was more easily formed in vacuum than at atmospheric pressure. Therefore, CuInSe@sub 2@ films selenized in vacuum showed large grain size, smooth surface, dense microstructure, high Raman peak intensity and no secondary phases with near-stoichiometric composition. Since CuInSe@sub 2@ films selenized in vacuum could hardly release the intrinsic stress due to dense structure, Raman peak of 173 cm@super -1@, A1 mode of CuInSe@sub 2@ charcopyrite phase, shifted to higher frequency and had a broad full width of half maximum.

TF-MoP9 Growth and Characterization of Epitaxial Films of Tungsten-Doped Vanadium Oxides on Sapphire (110) by Reactive Magnetron Sputtering*, P. Jin,* *M. Tazawa, M. Ikeyama, S. Tanemura,* National Industrial Research Institute of Nagoya, Japan*; K. Macak, X. Wang, U. Helmersson,* Linkoping University, Sweden

Some vanadium oxides undergo a semiconductor-to-metal phase transition with significant changes in optical, electrical and magnetic properties. Replacement of V by metals such as W, Mo affects greatly the properties. Since thin films of such materials are candidates for switching or memory devices, it is necessary to investigate the growth, structure and properties of the metal-doped vanadium oxides particularly in the form of epitaxial film. In this study, films of W-doped vanadium oxides were epitaxially grown on sapphire (110) by reactive sputtering a V-W alloy target. With computer control of deposition parameters, especially the oxygen flow into the Ar+O@sub 2@ discharge, a series of epitaxial films having structures of not only the best known MO@sub 2@ (M=V+W) but also others from M@sub 2@O@sub 3@ to M@sub 2@O@sub 5@ were obtained. The films were studied with X-ray diffraction (XRD), atomic force microscopy (AFM), Rutherford backscattering spectrometry (RBS), etc. The XRD theta-2theta scan shows only pairs of peaks corresponding to those from the film and the substrate. Furthermore, a series of films formed by varying slightly the oxygen flow exhibit a continuous shift of the XRD peaks in response to their metal-to-oxygen ratio. In other words, a continuous structural change was obtained by precise process controlling. The XRD pole figure study confirmed the epitaxial relationships. The phase transition properties were studied from the change in electrical resistivity against temperature. The results demonstrate strong influences both from the metal-to-oxygen ratio and the tungsten doping amount.

TF-MoP10 Stability of Transparent Conducting Oxide Films for Use at High Temperatures*, T. Minami, T. Miyata,* ***T. Yamamoto,*** Kanazawa Institute of Technology, Japan

The stability of transparent conducting oxide (TCO) films in various atmospheres at high temperatures is important for applications such as transparent heaters and also in optoelectronic device fabrication processes. However, the electrical, optical and chemical properties of TCO films at high temperatures above 500 ° C have not been investigated because of the melting point of glass substrates. In this paper, we describe the stability of various TCO films at high temperatures in various atmospheres. Various TCO films consisting of binary compounds such as ZnO, In@sub 2@O@sub 3@ and SnO@sub 2@, ternary compounds such as Zn@sub 2@In@sub 2@O@sub 5@, In@sub 4@Sn@sub 3@O@sub 12@, GaInO@sub 3@, ZnSnO@sub 3@ and MgIn@sub 2@O@sub 4@ or multicomponent oxides composed of two binary compounds or two ternary compounds were tested in this work. The TCO films were deposited by magnetron sputtering on quartz substrates at room temperature or 350 ° C. The tests were carried out in various atmospheres such as air, argon gas and vacuum at temperatures up to 1000 ° C. The SnO@sub 2@, In@sub 2@O@sub 3@ and In@sub 4@Sn@sub 3@O@sub12@ thin films were found to be more stable than other materials. It can be concluded that stability at high temperatures was mainly determined by the metal elements contained in the TCO film; high stability was obtained in TCO films rich in Sn and In.

TF-MoP11 Texture and Grain Size Modification through the Different Sintering Conditions for Ceramics of the Sr@sub 0.5@Ba@sub 0.5@TiO@sub 3@ Type*, J.M. Siqueiros,* UNAM, Mexico*; J. Portelles, S. Garcia,* Universidad de la Habana, Cuba*; S. Aguilera,* Universidad de Catolica de Norte, Chile*; M. Xiao,* UNAM, Mexico*; A. Fundora,* Universidad de la Habana, Cuba

The variation of the sintering conditions: temperature and sintering time, strongly modify the texture and grain size of the SBT ferroelectric compound (Sr@sub 0.5@Ba@sub 0.5@TiO@sub 3@). In this report, the sintering time is varied from 1 to 5 hours. The grain size increases as the sintering temperature is varied from 1200 to 1450 @super o@C. SEM studies allow us to determine the corresponding microstructure for each temperature and sintering time. A linear dependence of logarithm of the grain size with the sintering temperature is found. A change in the dielectric permittivity and the polarization with the sintering conditions is also reported. The analysis of the results is supported with XRD, thermoelectric and dielectric hysteresis measurements

TF-MoP12 Microstructure Study of PMN-PT Films Grown on Metal Electrodes by PLD*, J.M. Siqueiros,* UNAM, Mexico*; J. Portelles, A. Fundora,* Universidad de la Habana, Cuba*; S. Aguilera,* Universidad de Catolica de Norte, Chile

Thin ferroelectric films obtained by PLD from non-stoichiometric Pb(Mg@sub 1/3@Nb@sub 2/3@)O@sub 3@-PbTiO@sub 3@ (PMN-PT) ceramic targets are studied. The morphology of the resulting films for the 2.7PMN-0.1PT composition obtained in N@sub 2@ and O@sub 2@ atmospheres at room temperature obtained by SEM is reported. It is observed that, for similar deposit conditions, thicker films with columnar structure are produced in the O@sub 2@ atmosphere as compared with those grown on N@sub 2@ where very low crystallinity was detected. The film composition was determined by Auger electron spectroscopy and XPS. TEM measurements of the N@sub 2@ grown films showed scattered nanostructures embedded in a dominion structure in the paraelectric state, since the measurements were performed at room temperature, above the Curie temperature of the ceramic (15 @degree@C). This result seems to imply a diffuse phase transition associated to the film. Regions of high concentration of Niobium were detected by XPS evidencing the presence of pyrochlores, a situation confirmed by XRD. The PMN-PT/electrode interface is analyzed by TEM for samples annealed at different temperatures and the results are correlated with those obtained by XRD and SEM.

TF-MoP13 Columnar Growth of Tin from Liquid Metal Ion Source Studied by In-situ Transmission Electron Microscopy*, H. Kimata,* *Y. Kondo,* ERATO, Japan Science and Tech. Corp., Japan*; K. Takayanagi,* Tokyo Institute of Technology, Japan

A miniaturized liquid metal ion source (LMIS) built in a conventional transmission electron microscope (TEM) was developed to observe field desorption of tin ions and droplets, and growth of deposit from them on substrates in-situ. The LMIS has a reservoir, a needle and a filament which heats the liquid tin in the reservoir. The needle is faced to an extraction electrode with a small hole. A shield plate, with a small hole, is placed behind the extraction electrode. The substrate is placed behind the shield plate. Potentials of the LMIS and the extraction electrode are ground and negatively high, respectively. The shield plate and the substrate are usually ground. Thus emitted ions are decelerated to have near zero energy at the substrate, and they land the substrate very softly. Positive bias is occasionally applied to the shield plate and the substrate, to repel positive ions for selecting neutrals from mixture of ions and neutrals. Tin ions and neutrals were emitted from the LMIS at extraction voltage ranged from 4 to 6kV, with an emission current of about 40x10@super -6@A. We observed growth of tin on a substrate in-situ. The substrate was an amorphous carbon film on a thin tungsten wire. We found that columnar tin grew; typically 500nm in length and 50nm in width, when the substrate and the shield plate were ground. Columnar growth was not found when +100V bias was applied to the substrate and the shield plate, to repel the ions. The experiments showed that ions are essential for the columnar growth. The strong magnetic field (~2T) of the objective lens in the TEM, might play a role for the growth.

TF-MoP14 Characterization of TiOx Film deposited on Ti-6Al-4V Alloy by Reactive Sputtering in Oxygen Atmosphere*, T. Sonoda,* *M. Kato,* National Industrial Research Institute of Nagoya, Japan

Coating of Ti-6Al-4V alloy substrates with TiOx films by reactive sputtering in oxygen atmosphere was examined, not only to improve the biocompatibility of the alloy@footnote 1@ but also to enhance the bonding of the alloy implants to living bone.@footnote 2@ The reactive sputter deposition was carried out in oxygen gas using a magnetron d.c. sputtering apparatus with a pure titanium target. Thus the TiOx films were deposited on the alloy substrates at the rate of 300Å/min by the magnetron sputtering, even under the surface condition at the target to be in the reactive mode,@footnote 3@ due to reactive products covering the surface. The characteristics of the deposited TiOx films were investigated. Under visual observation, the deposited films looked light gray and appeared to be uniform and adhesive. Under SEM, the surface of the films was found to have a net-like microstructure which looked like a net consisting of micron-ordered fine meshes. Under AES, the Ti/O ratio of each film was constant in depth direction of the film. Based on XRD, it was concluded that not only the oxides(TiO@sub 2@) such as rutil and brookite but also the suboxides such as Ti@sub 4@O@sub 7@ and Ti@sub 6@O@sub 11@ were formed in the film. Therefore, it was assumed that the obtained TiOx films improved the biocompatibility of the alloy and enhanced the bonding of the alloy to living bone. Furthermore, the hardness of the TiOx films reached over Hv=800 under the film thickness of 0.8µm, concluding that the coating with the films improved the hardness of the alloy. @FootnoteText@ @footnote 1@A.Wisby et al., Biomaterials 12(1991)470. @footnote 2@T.Kitsugi et al., J. Biomed. Mater. Res. 32(1996)149. @footnote 3@S.Schiller et al., Thin Solid Films 111(1984)259.

TF-MoP15 Photoconductivity of Free-standing Diamond Film*, S.-H. Kim,* Silla University, South Korea*; I.T. Han,* Samsung Advanced Institute of Technology, South Korea*; **T.-G. Kim**,* Miryang National University, South Korea

Thick diamond film having 700 µm thickness was deposited on polycrystalline molybdenum (Mo) substrate using high power (4 kW) microwave plasma-enhanced chemical vapor deposition (MPECVD) system. We could achieve free-standing diamond film by detaching as-deposited diamond film from the substrate. Parallel-type diamond photoconductors were fabricated on either the growth side or the susbtrate side of free-standing diamond film via ohmic contact metallization. We investigated the variation of photoconductivity after exposing the film surface to either oxygen or hydrogen plasma. At as-grown state, the growth side showed noticeable photoconductivity, while the substrate side gave little photoconductivity, The oxygen plasma treatment of these sides led to the insulators. After exposing the film surfaces to hydrogen plasma, on the other hand, we could observe not only distinct photoconductivity at the substrate side but also the reappearing of photoconductivity at the growth side. Finally, we suggest that the dangling hydrogen bond on the film surface may play an important role to create the photoconductivity of this film surface.

TF-MoP16 Target Compound Layer Formation during Reactive Sputtering*, **L.B. Jonsson**, T. Nyberg, S. Berg,* Uppsala University, Sweden

It is well known that a compound layer may form at the target surface during reactive sputtering. However, the significance of this layer for the response to a change in target conditions has so far not been carefully investigated. The standard model for the reactive sputtering process @footnote 1@ does not allow for calculations of the compound thickness at the target surface. For simplicity it has been assumed that a single monolayer is responsible for the poisoning of the target. However, experiments clearly indicate that the compound layer thickness may be significantly thicker than one monolayer. For several reasons it is important to be able to quantify the thickness of this layer. The formation of the compound layer introduces memory effects into the system when the processing conditions are changed. The delay time for sputter erosion of the compound layer depends strongly on the thickness of the layer. We will present an extension of the basic reactive sputtering model that explains the formation of an arbitrary thickness of the compound layer at the target surface. From this model it is possible to examine the layer thickness dependence on the major processing parameters (reactive gas supply, sputtering power etc.). Optical emission spectroscopy studies of sputtered target material and transient target voltage response measurements confirm the validity of the new model. @FootnoteText@ @footnote 1@ S. Berg, H.-O. Blom, T. Larsson, and C. Nender, J. Vac. Sci Technol. A 5, 202-207 (1987).

TF-MoP17 Characterization of YSZ(Yttria-Stabilized Zirconia) Thin Films Prepared by RF-Magnetron Sputtering for Oxygen Gas Sensor*, **J.W. Bae**, J.Y. Park, G.Y. Yeom,* Sungkyunkwan University, Korea*; K.D. Kim,* Korea Gas Corporation, KOREA*; Y.A. Cho, J.S. Jeon, D.S. Choi,* Korea Gas Corporation, Korea

Yttria-stabilized zirconia(YSZ), a well known oxygen ion conductor, is one of the many solid state ionic materials utilized in the variety of electrochemical devices including fuel cells, oxygen pumps, and chemical gas sensors. Commercial YSZ oxygen gas sensors rely on the traditional bulk ceramic fabrication and require temperatures above 600 @degree@C to achieve sufficient ionic conductivity. However, if the YSZ could be applied as a thin film, it would offer many advantages including compact dimensions with smaller power consumption, reduced ohmic losses, and lower operating temperatures. In this experiment, yttria-stabilized zirconia(YSZ) films(0.5-1.5µm) were deposited on Pt/NiO-Ni mixed reference layer/SiO@sub 2@ substrates to characterize films properties using an RF-magnetron sputter deposition system and zirconia stabilized with 8mol% yttria(Y@sub 2@O@sub 3@) was used as a sputter target. The plasma atmospheres were pure Ar or mixtures of Ar and O@sub 2@. We employed X-ray diffraction to study the structure of YSZ films and scanning electron microscopy(SEM) to examine the film surface morphologies. Analyses by Auger electron spectroscopy(AES) and X-ray photoelectron spectroscopy(XPS) were performed to examine Zr, Y, and oxygen compositions in YSZ thin films and the uniformity in compositions. Transmission electron microscopy(TEM) was employed to examine the microstructural details and crystallography of the films. Gas-sensing test was carried out for Pt/YSZ/Pt/NiO-Ni/SiO@sub 2@ film structures exposed to an atmosphere of oxygen controlled composition. The deposition rates of YSZ thin films increased with increasing rf power and total pressure, and decreased with increasing O@sub 2@ concentration. The preferred orientation of deposited YSZ films changed from (111) to (220) with increasing thickness. O/Zr ratio analyzed by XPS was increased from 1.94 to 2.4 with increasing O@sub 2@/(Ar+O@sub 2@) ratio. But yttria atomic percentage in the YSZ films were not changed. More detailed physical and chemical characteristics of YSZ thin films and their relations to gas-sensing properties will be discussed in the presentation.

TF-MoP18 Growth Characteristics and Deposition Mechanism of SrTiO@sub 3@ Thin Films by Plasma Enhanced MOCVD*, Y-.B. Hahn, **D.O. Kim**, K.S. Nahm,* Chonbuk National University, Korea

Dielectric SrTiO@sub 3@ ultra thin films having 30 - 75 nm thickness were deposited on Pt/Si and Ir/Si substrates by plasma enhanced MOCVD using high purity Ti(O-i-C@sub 3@H@sub 7@)@sub 4@, Sr(tmhd)@sub 2@ and O@sub 2@. Depositions were carried out under various operation conditions. The deposition rates were substantially influenced by bubbler temperature (T@sub b@), substrate temperature (T@sub s@) and rf power. The optimum conditions of deposition were T@sub b@ = 60 @super o@C for Ti(O-i-C@sub 3@H@sub 7@)@sub 4@ and 220 @super o@C for Sr(tmhd)@sub 2@, T@sub s@ = 550 @super o@C, 130 sccm O@sub 2@, and 160 W rf with carrier gas flow rates of 40 sccm for Ti(O-i-C@sub 3@H@sub 7@)@sub 4@ and 130 sccm for Sr(tmhd)@sub 2@. The deposition process was controlled by chemical reaction at < 500 @super o@C, and by mass transfer above 550 @super o@C. Decomposition of Ti(O-i-C@sub 3@H@sub 7@)@sub 4@ was enhanced with increasing rf power, but that of Sr(tmhd)@sub 2@ was greatly affected by the substrate temperature. A deposition mechanism of SrTiO@sub 3@ was proposed based on the decomposition rates of Ti(O-i-C@sub 3@H@sub 7@)@sub 4@ and Sr(tmhd)@sub 2@.

TF-MoP19 Investigation of Ti and Cu Atom Density in Magnetron Sputtering Process Using Atomic Absorption Spectroscopy*, **E. Augustyniak**, S.V. Filimonov, C. Lu,* Intelligent Sensor Technology

A hollow cathode lamp based atomic absorption monitor is applied to measure the relative atom density in a planar DC magnetron sputtering system for various Argon pressures (from 1 to 30 mTorr) and input powers (from 0.3 to 20 W/ cm@super 2@). Deposition rates for Ti and Cu are monitored with a piezoelectric microbalance in order to infer the absolute atom densities. Absorption versus deposition data obtained from thermal evaporation of the same materials at Argon pressures in the range from 10@super -6@ to 10@super -3@ Torr are used to estimate the degree of thermalization in sputtering process. Near the target, at distance shorter than one mean-free path of sputtered atoms, the film grows mostly due to deposition of energetic atoms. However, even in this region the thermalized atoms have a significant contribution to the total absorption of resonant radiation. The experimental data show that the reduction of local number density caused by the introduction of a nearby sink for sputtered atoms, e.g., a substrate or a sensor, can be as much as 50%. Ambient gas heating in the vicinity of the target at high input power results in suppressed thermalization and decreased sensitivity of atomic absorption. The combination of atomic absorption spectroscopic and gravimetric (by piezoelectric microbalance) measurements can be a powerful tool for sputtering process characterization.

TF-MoP20 A Study of the Effect of Low Dielectric Constant PAE-2 by Plasma Treatment*, T.C. Chang,* National Nano Device Laboratory, Republic of China*; **M.F. Chou**,* National Chiao Tung University, Republic of China*; T.W. Hsiao,* National Yun-Lin University, Republic of China*; J.Y. Lin,* National Yun-Lin University, Republic of China, Taiwan, Republic of China*; C.Y. Chang,* National Chiao Tung University, Republic of China, Taiwan, Republic of China*; M.S.K. Chen, A. Tuan,* Air Product Company, Republic of China, Taiwan, Republic of China*; S. Chou,* San Fu Company, Republic of China

As the device dimensions continue to shrink to 0.25um and below, the interconnect delay becomes a limiting device factor and increases device speed. Integrating a low dielectric constant ILD into device is a way to reduce the interconnect delay time constant. Low density material such as PAE-2 can offer lower dielectric constant than conventional silicon dioxide insulator. The PAE-2 film has the functional groups with oxygen linkage, so an oxidative post treatment could enhance the properties of PAE-2 film. In this work, we study the effect of post-plasma treatment of PAE-2 film characteristics. The dielectric constant of PAE-2 film is found to be reduced with the application of O@sub 2@ plasma treatment. Also, the optimized condition of O@sub 2@ plasma treatment is obtained. A model is proposed to explain the effect of post-plasma treatment in PAE-2 film.

TF-MoP21 Porous Polycrystalline Silicon Micro-Electronic Sensor*, **P.G. Han,*** The City University of Hong Kong, China*; H. Wong,* The City University of Hong Kong, China, Hong Kong, China*; M.C. Poon,* The Hong Kong University of Science & Technology, China, Hong Kong, China*; N. Wang,* The City University of Hong Kong, China, Hong Kong, China

Porous Polycrystalline Silicon(PPS)-based microelectronic sensors have been explored in our laboratory. Using n-type epitaxial silicon wafer as the substrate, undoped poly-Si films with thickness of 700 nm were deposited by thermal decomposition of silane gas(SiH@sub2@) in a low pressure chemical vapor deposition(LPCVD) reactor. Boron was then diffused into the samples at 950°C for 20 min to form a p-type polycrystalline silicon film. The poly-Si film was selectively anodized in HF(50%vol):C@sub2@H@sub5@OH(96%vol)=1:1 solution with Pt eletrode at a current density of 10mA/cm@super2@ for 10 min at room temperature.The sensitivity of the sensors based on this PPS has been characterized and annlyzed at different ambient pressures and temperature as well as gas species. Results show that the current increases remarkably as the pressure decreases and over two order of magnitude change has been detected when the vacuum pressure was pumped to 10@super -2@ ATM. We find that both ethanol and acetone vapors can make the current increase obviously. In acetone vapor, the device even behaves like a diode. The analysis of the electrical conduction mechanisms of the sensors in vaccum envirement and organic vapors will be conducted in this paper. In addition, since the fabrication process is simple, and the sensor characteristics are repeatable and reproducible, it can be easily integrated with the VLSI technology.

TF-MoP22 Thickness and Index Measurement of Transparent Thin Films using Neural Network processed Reflectance Data*, **M.F. Tabet**, W.A. McGahan,* Nanometrics Inc.

Artificial neural networks and the Levenberg-Marquardt algorithm are combined to calculate the thickness and refractive index of transparent thin films from spectroscopic reflectometry data. A neural network is a set of simple, highly interconnected processing elements imitating the activity of the brain which are capable of learning information presented to them. Reflectometry has been used by the semiconductor industry to measure thin film thickness for decades. Modeling the optical constants of a film in the visible region with a Cauchy dispersion model allows the determination of both thickness and refractive index of most transparent thin films from reflectance data. In this work Artificial neural networks are used to obtain good initial estimates for thickness and two Cauchy parameters An and Bn, these estimates are then used as the starting point for the Levenberg-Marquardt which does a few iterations to find the final solution. This measurement program was implemented on a Nanometrics NanoSpec 8000XSE and will measure thickness and index of transparent films in the range of 1000 to 16000 Å in an average of four seconds.

TF-MoP23 Characterization of PECVD Hydrogenated Amorphous Silicon (a-Si:H)*, **T.C. Ang,*** Nanyang Technological University, Singapore, Republic of Singapore*; M.S. Tse,* Nanyang Technological University, Singapore*; L.H. Chan,* Chartered Semiconductor Manufacturing Ltd., Singapore, Republic of Singapore*; J.L. Sudijono,* Chartered Semiconductor Manufacturing Ltd., Singapore

Unhydrogenated amorphous silicon has a high defect density and this prevents it from being useful for electronic devices. Hydrogen incorporation in a-Si eliminates defects and the quality of a-Si:H depends on the way the hydrogen is incorporated rather than its content in the film. The type of plasma used and the deposition conditions determine the nature of the hydrogen bonding and the film quality. In this paper, the film characteristics of PECVD a-Si:H deposited using pure silane plasma and silane plasma diluted with argon at different deposition temperatures are studied in terms of the deposition rate, hydrogen content, refractive index and film morphology. Fourier transform infrared spectroscopy (FTIR) spectra showed that in a-Si:H films deposited with argon dilution of the silane plasma, hydrogen is bonded to Si only in monohydride groups (SiH) whereas with a monosilane glow discharge plasma, the spectra revealed the presence of SiH, SiH@sub 2@ and (SiH@sub 2@ + SiH@sub n@) bonds. Higher hydrogen content was measured in low temperature deposited films. The RI and absorption coefficient (n, k) values of low temperature deposited films were lower and are consistent with the higher hydrogen content observed in the FTIR spectra. This is mainly due to the decreasing Si densities of the films due to the formation of Si-H and SiH@sub n@ (n>1) bonds in the films. Atomic force microscopy (AFM) was used to investigate the effect of deposition temperature on the film morphology and results showed that smaller grain sizes and tighter packing densities were characteristic of higher temperature deposited films. Results obtained through FTIR and spectroscopic ellipsometry (SE) show a correlation between the hydrogen content and the RI. Films deposited at higher deposition temperatures have lower H content and higher RI values as compared to lower temperature deposited films. Results from electrical tests on a-Si:H films deposited at different temperatures revealed changes in film quality which are consistent with the FTIR and SE observations. @FootnoteText@ W. Beyer and H. Wagner, J. non-crystall. Solids 59/60, 161 (1983). W. Beyer, Tetrahedrally-Bonded Amorphous Semiconductors, Ed. D. Adler and H. Fritzsche, Plenum Press, New York, 129, 1985. W. Beyer, Physica (Utrecht), 170B, 105,1991. R. A. Street, Hydrogenated Amorphous Silicon, Cambridge Solid State Science Series (Cambridge University Press, Cambridge, 1991). Akihisa Matsuda, Plasma Physics Control Fusion, 39, pp.A431,1997.

TF-MoP24 The Analysis of Silicon Oxynitrides with Spectroscopic Ellipsometry and Auger Spectroscopy, Compared to Analyses by RBS, and FTIR*, **H.G. Tompkins**, R. Gregory, P.W. Deal, S.M. Smith,* Motorola, Inc.

This work addresses the issue of whether spectroscopic ellipsometry, using the effective medium approximation (SE-EMA), may be used meaningfully to analyze PECVD silicon nitride films. We use RBS and FTIR as reference methods and compare the results to the results of SE-EMA analyses and Auger analyses. The results are that Auger analysis, using properly determined sensitivity factors, gives compositions which are within the uncertainty of the reference methods. SE-EMA, on the other hand, always overestimates the oxide contribution and underestimates the nitride contribution. Probable causes are discussed.

TF-MoP25 Density Measurement of Thin Glass Layers for Gas Barrier Films*, **N. Fukugami**, H. Nishino, M. Yanaka, Y. Tsukahara,* Toppan Printing Co., Ltd., Japan

In the food packaging industry, there is an increasing demand for transparent gas barrier films consisting of a 10 ~ 100 nm thick glass layer deposited on a polymer substrate. An advantage of such films is that microwaves and light waves can penetrate. It was confirmed that our glass layer had no macro defects or pinholes, and the gas penetration mechanism was mainly due to a nano structure of the glass layer.@footnote 1@ It is anticipated that the density of the glass layer is an important factor to characterize such nanostructures. Therefore, an accurate density measurement of thin layers with thicknesses ranging from 10 nm to 100 nm was needed. We used a weight-volumetric method, and obtained the density with three digits accuracy. First, densities of SiOx layers which were deposited by vacuum evaporation on Si (100) surfaces were measured. The Si surfaces were used because they were well-characterized and smooth. The volume of a layer was obtained as a product of the layer thickness and its area. The area was defined by a window which was located in front of the Si substrate during the deposition. The thickness was obtained by measuring the edge height of stripes made over the entire surface by photolithography process. Dektak (Dektak3030, Nihon Shinku Gijutsu Inc.) was used for the edge height measurement. A weight of the layer was measured by Ultramicrobalance (Sartorius supermicro, Sartorius Inc.). The densities thus obtained were 2.15±0.01g/cm@super 3@ and 2.16± 0.03g/cm@super 3@ for layers with slightly different deposition conditions. Next, a novel method was invented for the density measurement of thin glass layers deposited on polymer substrates. The method made use of the fact that parallel multiple cracks were induced in the glass layer when the film was stretched.@footnote 2@ The thickness of the glass was obtained by measuring the depths of crack openings. The accuracy of the measurement was also investigated. @FootnoteText@ @footnote 1@B. Henry, et. al., presented at the 41st Society of Vacuum Coaters Technical Conference (April 1998). @footnote 2@M. Yanaka, Y. Tsukahara, N. Nakaso and N.Takeda, accepted to the J.Mat.Sci., 1998.

TF-MoP26 Accurate and Rapid Determination of Thickness, n and k Spectra, and Resistivity of ITO Films*, K. Zhang,* EG&G, US*; **R. Forouhi**, I. Bloomer,* n&k Technology, US

The transparent conductor, indium tin oxide (ITO), is an important thin film component of flat panel displays. An optimum ITO film should be both highly transparent to visible wavelengths and at the same time, conductive. In practice, however, a trade-off exists between these two attributes, making it difficult to produce a film that simultaneously meets both demands. In order to achieve the optimum balance between these properties, an effective method of characterizing ITO films is necessary. In this talk we will present results of a new measurement technique that simultaneously determines, thickness, the spectra of the refractive index (n) and extinction coefficient (k) from 190 to 1100 nm, and the energy band gap, of ITO films deposited on either transparent or opaque substrates. In addition, we will demonstrate how the film's resistivity can be correlated to the film's extinction coefficient. This technique is based on wide-band spectrophotometry, combined with spectral analysis incorporating the Forouhi-Bloomer dispersion equations for n and k.@footnote 1,2@ The measurement technique is non-destructive and takes only a few seconds. @FootnoteText@ @footnote 1@A.R. Forouhi and I. Bloomer, Phys. Rev. B, 34, 7018 (1986). @footnote 2@A.R. Forouhi and I. Bloomer, Phys. Rev B, 38, 1865 (1988).

TF-MoP27 Mechanical Properties and Strengthening Mechanisms of Pure Iron Implanted with Metal Ions, ***D. Yang,*** University of Alabama*; Q. Xue,* Lanzhou Institute of Chemical Physics, China

Ion implantation can alternates surface composition and microstructures of metals dramatically, consequent change of physical and chemical properties of ion implanted layers appears as a result of it. The first noticeable effect of implantation is variation of surface residual stress and microhardness. To further understand the effect of metal ion implantation on mechanical properties and strengthening mechanisms, Cr, Mo, W, Ni, Al ion implantation into pure iron was performed on a Metal Vapor Vacuum Arc (MEVVA) source implanter at doses of 5×10@super 16@ ions/cm@super 2@, 1×10@super 17@ ions/cm@super 2@ and 3×10@super 17@ ions/cm@super 2@. The atomic concentration, element distribution, phase structure, surface residual stress and microhardness were measured by Auger Electron Spectroscopy (AES), X-ray Diffractometry and microhardness tester respectively. The relationship among the atomic radius, residual stress and hardness was studied and discussed. It was shown that the highest atomic concentrations in the implanted layers were between 6 at.% to 38 at.% depending on the elements implanted and implantation doses. The higher and bigger the implantation doses and differences in radius between pure iron and implanted element atoms are, the larger the highest atomic concentration in the implanted layers. In addition, the ion implantation resulted in residual compressive stresses of 663-957 MPa and an increase of 5%-43% in microhardness of pure iron surface. Ion implantation dose was not the only factor influencing surface stress and hardness. The decisive factor was the existing format of ion implanted element, i. e. if the implanted element existed as solid solute the residual compressive stress would be higher and the hardness would be lower; if it existed mainly as compounds then the stresses would be lower and the hardness higher.

TF-MoP28 The Dislocation Network Developed Deep in Titanium Nitride by Ion Implantation, ***A.J. Perry,*** A.I.M.S. Marketing, Japan*; D.E. Geist,* Analytical Reference Materials International*; Y.P. Sharkeev,* Russian Academy of Sciences, Russia*; S.V. Fortuna,* Tomsk State University of Architecture & Building, Russia

After treatment by ion implantation, the implanted ions in metallic materials reside in an implanted zone, IZ, extending to a depth of some hundreds of nanometers. Earlier work has shown that the momentum carried by the ions affects the material to far greater depths with a dislocation network extending many microns deep. Dense, thick coatings of titanium nitride can be deposited with low residual stress and low dislocation densities at high temperatures, some 950 C, without the application of substrate bias. Normally used for wear resistance, these coatings are an ideal model system for studying the nature of the IZ and the development of the dislocation network well below it. Studies have been carried out by TEM and glancing incidence XRD. The TEM study shows that implantation leads to the formation of sub-grains within the original grain structure without any grain comminution occurring. A mechanism is then proposed to explain the development of the dense dislocation network below the IZ which is studied by XRD as a function of ion species, acceleration voltage and dose in an extended series of samples. It is found that while any ion bombardment produces a dislocation network, there is a momentum threshold level before a compressive residual stress is developed. This stress is proportional to the ion momentum, reaching values as high as 3-4 GPa, i.e. as high as that found in materials made by PVD methods. Finally we find that there is a significant change in the stress in the substrate below the titanium nitride coating which, surprisingly, can be tensile or compressive and is sensitive to the ion species implanted.

Vacuum Metallurgy Division
Room Hall A - Session VM-MoP

Vacuum Metallurgy Division Poster Session

VM-MoP1 Studies on Corrosion, Wear and Erosion-Corrosion of Aluminum Coated Steel before and after Nitrogen Ion Implantation*, M. Ghoranneviss,* ***M. Abyar Monfared Kashani****, S. Meery, H. Parcharmi, A. Shokohi,* Islamic Azad University, Iran

Aluminum base coatings have been used many years as a protective layer on steels, but application of this coating is limited due to its poor wear and corrosion resistance. The main goal of this work is increasing corrosion and consequently erosion-corrosion resistance of these coatings. Steel samples were coated with different aluminum alloy by means of ion beam sputtering and then implanted by different dose and energy nitrogen ion beam. We studied properties of this coating before and after ion implantation by potentiodynamic polarization, pin on disk and rotating coupon tests. Optical and electron microscopes were also used. The results of these tests are discussed in the paper.

VM-MoP2 Deposition of bcc Ta and beta-Ta Films using Different Underlayers, ***L.V. Kozlovsky,*** *A. Antinsh,* University of Daugavpils, Latvia

The formation of crystalline phases in sputtered Ta films can be attributed to the deposition conditions as well as to the nature of the substrate. We deposited 100 nm Me / X nm Ta (Me: Mo, W, Nb, Ti, Zr, Hf, Dy, Fe, Al; X = 40,100, 200 nm) bilayers on room-temperature glass substrates in a Xe discharge at a pressure of (5 - 8) x10@super -4@ Torr using Penning discharge sputtering devices @footnote 1@. The base pressure was nearly 5x10@super -9@ Torr. 10 nm C underlayers were deposited on substrates at the same vacuum conditions before bilayers deposition. The structure of the films was investigated by X-ray diffraction (XRD). XRD profiles revealed peaks corresponding to (110), (220), (211) reflections of bcc Ta, peaks at d = (0.2665 0.2672) nm and the second orders of these reflections. The peaks were attributed to the beta-Ta phase in the films. Ta films on Nb, W, Mo, Ti, Al had bcc structure. Ta/Dy, Ta/Fe films structure was characterized as beta-Ta and Ta/Zr and Ta/Hf films consisted of a mixture of bcc Ta and beta-Ta. The Me and Ta layers had preferred orientation of close-packed planes parallel to the substrate plane (the [111], [110], [001] planes for the fcc, bcc, hcp metals correspondingly). The shortest interatomic distances (SID) in the Me are the shortest distances between the atoms in these planes. The correlation between beta-Ta formation in Ta/Me bilayers and mismatching of the SID in bcc Ta and in Me was found. Results of Ta films crystal structure investigations will be presented and discussed. @FootnoteText@ @footnote 1@ 1. L.V. Kozlovsky. Istrum. Experim. Techniq., 38, iss. 3, pt. 2, 417, (1995).

VM-MoP3 Graded TiAlN Layers Deposited by ECR Assisted Reactive Sputtering*, A. Raveh,* ***M. Weiss****,* Nuclear Research Center-Negev, Israel

Graded layers have been reported to reduce property discontinuities at the interface. TiAlN layers were deposited by plasma reactive sputtering employing dual cathode radio-frequency sputtering targets, Ti and Al, assisted by electron cyclotron resonance (ECR). The layers were deposited using various combination of parameters such as power input, bias substrate voltage and gas feed composition. The deposition process was monitored by optical emission spectroscopy (OES). The OES results indicate that microwave excitation added to radio-frequency plasma has contrasting effects on Ti and Al concentration in the gas phase, enhancing titanium and quenching aluminium species reaching to the deposited substrate. Thus, by the regulation of the ECR power and the ratio of nitrogen flow to nitrogen plus argon flow, the formation of graded layers is allowed. Hence, this approach was found appropriate for controlling and tailoring the interface between a metallic substrate and hard coating. The layers formed in this way were characterized with regard to structure, composition, and mechanical properties using X-ray diffractometer, Auger electron spectroscopy microscope, and Vickers microhardness and scratch tester (adhesion). It was observed that layers deposited at a low ECR power (@<=@100 W) yielded oriented (111) crystalline structure with good adhesion (failure load >70 N). These layers displayed a higher microhardness (~25 GPa) at bias substrate voltage (-50 VDC) than that of grounded substrate (10-15 GPa). However, layers deposited at an ECR power higher than 100W showed a random or amorphous structure with an intermediate adhesion range (failure load 30-50 N). The relationship between the processing parameters, the structure, and the properties of the layers formed will be presented and discussed.

VM-MoP4 Microwave Plasma Nitriding of Pure Iron*, **E. Camps**,* Instituto Nacional de Investigaciones Nucleares, Mexico, México*; S. Muhl, O. Alvarez-Fregoso, J. Chavez-Carvayar,* IIM, UNAM, Mexico*; O. Olea-Cardoso,* UAEM, Mexico

This paper presents the results of a study in which the performance of an electron cyclotron resonance (ECR) plasma source has been evaluated in regard to it's use for the nitriding of pure Fe. Diagnostic measurements,using optical emission spectroscopy (OES), Langmuir probes and an ion analyzer, were recorded as functions of the working pressure (2 - 8 x 10@super -4@ Torr) and for two different configurations of the external magnetic field near the substrate (compressed and divergent plasma flux). It was observed that the plasma source is capable of producing high density discharges, about 5 x 10@super 11@ cm@super -3@ and ion energies about 15 25 eV. Although the average ion energy was higher for the case of a divergent plasma flux (~ 45 eV). The most abundant radicals produced in the N/H discharges were NH, N@sub 2@ and N@sub 2@ @super +@ species. Experiments for nitriding of Fe showed the formation of distinct material structures when using different plasma conditions. Under certain conditions it was possible to form almost single phases of Fe@sub 3@N and Fe@sub 16@N@sub 2@ in the sample surface.

Vacuum Technology Division
Room Hall A - Session VT-MoP

Vacuum Technology Poster Session

VT-MoP1 Behavior of the Negative Collector Current in Ionization Vacuum Gauges*, **K. Kokubun**, M. Hirata,* Electrotechnical Laboratory, Japan

In or near XHV pressure region, negative collector currents have been observed in the Extractor vacuum gauges that several times experienced a baking at 573 K for about 70 hours.@footnote 1@ It was found that the negative collector current continued to flow even when the gauge was not in operation. Authors confirmed that in these gauges a negative electromotive force of - 1 V to - 100 mV was formed in the system including the collector electrode and the gauge body, and simultaneously the insulation of the collector electrode degraded due to unknown causes. These results suggested that some new structure was formed in the gauge head system by the bakings. This conjecture was supported by measuring the temperature dependences of the negative collector current, the negative e.m.f., and the insulation resistance. These temperature dependences were remarkably different from those of a normal gauge. Especially, the insulation resistance drastically increased to about 330 K, and then abruptly decreased. This behavior was in strong contrast to that of the normal gauge. On the other hand, in the normal gauge a significantly larger positive e.m.f. was observed. But it was found that only a small positive current flowed because of the very large insulation resistance of the collector electrode. @FootnoteText@ @footnote 1@K.Kokubun and M.Hirata, J. Vac. Soc. Jpn, 40, 137(1997).

VT-MoP2 Compatibility of a Control Unit and a Sensing Coil Unit with a Rotor Ball of a Spinning Rotor Gauge*, **M. Hirata**,* Electrotechnical Laboratory, Japan

A spinning rotor gauge is one of the most reliable vacuum gauge. The gauge is a noble viscosity gauge which is essential to a transfer gauge and a reference gauge in high vacuum. The gauge consists of a control unit, a sensing coil unit and a rotor ball installed in a tube. The rotor is operated frequently in a different pairing of the control unit and the sensing coil unit for convenience of transportation and use. In order to clarify the interchangeability of the electronic unit and the sensing coil unit with the rotor ball, accommodation coefficient of the rotor ball in the different pairing was measured preciously by a direct comparison with a reference spinning rotor gauge. Pressure measurements by the two gauges was simultaneously done by using a personal computer. While repeatability within 0.1% was obtained in the measurement of the relative accommodation coefficient, the rotor showed a slightly high value, 0.5%, in the coefficient in special pairings. Consideration of the experimental results in detail showed that one of seven coil units gave slightly high value in the coefficient. The coefficient did not depend on the control unit. Big tilt of the sensing coil units, about 15@degree@ from the normal vertical axis, also gave a slightly high value in the coefficient. Remagnetization changed the value of the coefficient occasionally. It seems that the coefficient depends on the mode of the rotation of the ball. A fixed pairing of the rotor with the sensing unit is preferable for a reliable pressure measurement by the gauge.

VT-MoP3 A New High-Power Ion Source Based on Magnetically Neutral Loop Discharge*, **F. Shimokawa**,* NTT Opto-electronics Laboratories, Japan

We developed a new high-power ion source based on the high-density plasma formation method that is known magnetically neutral loop discharge (NLD). Our original ion source consists of three separate electromagnetic coils, as well as ion extracting grids and a quartz vessel chamber with a one-turn RF antenna coil, which is the main component of the conventional RF ion source. The three separate electromagnetic coils are located around the periphery of the chamber. The current in the middle coil flows in the opposite direction of the currents in the top and bottom coils. By using these source configurations, a magnetically enhanced plasma that is known as NLD occurs in the chamber. Our source produces a high plasma density of 10@super 11@ cm@super -3@, which is 10 times higher than that of the conventional source under a lower gas pressure of 0.1 Pa. Also, it is possible to control both the ring-like plasma diameter and the high-density plasma generation position in the chamber. As a result, we achieved the high ion current density (10 mA/cm@super 2@) at 300 V of ion extracting voltage, which is almost 10 times higher than the conventional source. Furthermore, we also obtained a high ion current uniformity of about 3% over a 6-inch diameter by using our source's plasma space controllability. A processing system that uses this new source will contribute to faster processing, excellent uniformity processing, and high quality processing for ion beam etching, ion beam deposition, and ion beam sputter deposition. Many other applications are also expected to come about from this method.

VT-MoP4 Stabilization of Long Travel - Single Bellows - Horizontal Manipulators*, **V.S. Smentkowski**, A.L. Linsebigler,* General Electric Corporate Research and Development Center

Single bellows, long travel, horizontal manipulators are required for many experiments in surface science. Unfortunately, the gravitational force exerted on long travel - single bellows - horizontal manipulators results in stability problems including, but not limited to unwanted sample vibrations and non-reproducible sample positioning. We have designed, built, and tested a simple add on device that efficiently alleviates such problems. The device that will be described can be used with any manipulator, regardless of age. The cost to implement this device (machining and parts) is minimal.

VT-MoP5 Pressure Wave Propagation by Gas Expansion in a High Vacuum Tube*, **T. Takiya**,* Hitachi Zosen Corporation, Japan*; F. Higashino,* Tokyo Noko University, Japan*; Y. Terada, A. Komura,* Hitachi Zosen Corporation, Japan

This paper describes an unsteady tube flow model which accounts for the effect of contracted flow around the entrance orifice of a tube. The sudden expansion of gas introduced into a vacuum tube is an important phenomenon, which has to be studied in relation to leakage accidents of vacuum devices. In order to predict the pressure wave propagation speed, it is necessary to model the gas expansion in a vacuum tube. So we proposed an analytical model for gas expansion in a high vacuum tube, with the aim of preventing vacuum hazards at scientific experimental facilities. Setting a very high pressure drop between the outside and inside of the vacuum tube makes the model applicable to high vacuums, although the model is based on continuous fluid dynamics. We installed an orifice on the inlet end of the tube in the model, and investigated the orifice aperture effect on the propagation velocity of pressure waves. It was found that a rarefaction wave rather than a shock wave was primarily involved in vacuum accident damage, and that orifice aperture controls pressure increase rate in the low pressure regime more sensitively than in the high vacuum regime. This study was carried out to provide necessary data in designing vacuum protection for long tube-like devices, such as the beamline for synchrotron radiation, by solving the set of basic equations that incorporates important conditions.

VT-MoP6 Measurement of Secondary Electron Yields of Copper Materials and the Surface Analysis*, **S. Kato**, K. Kanazawa,* KEK, Japan*; N. Kitano, N. Matsuda,* Tokyo Denki University, Japan

Photoelectron instability is one of serious problems in a positron storage ring of colliding accelerators such as PEP-II and KEKB where a current of a couple of amps is stored. It occurs in a manner that the positron beam interferes with an enormous amount of secondary electrons emitted from surfaces of vacuum pipes bombarded by a large amount of photoelectrons due to synchrotron radiation. This instability considerably disturbs beam operation. In this study, secondary electron yields from copper materials where some surface treatment techniques were performed were measured to make a comparison with other materials. Target samples were prepared by three different chemical polishing techniques using a) a water solution of sulfuric acid and hydrogen peroxide, b) a water solution of citric acid and c) a) and subsequent b). These samples were treated in the same condition as the extruded copper chambers for KEKB electron-positron collider. The secondary electron yields were measured at a typical condition of a kinetic energy ranging from 0.1 keV to 2.0 keV at a normal incident and a sample temperature of 23 ° C. The residual gas pressure of the sample chamber was less than 2x10@super -7@ Pa during the measurements. In order to avoid electron beam induced contamination at the sample surface from the residual gas even so, a total dose of electrons for a measurement was limited to be 1x10@super 12@ electrons/cm@super 2@ by use of a pulsed beam. Characterization of those surfaces was also done by Auger electron spectroscopy with argon ion sputter etching. This gives information about depth profiles of atomic compositions in an altered surface layer due to the treatment discussing the interrelation between the secondary electron yields and the surface atomic compositions. The lowest maximum yield of secondary electrons of 1.05 was observed at the surface treated as (a) where the oxidized layer was found to be the most stable against a long exposure to air in contrast to the surface treated as (b).

VT-MoP7 Study of Field Emission Properties of GaN grown by ECR MBE*, **I.E. Berishev**, O. Kameli, D. Starikov, A. Bensaoula, I. Rusakova,* University of Houston*; V.P. Ageev, M.V. Ugarov, A. Korabutov,* General Physics Institute, Russia

GaN thin films were grown by electron cyclotron resonance (ECR) molecular beam epitaxy (MBE) on Si (111) wafers. X-ray diffraction and both scanning and transmission electron microscopy were used to characterize the thin films in order to determine their crystal structure and surface morphology. The films consisted from clearly defined columns about 100 nm in diameter. Despite the large defect density, a strong room temperature photoluminescence signal was observed from these samples. The origin of this luminescence and its role on field emission will be discussed. The surface of the films exhibited random array of sharp tips at the microscopic level with about 5x109 tips/cm2 density. The field emission characteristics, voltage threshold and emission current, of these thin films were order of magnitude higher than any published data. The dependence of the emission characteristics on the doping level, substrate orientation, film thickness, and post-growth surface modification were investigated. Potential GaN/Si-based field emission devices will be discussed and preliminary results will be presented.

VT-MoP8 Outgassing Tests on Materials Used in the DIII-D Tokamak@footnote 1@*, **K. Holtrop**, M. Hansink, A.G. Kellman,* General Atomics

In order to achieve high performance plasma discharges in the DIII-D tokamak, impurity levels must be carefully controlled. Since first wall materials can desorb volatile impurities during these discharges, it is important to characterize and control the outgassing of these materials. An outgassing chamber was built to measure the outgassing properties of various materials used in the DIII-D vessel. The results of pump-down tests performed on ATJ graphite, thin grafoil gaskets, and MGO coaxial cables will be presented. In addition, to pumpdown tests it was desired to study the behavior of the materials at temperatures up to 400°C, which is the maximum temperature to which the DIII-D vessel is baked. The station was modified to include independent heating control of the sample and a simple load-lock chamber. @FootnoteText@ @footnote 1@Work supported by the U.S. Department of Energy under Contract No. DE-AC03-89ER51114.

VT-MoP9 Simple Catalytic Cell for Restoring He Leak Detector Sensitivity on Vacuum Systems with High D@sub 2@ Backgrounds**, **J. Busath**, H.K. Chiu,* General Atomics

The DIII-D National Fusion Facility at General Atomics focuses on plasma physics and fusion energy science. The DIII-D tokamak is a 35 M@super 3@ toroidal vacuum vessel with over 200 ports for diagnostic instrumentation, cryogenics, microwave heating, and four large neutral beam injectors. Maintaining vacuum in the 10@super -8@ Torr range is crucial for producing high performance plasma discharges. He leak checking the DIII-D tokamak and the neutral beamlines has historically been difficult. D@sub 2@ is used as the fill gas in most plasma discharges. After plasma operations, D@sub 2@ out-gassing from the torus walls and internal beamline components can exceed 10@super -4@ Torr l/s. The mass of D@sub 2@ molecule (4.028 amu) is indistinguishable from that of the He atom (4.003 amu) to a standard mass spectrometer leak detector. High levels of D@sub 2@ reduce leak detector sensitivity and effectively mask the He trace gas signal rendering normal leak checking techniques ineffective. A simple apparatus was developed at GA to address these problems. It consists of a palladium based catalyst cell and associated valves and piping placed in series with the leak detector. This reduces the D@sub 2@ throughput by a factor greater than 10,000, restoring leak detector sensitivity. This paper will briefly discuss the development of the cell, the physical processes involved, the tests performed to quantify and optimize the processes, and the operational results at DIII-D. @FootnoteText@ *Work supported by the U.S. Department of Energy under Contract No. DE-AC03-89ER51114.

Applied Surface Science Division
Room 307 - Session AS-TuM

Sample Preparation and Tricks of the Trade

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am **AS-TuM1 Using a Focused Beam XPS System for Analysis of Oxides, Insulators and Beam Sensitive Materials@footnote 1@***, **M.H. Engelhard**, L.-Q. Wang, B.J. Tarasevich, D.R. Baer,* Pacific Northwest National Laboratory

Experience gained during use of a Physical Electronics Quantum 2000 XPS system for the analysis of some oxides, insulators and beam sensitive materials is reported. This instrument, which is part of a Department of Energy user facility, uses an internal monochromatic focused x-ray beam that can be focused, raster scanned, and changed in intensity. Some of our initial studies with this instrument involved comparison of data from the Quantum with measurements made on older systems. These comparisons included an examination of line widths, x-ray damage, and effectiveness of the neutralization methods. In addition to the normal Quantum specimen handling system, the spectrometer can interface with a special specimen handling system that allows interchange among 15 different locations in the user facility. This extra capability allows conduct of a variety of experiments (involving heating, film deposition, electrochemistry or corrosion) but introduces a variety of challenges for specimen mounting. Specific data to be reported include measurements of line-width and the ability to observe defects on the rutile (110) surface and damage observed during analysis of self assembled monolayer and polymer systems. This system now includes the newly developed ion-neutralization capability (U. S. patent 5432345). Because this neutralization system includes the use of both an electron gun and low energy Ar ions, a test was made to determine if the neutralization method introduced defects on a "defect free" rutile surface. No introduction of defects was observed for the period of our test. @FootnoteText@ @footnote 1@This research was conducted at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) with funding provided by the U.S. Department of Energy, Office of Basic Energy Sciences. The EMSL is a new DOE scientific user facility located at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. PNNL is operated by Battelle for the Department of Energy.

8:40am **AS-TuM2 Implementation and Application of a Ag L@sub alpha@ Monochromatic Source on a Magnetic Lens Based Spectrometer***, **C.J. Blomfield**, B.J. Tielsch, S.P. Page,* Kratos Analytical Ltd, United Kingdom

High energy Ag L@sub alpha@ X-rays have several advantages over the more commonly employed Al K@sub alpha@ source. A photon energy of 2984.3 eV means that a Ag source can generate higher 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@sub alpha@ monochromator body with only minor modifications. Such an approach has previously resulted in a workable source although the sensitivity was reduced in comparison to the Al K@sub alpha @source.@footnote 1@ We have now for the first time implemented a Ag monochromator as a modification to the standard Al mono on a modern magnetic lens based electron spectrometer, the Axis Ultra. The great improvements 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 functionality will be demonstrated with examples of Auger parameter and high energy core level spectroscopy. @FootnoteText@ @Footnote 1@K Yates RH West Surface and Interface Analysis Vol 5 No 4 1983 133-138

9:00am **AS-TuM3 The Good and the Bad About XPS Peak Fitting***, **N.H. Turner**,* Naval Research Laboratory

Fitting XPS peaks is done to identify different elemental components or atomic sublevels in cases where there is a complex peak shape. Also, fitting is performed to determine parameters such as peak position, height, and FWHM even for a simple, one component line. Usually Gaussian or Lorentzian line shapes (or a combination of these functions) are used for fitting purposes. Often from these determinations relative atomic amounts of the detected species are computed for the sample being studied. There are many factors that contribute to an observed peak, and a blind acceptance using curve fitting potentially can lead to erroneous interpretations of the experimental data. These mistakes can include physically unrealistic situations and the number and types of components present. In this presentation methods to better use curve fitting will be presented to minimize many of the possible problems. These practical approaches include considering the chemistry and physics of the system being studied, employing reasonable fitting criteria where appropriate, e.g., peak widths and energy separations, relative atomic area ratios, number of variables, curve types, other elements present, and the experimental conditions under which the data were obtained.

9:20am **AS-TuM4 Auger Depth Profiling at Extreme Low Ion Energy***, **M. Menyhard**, A. Barna, A. Sulyok,* Research Institute for Technical Physics and Materials Science, Hungary

To obtain good depth resolution the sputtering induced surface roughening as well as the ion mixing should be reduced. It is well known that applying Zalar rotation with grazing angle of incidence the surface roughness is considerably reduced and the depth resolution is mainly determined by ion mixing. We have shown previously that the ion mixing proportional to the square root of the ion energy, in the energy range of 4-0.25 keV, thus the best depth resolution can be obtained by applying the lowest possible ion energy. To improve further the depth resolution we have constructed a new ion gun operating down to 0.1 keV. We will report on the experimental findings using this extreme low ion energy for depth profiling, and a novel evaluation procedure (based on dynamic TRIM simulation considering the experimentally determined roughness values) of the depth profiles. We will show that the sputtering induced surface roughness (specimen is rotated during sputtering) depends on the ion energy; e.g. in case of GaAs we have found 1 nm and non roughness for 1 keV and 0.25 keV ion energy, respectively [1]. We will also show that the square root of ion energy dependence is also valid for this 0.25 - 0.1 keV ion energy range. We will demonstrate the capability of the method on several examples. E.g. we will show that using extreme low ion energy and our novel evaluation method for the depth profiling of a GMR structure, consisting of 1 nm thick Co/Cu layer, the demixing of Cu and Co can be demonstrated. This work was supported by grant OTKA 15880. 1. A. Barna, B. Pécz and M. Menyhard, Ultramicroscopy 70 (1998) 161-171

9:40am **AS-TuM5 Sample Preparation and Practical Surface (and Interface) AnalysisTricks of the Trade***, **D.F. Reich**,* Physical Electronics **INVITED**

In applied surface science, instruments are now available with 'push-button' tuning of spectrometers and primary beam columns, automated analysis capabilities, and so on. Nevertheless, far from becoming less important to the analytical process, the analyst remains as critical as ever to the success of the whole enterprise. The aim of this presentation is to discuss some 'practical' knowledge, particularly in relation to sample preparation and instrument operation for surface analysis. My own area of practice is dynamic and static SIMS, using quad and time of flight SIMS instruments. However, the general sample preparation requirements for SIMS are equally encountered in AES, XPS etc. The practical methods discussed should hopefully be of interest to all, not just SIMS practitioners. (1) The following types of sample preparation will be addressed: Cryo-preparation of volatile and organic materials: freeze-drying, cryo-microtoming. Cold introduction and cold stages. X-section preparations: fracture methods, microtoming, 'clean' polishing. Mounting of awkward geometry samples: powders, tubes, rods, fibers: woven; strands; loose mats, etc. Solvent cleaning: which solvents to use in the event of contamination, either on samples or on contaminated sample holders. Potential problems for polymers and organic surface treatments. Use of adhesives for sample mounting: forbidden territory? Which products are acceptable and which are not. (2) Certain instrumental parameters will also be addressed: Primary beam probe size effects: flux densities and beam damage. Requirements for charge compensation on insulators. Tricks of the trade. Practical limits. Spectrometer issues: the importance and influence of the energy window of whatever spectrometer (electron or ion) is in use. In summary, the presentation will aim to give you, a fellow analyst, some ideas that may be of use in increasing that part of your knowledge of surface science that is 'practical'.

10:20am **AS-TuM7 Physical Influences on Chemical Identification using TOF-SIMS***, **T.J. Schuerlein**, G.S. Strossman, K.J. Wu, T.F. Fister,* Charles Evans & Associates

Time of flight secondary ion mass spectrometry (TOF-SIMS) is rapidly becoming a standard tool for failure analysis and identification of surface contamination. One requirement of a tool used for these purposes is to be able to use reference spectra to help identify unknowns, as is typically done in other techniques such as FTIR. Although TOF-SIMS has had great success in addressing such identification issues, there are some possible pitfalls that are to be avoided when acquiring reference spectra and making subsequent comparisons to analytical data. We have observed a series of physical parameters that can alter mass spectra that are not related to the chemical nature of the analyte. In some cases these effects are subtle, in others the changes observed in the mass spectrum are significant. Data will be shown which illustrates these effects for physical parameters such as contaminant thickness, sample temperature and the interaction between surface species. We will also demonstrate how the intentional introduction of a reagent can be used to increase the molecular ion yield of high molecular weight species.

10:40am **AS-TuM8 SEM Sample Preparation Using Ion Sputtering**, ***J.R. Kingsley***, *X. Lu,* Charles Evans & Associates

Wet chemical etching has long been the preferred method for the delineation of features in cross sections of Integrated Circuits. Dry chemical etching, or plasma etching, has also been used as an effective tool for the selective removal of material. One limitation of these techniques is a lack of reproducibility due to such factors as wet etch age, temperature, etch time and composition. Plasma condition changes due to the size and number of samples, the other materials present, and the long time stability of the plasma adversely affect dry chemical methods. In this paper we characterize the use of focused ions, in combination with electron microscopy, to circumvent the inherent inconsistent results noted above. By using focused ions as the etching source in the same vacuum as the imaging source, a reproducible stop point can hopefully be obtained.

11:00am **AS-TuM9 The Correlation Between Ion Beam/Material Interactions and Practical FIB Specimen Preparation**, ***B.I. Prenitzer***, *L.A. Giannuzzi,* University of Central Florida*; S.R. Brown,* Cirent Semiconductor*; T.L. Shofner,* Bartech Group*; R.B. Irwin, F.A. Stevie,* Cirent Semiconductor

Nanometer scale, high resolution Ga@super+@ ion probes, attainable in commercially available focused ion beam (FIB) instruments, allow sputtering/deposition operations to be performed with a high degree of spatial precision. In addition to semicondutor applications, FIB methods have been applied to the preparation of SEM and TEM specimens from a host of materials that have traditionally proven to be challenging from the standpoint of either composition or geometry. As FIB applications increase in diversity, it becomes necessary to examine the interrelationships between target material, variable processing parameters, and process efficiency of the milling phenomena. The roles of incident ion attack angle, beam current, raster pattern, and target material dependent removal rate are considered as applied to the FIB lift-out method. Careful characterization of such relationships is used to explain observed phenomena and predict expected milling behaviors, thus expediting the fine tuning process for new or novel applications and allowing the FIB to be used more efficiently with reproducible results. Applications involving fibers, powders, and interfaces in metal, ceramic, and biological materials are presented.

11:20am **AS-TuM10 Use of Micro-Craters and Extended Rotational Profiling for Auger Analysis of Difficult Samples**, ***R.E. Davis,*** IBM Corporation, East Fishkill Facility

When designing, evaluating or operating an Auger electron spectrometer, it is common and appropriate to turn ones attention first to the performance of the primary excitation, and second to the spectrometer. However, in certain types of difficult samples, the desired experimental outcome depends in many cases more on other factors. This paper will describe several examples of such difficult problems which were successfully analyzed by focusing on the sputtering process and the ion gun, with only ordinary emphasis on the electron column and spectrometer. The first example overcomes a common problem for Auger analysts, dealing with very small electrically conductive features that are surrounded by insulating material. With these samples one can make good use of the higher brightness of a magnetically-confined ion source, or duoplasmatron, to depth profile with very small sputtered areas, on the order of ten microns across. Examples of the application of this technique will be drawn from studies of semiconductor technology. The second application involves very thick multilayered stacks of metals, with a thin (200Å) but crucial adhesion layer of chromium buried under seven microns of gold, nickel and copper. By attacking the buried layer from the top, one can establish a baseline for how much oxygen and carbon are present at the bottom of the chromium layer without exposure to ambient, even for films with excellent adhesion. Another example of extended depth profiling will be presented which involved subtle changes in the distribution of @theta@-phase aluminum copper within Al-2% Cu semiconductor interconnects, which had important ramifications in terms of chemical-mechanical polishing.

11:40am **AS-TuM11 Two-Dimensional Surface Roughness Measurements of Sidewalls of High Aspect Ratio Patterns Using the Atomic Force Microscope**, *K.-J. Chao,* ***R.J. Plano,*** *J.R. Kingsley,* Charles Evans & Associates

Methods of measuring the surface roughness of the sidewalls of high aspect ratio patterns are presented. Cleaving developed resist and etched silicon samples parallel to the long direction of the patterns and tipping over the sample 90 degrees fully exposes the sidewall surfaces, allowing investigation by either the Scanning Electron Microscope (SEM) or the Atomic Force Microscope (AFM). Another method, simply tipping over the lines in the developed resist samples, also allows full access to the resist sidewall. While the SEM can be used to confirm the sidewall surface features, the AFM provides quantitative information such as the Root-Mean-Square (RMS) roughness, unobtainable through other methods.

Biomaterial Interfaces Group

Room 326 - Session BI-TuM

Biosensor-Biology Interface

Moderator: B.D. Ratner, University of Washington

8:20am **BI-TuM1 Gated Ion Channel Devices within Synthetic Tethered Membranes**, ***B.A. Cornell***, *L. Braach Maksvytis, L. King, P. Osman, B. Raguse, L. Wieczorek,* Cooperative Research Centre for Molecular Engineering, Australia*; R. Pace,* Australian National University, Australia **INVITED**

A novel biosensor based on switching the conductance of a population of molecular ion channels is described. . The active elements of the ion channel switch comprise a gold electrode to which is tethered a lipid membrane containing ion channels linked to an appropriate receptor. The approach can be used with most types of receptor including antibodies and nucleotide probes. In its simplest form the technique is sensitive to below 1 picoMolar concentrations of proteins in 5 minutes. The sensor can readily be incorporated as an integral component of a microelectronic circuit and can used in multi-element arrays. It has a wide range of applications and operates in complex media including whole blood. Examples include: cell typing, the detection of proteins, bacteria, viruses, antibodies, DNA targets, electrolytes, drugs, pesticides, heavy metals and other high and low molecular weight compounds. The device has been used to detect the equilibrium and kinetics of the binding of analytes from solution, the kinetics and number association of molecules at the surface of the tethered membrane and the kinetics and conduction of ion channels within the membrane. A description will be given of the assembly and characterisation of the device over a range of applications.

9:00am **BI-TuM3 Interaction of Lipid Vesicles and Cell Membranes with Alkylthiol Monolayers**, ***A.L. Plant,*** National Institute of Standards and Technology*; V. Silin,* Georgetown University **INVITED**

Surface plasmon resonance (SPR) studies provide real-time information about the nature of the interaction of phospholipid vesicles and red blood cell ghosts with alkylthiol modified surfaces. By using a focussed beam, a range of incident angles are detected simultaneously at a linear CCD array, and the reflectivity response is evaluated at each time point. With this approach it is possible to observe time-dependent changes in the width of the reflectivity response as well as in the angular dependence of the reflectivity minimum. The width of the reflectivity response is an indicator of surface roughness, and helps to elucidate the details of the surface reaction. At a hydrophobic surface, vesicles disassemble and add a monolayer of lipid to the surface, forming a smooth hybrid bilayer that is a model of a cell membrane. This process occurs with vesicles that are net neutral or carry a net negative charge. The interaction of red blood cell ghosts with the surface results in increases and then decreases in the width of the reflectivity response, presumably as a result of initial binding of the cell membrane particles, and then reorganization of the cell membrane into a discrete layer at the hydrophobic surface. The interaction of vesicles with a charged surface is distinctly different from their interaction at a hydrophobic surface. Instead of addition of a layer of lipid, vesicles apparently remain intact at the charged surface, resulting in a large shift in the angle of minimum reflectivity, and an increased and sustained broadening of the reflectivity response. This broadening reflects heterogeneity in the surface coverage, suggesting the long-term presence of intact vesicles at the surface.

9:40am **BI-TuM5 Stabilizing Supported Lipid Bilayers for Biomaterial Applications***, **O. Dannenberger**, M. Boeckl, J.A. Bassuk,* University of Washington*; P.L. Valint,* Bausch & Lomb*; T. Sasaki, V. Vogel,* University of Washington

Supported phospholipid bilayers are promising biomembrane model systems.@footnote 1@ Our special interest is to extend their application to investigate the interactions of cells with specific recognitions sites on synthetic surfaces. Bilayers are ideally suited to stabilize and expose cell receptors and membrane anchored proteins. The fluid character of supported bilayers further allows cells to spatially reorganize recognitions sites. As one major drawback of lipid bilayers is their instability we have assembled phospholid (PL) bilayers on a smooth hydrogel cushion and partially crosslinked the inner layer to the cushion and the layers themselves. The hydrogel mimics the cytoskeletal network that stabilizes the lipid membranes in living cells. HEMA was selected as the major polymer constituent due to its biocompatibility. The PL bilayers were formed using Langmuir Blodgett and Schäfer techniques. The hydrogels were investigated with AFM and angle-resolved XPS, the mono- and bilayers were studied with fluorescence and Brewster angle microscopy. We covalently linked our inner layer to the reactive groups provided on the polymer cushion. While partial linkage stabilized the inner leaflet it still exhibits a high membrane fluidity since direct interactions with the solid substrate are prevented. Bifunctional lipid-like surfactants were used to improve the stability of the outer PL leaflet through layer-to-layer crosslinking. In addition we will present the results of the attachment and spreading behavior of endothelial cells on our model surfaces. @FootnoteText@ @footnote 1@E. Sackmann, Science 271 (1996), 43-48.

10:00am **BI-TuM6 Patterning Multiple Antibodies onto a Surface***, **R.A. Brizzolara**,* NSWC, Carderock Division

Patterning multiple antibodies (each to a different antigen) on a single substrate is an important step in the development of multi-analyte biosensors. The envisioned device requires patterning antibodies onto a substrate in discrete pixels, with adjacent pixels containing antibodies against different antigens. In this paper, a new method for forming patterns of different antibodies on a surface is described. The method utilizes hydrophobic interactions to immobilize antibodies on a polystyrene surface. Prior to incubation in the antibody, the substrate is coated with bovine serum albumin (BSA) to prevent nonspecific adsorption. The BSA is then selectively removed from the region where antibody adsorption is desired. Results will be presented demonstrating several methods of selective BSA removal, including ion-beam sputtering and mechanical scribing. Ion beam sputtering has been used to form a rudimentary, millimeter-scale pattern of two antibodies on a polystyrene surface. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used to detect the spatial distribution of 10 nm gold labeled antigen on the surface. Mechanical scribing has been used to form a 0.1 mm-scale pattern of two antibodies on a surface. Fluorescence Microscopy was used to visualize the FITC labeled antigen on the surface. Finally, results will be presented showing the use of the AFM as a lithographic tool for antibody patterning. The NSWC, Carderock Division In-House Laboratory Independent Research Program provided funding support for this work.

10:20am **BI-TuM7 Biological Applications of Colloidal Au-Amplified Surface Plasmon Resonance***, **M.J. Natan**,* The Pennsylvania State University **INVITED**

The ability to rationally control surface topography of thin noble metal films has an enormous impact on the utility of such films for biosensor signal transduction. Nowhere is this more evident than in surface plasmon resonance (SPR), where changes in surface roughness of a few nanometers are easily detected. Accordingly, when immobilization of colloidal Au nanoparticles from solution is brought about by a biomolecular recognition event on an SPR substrate, dramatic changes in reflectivity are observed. This talk will focus on fundamental aspects of this phenomenon, including the dependence on colloidal Au particle size, particle coverage, and particle spacing, as well as on applications to ultrasensitive detection of proteins, nucleic acids, and small molecules.

11:00am **BI-TuM9 Structure of Single- and Double-Stranded DNA Monolayers on Gold from Neutron Reflectivity***, R. Levicky, T.M. Herne, **M.J. Tarlov**, S.K. Satija,* National Institute of Standards and Technology, US

Neutron reflectivity was used to determine the concentration profiles of oligomeric DNA monolayers on gold under conditions of high salt (1M NaCl). These monolayers are of interest as model DNA probe systems used in diagnostic devices. To facilitate its attachment, the DNA was functionalized at the 5' end with a thiol group connected to the oligonucleotide by a hexamethylene linker. Concentration profiles determined from neutron reflectivity indicate that adsorbed layers of single-stranded DNA (HS-ssDNA) on bare gold are compact, suggesting the presence of multiple contacts between a DNA strand and the surface. After treatment with mercaptohexanol, a short alkanethiol with a terminal hydroxy group, the DNA "stands-up" and extends farther into the solvent phase. These changes are consistent with the DNA remaining attached through its thiol endgroup while contacts between DNA backbones and the surface are limited by the formation of a mercaptohexanol monolayer. The end-tethered HS-ssDNA layer readily hybridizes to its complementary sequence, resulting in DNA helices with a preferred orientation toward the substrate normal.

11:20am **BI-TuM10 XPS Analysis of Oligonucleotides for DNA Microarrays***, **E.C. Carr**, K.J. Luebke, S.M. Lefkowitz, N.M. Sampas, S.S. Laderman, E. Poon,* Hewlett-Packard

In recent years, a vast amount of DNA sequence information has been provided by the Human Genome Project. To make intelligent and efficient use of this information requires new analytical techniques capable of massively parallel interrogation. Microarrays of DNA have emerged as one of the most promising molecular recognition technologies for high sensitivity, multiplex analysis of DNA. It has been demonstrated that specific sequences of DNA can be synthesized directly on a planar surface, however the density and fidelity of the resulting oligonucleotides are of primary importance to the effectiveness of the array. We have used X-ray Photoelectron Spectroscopy (XPS) to measure phosphorus signal, and thus nucleotide density, of oligonucleotides synthesized on a silylated glass surface. We derive a coupling yield for the attachment of each nucleotide in the sequence that is in good agreement with yield derived from optical transmittance of dye bound to the final nucleotide. Coupling yield measured by these techniques is consistent with that achieved in standard DNA synthesis on porous glass beads using cleavable linkage to the bead and High-Performance Liquid Chromatography for measurement. Issues associated with the accuracy of making quantitative measurements on microarrays using XPS will be discussed.

11:40am **BI-TuM11 Multifunctional Molecular Multilayer Assemblies for Reagentless, Fluorescence-Based Biosensing***, M.M.A. Sekar, P.D. Hampton, **G.P. Lopez**,* University of New Mexico

This report describes the development of self-assembled monolayers (SAMs) and surface modified SAMs to create model, multifunctional organic surfaces for reagentless, fluorescence-based biosensing. We describe the formation of modular molecular assemblies that display biospecific ligands, luminescent probes and highly-hydrated oligomeric species that inhibit nonspecific adsorption of biomolecules and cells [e.g., oligo(ethylene glycol)]. SAMs can be formed by the serial chemisorption of amine-terminated alkylthiolates to gold or alkylsilanes to silica, and can be serially modified by reaction with di-aldehydes, and subsequently di-amines, to form layered molecular assemblies that can be terminated with bioreceptive ligands, luminescent probes or oligo(ethylene glycol). This talk will present a detailed surface analytical characterization of these layered molecular assemblies and will discuss the efficacy of this method for constructing modular, multifunctional assemblies for interfacial modification of biomaterials. We demonstrate that protein-sensitive luminescent probes immobilized on such layered assemblies can be used to detect specific and nonspecific adsorption of proteins through steady-state and time-resolved fluorescence spectroscopy.

Electronic Materials and Processing Division
Room 316 - Session EM+SE-TuM

Critical Issues in Widebandgap Semiconductors

Moderator: M.R. Melloch, Purdue University

8:20am **EM+SE-TuM1 Gallium Nitride Structures for High Power Microwave Amplification***, **L.F. Eastman**, K. Chu, N. Weimann, J. Smart, J.R. Shealy,* Cornell University **INVITED**

Among the wide band-gap materials Gallium Nitride has yielded the best frequency response and efficiency for microwave amplifiers. Wurtzite Al@sub x@Ga@sub 1-x@N/GaN/SiC HEMT structures, with x < .50, yield a high two-dimensional electron gas density of ~ 1 x 10@super 13@/cm@super 2@ with no intentional doping, due to the piezoelectric effect. The drain-source breakdown voltage at pinchoff rises linearly with gate length, being > 200 V for 1 µm gates due to the 3-4 MV/cm breakdown field strength. Using SiC substrates having > 3 W/cm°K thermal conductivity, up to 20 W/mm periphery will be possible. The normalized drain current is > 1 A/mm, yielding a high normalized optimum load of ~ 200 ohm-mm for 1 µm gates. Large periphery HEMT's with reasonable load resistances will allow power levels > 100 W, with efficiency above 60%, for frequencies < 12 GHz. The impact of dislocations, with density of .5 - 2.0 x10@super 9@/cm@super 2@ for GaN on SiC, on electron mobility has been determined analytically, and is in the range of 1,500-2,000 cm@super 2@/V-s. These dislocations line up in the growth direction and thus do not substantially limit the electron mobility in vertical FET's such as the Static Induction Transistor (S.I.T.) The theoretical value of the peak electron velocity for GaN is 2.7 x 10@super 7@cm/s and is reached at 150-200,000 V/cm. Short gate (.15µm) HEMT's have unity current gain frequency of ~ 70 GHz, and unity power gain frequency of 140 GHz. Due to the large bandgap, operation with channel temperatures > 200°C is possible with no substantial reduction in performance.

9:00am **EM+SE-TuM3 HfN Films Grown on GaN by Reactive MBE using Ammonia@footnote 1@*, **A. Parkhomovsky**, B.E. Ishaug, A.M. Dabiran, P.I. Cohen,* University of Minnesota

Stoichiometric HfN has a sodium chloride structure which is lattice matched to GaN to within 1%, assuming a 45 degree rotation. It has a low work function and hence should be an abrupt ohmic contact to wide bandgap semiconductors that is stable at very high temperatures. In this work we report the epitaxial growth of HfN on the (000-1) plane of GaN thin films. Hf and Hf-N thin films of various nitrogen contents were grown by MBE using a Hf electron beam source and an ammonia leak. The films were studied using RHEED and AFM. It was found that epitaxial HfN could be grown on GaN even at room temperature. However, the surface morphology and structure are dependent upon the nitrogen content and on the substrate temperature. GaN films of about 0.2 microns thickness, also grown using ammonia, were used as the substrate for the HfN growth. The GaN was grown under conditions of excess ammonia. The surface was annealed in ammonia as the temperature was lowered, producing an N termination on this polarity. Hf and HfN were then deposited on top of GaN at temperatures between 20C and 730 C. Deposition of pure Hf at room temperature revealed an epitaxial, though bulk diffraction pattern. This was only slightly affected by annealing in vacuum to 700 C. Little change was observed when annealed in an ammonia flux. However, when Hf was deposited in an ammonia flux at room temperature, the diffraction pattern corresponding to HfN is observed. For this room temperature film, there is some evidence of faceting in the diffraction pattern. AFM indicated an rms roughness of 5 nm for 100 nm film. If HfN was deposited at substrate temperatures above 350 C, a polycrystalline diffraction pattern was observed. This consisted of arcs at the intersection of the Ewald sphere, which were not continuous, indicating some preferential ordering in the film. AFM indicated an rms rougnhness of 40 nm for a 100 nm film. The electrical properties of the contact as well as the role of the interfacial termination and the flux ratio on the film growth will be presented. @FootnoteText@ @footnote 1@Partially Supported by Air Force Office of Scientific Research and the Office of Naval Research.

9:20am **EM+SE-TuM4 Investigation of Metal / GaN Interface Properties using Photoemission Spectroscopy and I-V Measurements***, **C.I. Wu**, A. Kahn,* Princeton University

We present a systematic investigation of the formation of Schottky barriers between n- and p-GaN grown by MOCVD and a series of high and low work function metals (Mg, Al, Ti, Au and Pt). We compare interface Fermi level positions with measured transport characteristics (I-V). The interfaces are formed on well ordered (0001)-(1x1) surfaces. The initial band bending is 0.75 eV upward and 0.75 eV downward on clean n- and p-type surfaces, respectively. The chemistry and electronic properties of these interfaces are studied by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). Al, Ti and Mg are found to react at room temperature with nitrogen, as indicated by the appearance of a free Ga component in the Ga 3d core level spectrum, whereas Au and Pt form abrupt, unreacted interfaces. The Fermi level movements on both n- and p-GaN are consistent with the metal work functions, but limited by surface or interface states. The maximum metal induced band bending is 0.9 eV downward for Mg on p-GaN and 0.8 upward for Pt on n-GaN. Upon annealing, the incorporation of Mg increases the density of acceptors as seen on both n- and p-GaN. In spite of similar work functions and chemical reaction with nitrogen, Ti and Al form drastically different Schottky barriers. Ti causes an additional band bending of more than 0.5 eV for both n- and p-GaN whereas the Al-induced band shift is less than 0.2 eV. The difference is due to very different products of reaction, i.e. AlN is a wide band gap semiconductor whereas TiN is a metallic compound. The Schottky barrier heights are 1.2 eV (1.45 eV) and 1.1 eV (0.7 eV) on n- and p-GaN, respectively, for Au (Pt). We will present on-going measurements on the comparison between Schottky barrier heights obtained by photoemission spectroscopy and I-V measurements.

9:40am **EM+SE-TuM5 Mg Doping Studies of ECR-MBE GaN Thin Films***, **I.E. Berishev**, E. Kim, O. Kameli, D. Starikov, A. Bensaoula,* University of Houston

MBE of GaN is a rapidly progressing ultra high vacuum growth technique that allows the growth of high purity materials, at lower temperatures, in a clean and well characterized environment, and at high enough growth rates. Much of the recent work however was performed using RF nitrogen sources instead to previously popular ECR sources. Lower deposition rates for ECR sources being the major reason. In all growth technologies, p-type doping remains an issue for GaN device structures fabrication such as LED, LD, FET, etc. As grown p-type MBE GaN layers were however successively realized by several groups. In our study a modified ASTEX ECR source, allowing optically active GaN thin films at growth rates up to 1 micron per hour, was utilized in an MBE environment. Using this nitrogen source, Mg doping studies of GaN were undertaken. The effects of growth parameters and ECR source design on the Mg incorporation and its electrical activity were characterized by SIMS, electrochemical profiling, and photo-luminescence. The background concentration and major impurities are identified by time of flight SIMS. A direct correlation exists between Mg incorporation and the ECR power, nitrogen flow, Mg cell temperature, growth temperature and ECR exit aperture size. Using an optimized process, SIMS show sharp profiles between doped and undoped layers can be obtained. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061.

10:00am **EM+SE-TuM6 Deposition of AlN Gate Dielectrics***, **B. Gila**, S.M. Donovan, C.R. Abernathy, K.N. Lee, J.D. MacKenzie, F. Ren, S.J. Pearton,* University of Florida, Gainesville*; S.N.G. Chu,* Bell Laboratories, Lucent Technologies

The development of a suitable insulator for GaN is a critical step in developing a GaN MOSFET technology. Conventional dielectrics such as SiO@sub 2@ and Si@sub 3@N@sub 4@ have generally failed on III-V materials because of high interface state densities. AlN is an attractive alternative because of its large bandgap, high thermal conductivity and excellent thermal stability. Also, a high relative dielectric constant (8-9) alleviates the problem of high fields in the dielectric in high voltage applications. AlN has also been proposed as a potential replacement for silicon dioxide in high temperature MIS based silicon carbide device applications. In this study, 375Å AlN films were deposited in ultrahigh vacuum (UHV) using an RF nitrogen plasma and dimethylethylamine alane (DMEAA) on Si, SiC and GaN/Sapphire at temperatures ranging from 325° to 525°C. Prior to deposition various surface cleans were employed including hydrogen plasma exposure, BOE (Si) high temperature exposure to ammonia and nitrogen plasma (GaN and SiC). Cross-sectional TEM (XTEM), Auger electron spectroscopy (AES), reflection high energy electron diffraction (RHEED), C-V and I-V analysis were used to characterize the films as functions of deposition temperature and surface preparation. In spite of the low deposition temperatures, none of the films were found to contain oxygen or carbon within the detection limit of AES. Consequently, the reverse breakdown characteristics of the layers were found to be excellent. By contrast, the interface state density as measured by C-V was found to depend strongly on the nature of the initial substrate surface. Optimization of the initial starting surface via mass spectrometry and RHEED during in-situ chemical cleaning produced substantial reduction in the interfacial leakage current. As a result, initial GaN HIGFET devices show promising performance with improved breakdown and C-V behavior relative to conventional MESFET structures.

10:20am **EM+SE-TuM7 Progress in SiC: From Material Growth to Commercial Device Development***, **C.H. Carter**, V.F. Tsvetkov, D. Henshall, O. Kordina, K. Irvine, R. Singh, S.T. Allen, J. Palmour,* Cree Research, Inc. **INVITED**

Silicon carbide technology has made tremendous strides in the last several years, with a variety of encouraging device and circuit demonstrations in addition to volume production of nitride-based blue LEDs being fabricated on SiC substrates. The commercial availability of relatively large, high quality wafers of the 6H and 4H polytypes of SiC for device development has facilitated these exciting breakthroughs in laboratories throughout the world. These have occurred in numerous application areas, including high power devices, short wavelength optoelectronic devices, and high power/high frequency devices. This presentation will describe progress made in increasing the quality and size of SiC wafers, advances in SiC epitaxy and some of the resulting device demonstrations and commercialization by Cree Research. To meet the challenges required for commercialization of SiC semiconductors, we have made specific efforts towards larger diameter high quality substrates which have led to production of 50 mm diameter 4H and 6H wafers for fabrication of LEDs and the demonstration of 75 mm wafers. The latest results on micropipe reduction will be presented including a wafer which contains a total of 7 micropipes, yielding a density of 0.7 cm@super-2@. High voltage P-i-N diodes have been fabricated from hot-wall grown epitaxy using junction termination extension (JTE) edge termination. The highest breakdown voltage achieved for these diodes is >5.5 kV, which is a new world record for blocking voltage for a SiC device. In the microwave device area, a SiC MESFET with 42 mm of gate periphery on a single die which had a maximum RF output power of 53 watts CW with 37% power-added efficiency (PAE) at 3.0 GHz has been demonstrated. This unprecedented power from a die with an area of only 3 mm@super2@ demonstrates the extremely high power handling capability of SiC microwave devices. Additionally, SiC MESFETs showing 2.5 W/mm with 41% PAE at 8 GHz, demonstrate the utility of this technology at X-band.

11:00am **EM+SE-TuM9 Critical Development Issues for Deep (10 to 100 µm) Etching of SiC***, D.C. Sheridan,* Auburn University*; **J.B. Casady,*** Northrop Grumman*; C.E. Ellis,* Auburn University*; R.R. Siergiej,* Northrop Grumman*; J.D. Cressler,* Auburn University*; W.E. Urban, W.F. Valek, H. Buhay,* Northrop Grumman

Silicon carbide is a wide bandgap (3.2 eV for the 4H polytype) semiconductor gaining popularity in applications requiring high-power, high-frequency, and high-temperature performance@footnote 1@. Material quality improved significantly since the first commercial release of SiC substrates in 1991. Numerous SiC semiconductor devices have been developed, such as thyristors, diodes, JFETs, MESFETs, and static induction transistors. Because of its high bond strength, the etching of SiC has been quite difficult, performed almost exclusively using dry etching techniques. Most techniques have utilized fluorinated gas chemistries in reactive ion etch (RIE), electrocyclotron resonance (ECR) etch, or inductively coupled plasma (ICP) etch systems. Residue free etches have been developed with etch rates from 5 nm/minute up to 350 nm/minute@footnote 2,3@. For very deep etching of SiC, up to 75 µm, which would be required for selected applications, no suitable process has been reported on. The ideal process would optimize a combination of fast etch rate, good mask selectivity, and reproducibility. In this work, we compare five SiC etches used in commercial RIE systems with regard to the above criteria. The SiC etches examined are all residue-free, and posses etch rates ranging from 8 nm/minute up to 160 nm/minute. The etches utilize one or more of the following fluorinated gases: NF@sub 3@, SF@sub 6@, CHF@sub 3@, or CF@sub 4@. A more detailed characterization of the etch recipes will be given in the full paper, and partial details have been reported elsewhere@footnote 4,5,6@. Several inorganic and organic mask materials will also be evaluated. Each mask material is characterized and tabulated in terms of etch rate, selectivity, and residue-formation for each of the SiC etches. @FootnoteText@ @footnote 1@ J.B. Casady and R.W. Johnson, Solid-St. Elect., Vol. 39, No. 10, p. 1409, 1996. @footnote 2@ P.H. Yih, V. Saxena, and A.J. Steckl, Phys. Stat. Sol. (b) Vol. 202, p. 605, 1997. @footnote 3@ G. McDaniel, J.W. Lee, E.S. Lambers, S.J. Pearton, P.H. Holloway, F. Ren, J.M. Grow, M. Bhaskaran, and R.G. Wilson, J. Vac. Sci. Technol. A, Vol. 15 @footnote 4@ J.B. Casady, E.D. Luckowski, M. Bozack, D. Sheridan, R.W. Johnson, and J.R. Williams, J. Electrochem. Soc., Vol. 143, No. 5, p. 1750, 1996. @footnote 5@ P.H. Yih and A.J. Steckl, J. Electrochem. Soc., Vol. 140, p. 1813, 1993. @footnote 6@ J.B. Casady, S.S. Mani, R.R. Siergiej, W. Urban, V. Balakrishna, P.A. Sanger, and C.D. Brandt, J. Electrochem. Soc., Vol. 145, No. 4, p. L58, 1998.

11:20am **EM+SE-TuM10 Thermochemical Stability of Plasma-Deposited Silicon Oxycarbide Thin Films Subjected to Post-Deposition Rapid Thermal Annealing***, **D.M. Wolfe,** B. Ward, F. Wang, M. Xu, G. Lucovsky, R.J. Nemanich, D.M. Maher,* North Carolina State University

Low defect density gate dielectrics are of critical importance to maximize electrical performance/reliability in SiC high power devices. Under some growth conditions carbon atoms are trapped in thermally-grown oxides forming silicon oxycarbides@footnote 1@, and it has been suggested that these C-atoms degrade device performance. The bonding of C-atoms in silicon oxycarbides as well as their thermal stability is therefore addressed. Thin silicon suboxide (SiO@sub x@, x<2) and silicon oxycarbide (SiO@sub x@C@sub y@, x<2, y<<1) films were deposited at 250°C by remote-plasma enhanced CVD. Changes in the local chemical bonding and the onset of crystallization upon rapid thermal annealing at temperatures from 600-1100°C were investigated. XPS and RBS were used for compositional analysis; FTIR was used to track the extent of structural/chemical changes through shifts in Si-O and Si-C bond-stretching frequencies. Raman spectroscopy, and HRTEM/selective area diffraction were used to monitor crystallization products through the appearance of characteristic phonon modes and diffraction patterns, respectively. These studies showed a structural/chemical transformation occurred at about 900°C for silicon suboxide films. At this temperature, the end-product material was comprised of Si nanocrystals imbedded in an non-crystalline SiO@sub 2@ matrix. A similar structural/chemical transformation, in which Si nanocrystals were also formed, was observed between 1000 and 1050°C for the silicon oxycarbides. However, a siloxane-type Si-O-C bond was observed to form at intermediate temperatures (~900°C), and to disappear upon crystallization. No evidence for amorphous or crystalline C-C bonds, or other C-O bonding groups was found in the oxycarbide films before, or after annealing. Finally, concentrations of Si and O, and Si, O and C remained essentially the same for the respective as-deposited and fully-annealed films. @FootnoteText@ @footnote 1@ B. Hornetz, H-J. Michel, J. Halbritter, J. Mater. Res 9, 3088 (1994).

The Science of Micro-Electro-Mechanical Systems Topical Conference
Room 324/325 - Session MM+NS+SS-TuM
Micro-Science and Tribology of MEMS

Moderator: N.E. McGruer, Northeastern University

8:20am **MM+NS+SS-TuM1 Making a Bridge to the Nanoworld***, **S.R. Manalis,** S.C. Minne, J.D. Adams, K.B. Crozier, H.T. Soh, T.A. Sulchek, K. Wilder,* Stanford University*; G.G. Yaralioglu, A. Atalar,* Bilkent University, Turkey*; C.F. Quate,* Stanford University **INVITED**

Our vision for micro-electro-mechanical-systems (MEMS) is to provide a window to the microscopic world. Scanning probe microscopes with automated cantilever arrays now image surface areas in excess of one square millimeter with atomic resolution. We will present new types of cantilevers and transducers that improve the speed, sensitivity, and simplicity of scanning probe microscopes. Samples are imaged at video rates with an integrated piezoelectric actuator that bends the cantilever over surface topography at high speeds. The deflection sensor, which consists of a micromachined light modulator, monitors cantilever bending with a sensitivity near one percent of an atomic diameter. We also present approaches for microfabricated biological sensors based on mechanical, electrical, and optical methods of transduction.

9:00am **MM+NS+SS-TuM3 Nanotribology of Vapor-Phase Lubricants and Their Potential Applications to MEMS@footnote 1@***, **J. Krim,*** North Carolina State University **INVITED**

The concept of lubricating high temperature surfaces with organic vapors has existed for at least forty years, with substantial efforts beginning in the 1980's and continuing on to the present day. Vapor-phase lubricants are advantageous for use at high temperature, as well as in situations where the vapor can be used as a reservoir for replenishment of areas where the lubricant has been depleted in the course of device operation. While work in the area of vapor-phase lubrication has to date focussed on the lubrication of macroscopic systems, vapor lubrication mechanisms may ultimately prove to be of critical importance to sub-micron mechanical systems in cases where lubricant delivery and/or replenishment by other methods proves impractical. In order to examine the viability of vapor-phase lubrication at length scales commensurate with submicron-scale machinery, we have constructed a Quartz Crystal Microbalance which operates in combination with a Scanning Probe Microscope so as to form a simple nanometer-scale mechanical system whose response to a number of vapor-phase lubricants can be monitored for nanotribological performance. Our observations of organic and water-vapor films recorded with this device will be discussed. @FootnoteText@ @footnote 1@Work supported by NSF and AFOSR

10:20am **MM+NS+SS-TuM7 Vacuum Deposited Fluorinated Alkyl Siloxane Films for Adhesion Control in MEMS Devices***, **T.M. Mayer,** M.P. de Boer, N.D. Shinn, P.J. Clews, T.A. Michalske,* Sandia National Laboratories

Monolayer films of polymerized alkyl siloxanes have been employed for surface passivation and adhesion control in MEMS devices. However, reproducible film formation and properties have been difficult to achieve due to process sensitivity to substrate preparation conditions, presence of small quantities of adsorbed water, and the high aspect ratio structures typical of MEMS devices. In contrast to the normal solution coating process using alkyl trichlorosilane precursors, we have developed a vacuum-based film deposition process, using volatile fluorinated alkyl trichloro silane precursors. Reproducible substrate conditions are obtained by UV-ozone oxidation followed by sequential or simultaneous exposure to the chlorosilane precursor and water vapor. Efficient transport of reactants into high aspect ratio structures is accomplished by maintaining Knudsen flow conditions at low pressures. We measure kinetics of film growth by in-situ ellipsometric and quartz-crystal microbalance techniques, and evaluate film composition and structure by XPS and IR spectroscopies. We also measure the work of adhesion and surface energy of coated cantilever beams under equilibrium fracture mechanics conditions. We compare results to uncoated structures, and to structures coated from solution with alkyl and fluoro-alkyl siloxane films. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U. S. Dept. of Energy under contract DE-AC04-94AL85000.

11:00am **MM+NS+SS-TuM9 Adhesion Hysteresis of Polysilicon Beams in Controlled Humidity Ambients***, M.P. de Boer,* ***T.A. Michalske****, M.R. Tabbara,* Sandia National Laboratories*; R. Maboudian,* University of California, Berkeley*; T.M. Mayer,* Sandia National Laboratories

Auto-adhesion, or spontaneous sticking between MEMS structures, is currently a major limitation in bringing this new class of engineering devices to the broader market. MEMS are particularly susceptible to auto-adhesion because the structural members: 1) are constructed in close proximity to each other, 2) are highly compliant due to their extreme length to thickness aspect ratio and, 3) have large surface to volume ratios which increase the relative importance of adhesive surface forces. If the miniature structural members are brought together by surface (capillary, electrostatic) or inertial (shock, rapid air flow) forces, they may remain adhered after the external force is removed. If the structures remain adhered, bonding may increase over time, giving rise to the phenomena known as adhesion hysteresis. In this work we develop mechanical analysis for and report on measurements of adhesion hysteresis in surface micromachined polysilicon beams subject to dry and wet ambients. The electrostatically activated beams used in this study were tested directly after supercritical drying or after the application of hydrophobic molecular coatings such as octadecyltrichlorosilane (ODTS) or perfluorodecyltrichlorosilane (FDTS). Results indicate that both uncoated and coated beams show strong increase in adhesion after an incubation period in humid environments. This incubation time is shorter and occurrs at lower RH for uncoated beams than coated beams. For the case of uncoated beams, we are able to show that a model based on individual asperity contact forces can be used to predict the overall adhesion behavior in micromachined beams. The behavior of coated beams is compared with ellipsometric measurements indicating water adsorption on these nominaly hydrophobic surfaces after extended exposure at high RH conditions.

Manufacturing Science and Technology Group
Room 317 - Session MS-TuM
Overview: Integration for Manufacturing

Moderator: J.J. Sullivan, MKS Instruments, Inc.

8:20am **MS-TuM1 Reaction/Annealing Pathways for Forming Ultrathin Silicon Nitride Films for Composite Oxide-Nitride Gate Dielectrics with Nitrided Crystalline Silicon-Dielectric Interfaces for Application in Advanced CMOS Devices***,* ***G. Lucovsky****,* North Carolina State University **INVITED**

Aggressive scaling of CMOS devices requires gate dielectrics with oxide equivalent thicknesses of ~1 nm by 2012. Direct tunneling is a limitation in FETs when oxide thicknesses are reduced to <2 nm. In addition, boron diffusion from p+ poly-Si gate electrodes in PMOS FETs leads to additional electrical problems for oxide thicknesses <4 nm. Interfacial nitridation improves reliability in NMOS FETs; however, it is not effective in PMOS FETs due to of boron pile-up at the Si-dielectric interface. One solution to these problems is the integration of composite oxide-nitride composites with nitrided interfaces; NON dielectrics, into CMOS devices. The paper discusses: i) deposition of hydrogenated silicon nitride by remote plasma-enhanced chemical-vapor deposition (RPECVD); ii) characterization of plasma-deposited nitrides by IR and AES; and iii) effects of post-deposition annealing on the bonded-H content. Formation of nitride thin films for NON composite dielectrics requires two process steps: i) deposition of a hydrogenated silicon nitride film at 300°C by RPECVD, followed by ii) rapid thermal annealing in an inert ambient at 900°C. During the anneal H-atoms are evolved from near-neighbor SiH and SiNH bonds, and the resulting Si and N-atom dangling bonds combine to form new SiN bonds accounting for the device-quality electrical performance. Electrical performance of devices with composite i) oxide-nitride-oxide, ONO, dielectrics, and ii) ON dielectrics with fully nitrided interfaces, NON, is discussed. For example, we demonstrate that approximately 2 molecular layers of nitride, ~0.8 nm, at the top surface of the NON dielectric is sufficient to stop B-penetration out of p+ poly-Si gate electrodes during dopant drive-in/activation anneals. Finally, nitrides produced by the two step process are qualitatively different from CVD nitrides deposited at higher temperatures, ~500°C, and subjected to post-deposition anneals in oxidizing ambients.

9:00am **MS-TuM3 Process Mixing in Cluster Tools***,* ***R.A. Powell****,* Novellus Systems **INVITED**

Cluster tools are widely used in advanced microelectronic manufacturing because they offer high productivity and the ability to improve thin film and interface quality through vacuum-integrated processing. While such tools are often dedicated to a single technology such as plasma etching, PVD, or CVD, it is common to integrate a number of different process technologies within the same tool. For example, the integrated process sequence of wafer degas+ preclean + PVD Ti + PVD TiN + PVD AlCu + PVD TiN can be carried out in a PVD cluster tool without a vacuum break to deposit an AlCu interconnect line. Understanding and managing the interplay between successive steps is critical to successful process integration-which in turn has an important effect on tool performance, productivity and cost of ownership. Looking forward, there is growing interest in clustering fundamentally different deposition methods such as PVD and CVD onto a common wafer handling platform to take advantage of their complementary benefits. This talk will discuss the motivation and challenge of integrating these and other processes on advanced cluster tools with a focus on film deposition. Generic issues of mixing and matching different processes on a cluster platform will be discussed with regard to vacuum requirements, ambient purity, thermal cross-contamination, and the choice of single wafer versus batch processing. Specific examples from both PVD and CVD cluster tools will be used to illustrate the general points made.

9:40am **MS-TuM5 Process Integration Overview: Development and High Volume Manufacturing of Microprocessor Products***,* ***R.A. Gasser, Jr****,* Intel Corporation **INVITED**

Intel Corporation provides ~80% of worldwide demand for microprocessors. Continuing to meet this demand requires the development of high performance microprocessors using the most advanced process technology available. Meeting this demand also requires the ability to ramp the technology at high volumes in many factories at the same time. This talk will first present an overview of the economics of microprocessor manufacturing. This overview will show why it is imperative for the key participants in this industry to be able to consistently deliver both high levels of transistor performance and process integration using the most advanced equipment available. Next, there will be a review of methods for robust process design. Robust process design is key to laying the foundation for eventual process ramp. Finally, there will be an overview of methods for ramping the process technology to very high volumes, while achieving high product yields.

10:20am **MS-TuM7 Value Chain Integration***,* ***P.S. Peercy****,* SEMI/SEMATECH **INVITED**

Driven by continuously increasing competitive pressures from increasing globalization, the semiconductor industry has undergone major structural changes over the past few years. As recently as the early 1980s, most of the process and fabrication research and development was performed primarily in large vertically integrated companies in the industry. Mission-driven research in the central research labs and the R&D pilot lines of these companies yielded most of the technology required to keep the industry's productivity growing exponentially at a rate of 25-30% per year. Today, the semiconductor industry in the U.S. has largely stratified into systems companies, device manufacturing companies, and equipment, subsystem, component, and materials suppliers. In addition, competitive pressures and changing business conditions have shifted the focus of much of the research in the central research labs of the device companies away from fabrication equipment and processing technology. As a result, an increasing amount of the new processing equipment, process technology, and materials development comes from the supply chain today. Tomorrow, the suppliers will be expected to provide virtually all of the new processing equipment and technology required by the device manufacturing sector of the industry. With the increasing stratification of the supply chain, increased vertical communication and coordination is necessary. The efficiency of the supply chain, and the industry, can be greatly increased by close customer-supplier alliances at all levels in the supply chain. Such "value chain integration" can provide a common language for simultaneous communication of requirements to all levels of suppliers. Further, joint development of the technology permits optimization of the research and development efforts throughout the supply chain. It permits competitors to cooperatively perform the research for generic, pre-competitive technologies required for the continued advancement the technology. Additional optimization comes from relying on the expertise of suppliers at all levels in the supply chain; if the requirements are developed jointly, the expertise of suppliers of a given component or subsystem frequently permits redesign and implementation in a more cost-effective and reliable manner. We will examine value chain integration in general with examples of the benefits realized through true customer-supplier alliances, then examine application of value chain integration to the semiconductor industry.

11:00am **MS-TuM9 Factory Integration in the NTRS: Future Factory Level Issues and Needs***, **G.M. Gettel,*** SEMATECH / Texas Instruments, Inc. **INVITED**

The global challenge in the National Technology Roadmap for Semiconductors (NTRS) is to keep the semiconductor industry's productivity engine on track by staying on the 25-30% per year manufacturing cost reduction curve. The industry has been successful in the past in driving down the curve by using feature size reductions and wafer diameter increases. In the future, these two approaches will continue to be exploited but four factory level challenges will have to be addressed to keep the industry from getting derailed. The four challenges are: Escalating factory cost; Factory investment risk and time factors; Overall Factory Effectiveness; and Process / Factory complexity. Factory capital costs are escalating over time up an exponential curve. With the escalating factory costs comes escalating investment risk. Future factories will need faster design, construction, tool installation and ramp in order to pay back in a reasonable time period. Improved bottleneck and average tool OEE are needed. In the future, incoming equipment in an operation will need to have a higher initial OEE and reach maturity quicker. Processes (driven by smaller feature sizes and larger wafer diameters) and factories (driven by economy of scale) will be increasingly complex in the future. This complexity is increasing exponentially. The systems capability to deal with the complexity is evolving at a slower pace resulting in a "data overload gap". These factors drive the need for improved decision support capability. Future factories will require more tool to tool automation, better wafer and die traceability and improved material control systems. Software content in equipment is growing by more than 25% per year. To prevent this increased amount of software complexity from derailing effective factory operation, more reliable and predictable software will be required. This presentation will review the trends, issues and potential solutions for these four difficult factory level challenges.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS-TuM

Quantum Structures and Molecular Electronics

Moderator: C.R.K. Marrian, Naval Research Laboratory

8:20am **NS-TuM1 Quantum-Dot Cellular Automata***, **G.L. Snider**, A.O. Orlov, I. Amlani, G.H. Bernstein, C.S. Lent, J.L. Merz, W. Porod,* University of Notre Dame **INVITED**

Quantum-dot Cellular Automata (QCA) is a promising architecture which employs quantum dots for digital computation. It is a revolutionary approach which addresses the issues of device density and power dissipation. It represents a concrete device design, scalable down to atomic dimensions, with possible implementations in both metals and semiconductors. A basic QCA cell consists of four quantum dots coupled capacitively and by tunnel barriers. Two excess electrons within the four dots are forced to opposite "corners" of the four-dot system by Coulomb repulsion. These two possible polarization states of the system represent logic "0" and "1". Properly arranged, arrays of these basic cells can implement the Boolean logic functions and memory needed for general purpose computation. An introduction to the QCA architecture will be presented, along experimental results from a functional QCA cell built of nanoscale metal dots defined by tunnel barriers. The QCA cell to be presented consists of two Al double-dot islands defined by tunnel junctions, capacitively coupled to each other. Al/AlO@sub x@/Al tunnel junctions are fabricated using a standard e-beam lithography/shadow evaporation technique. In addition to the QCA cell, two single-dot Al islands are capacitively coupled to the QCA cell to act as electrometers. Direct measurements of the charging diagram of QCA cell, combined with electrometer measurements of the cell, show a controlled polarization switch of the QCA cell. These and additional results confirm the control of the switching of a single electron by a single electron, and demonstrates a non-linear, bistable response in the QCA cell. There is excellent agreement between the experimental results and theory.

9:00am **NS-TuM3 A Proposal of Atom/Molecule Switching Devices***, **Y. Wada,*** Hitachi Ltd., Japan **INVITED**

This paper describes the possibility of atom/molecule switching devices, Atom Relay Transistor (ART)@footnote 1@ and MOlecular Single Electron Switching transistor (MOSES),@footnote 2@ which would supersede present semiconductor devices beyond their ultimate limitations. ART consists of an atom wire, a switching atom, a switching gate and a reset gate. MOSES devices consist of a conducting molecule and an insulating molecule, the former being the quantum dot and the latter the tunnel barrier. ART and MOSES devices are evaluated on the basis of the five major characteristics necessary for information processing integrated circuit devices,@footnote 1@ and indicated that they are the most promising candidates for the future information processing. Scanning Tunneling Microscope (STM) should be the most probable tool to fabricate these devices. Technology development to realize these atom/molecule devices are described, including Beam Assisted STM (BASTM)@footnote 3@ which enables insulator observation, Needle Formation and Tip Imaging (NFTI)@footnote 4@ which directly evaluates STM tip apex for reliable atom/molecule manipulation, micromachine STM@footnote 5@ which makes possible the direct observation of vacuum tunneling gap. Gallium (Ga) atom wire was successfully fabricated on Si (100)-H surface by removing hydrogen atoms by STM and filling the dangling bond by Ga atoms,@footnote 6@ which is theoretically predicted to be conductive.@footnote 7@ Those technologies should lead to a successful ART/MOSES demonstration. @FootnoteText@ @footnote 1@Y.Wada, et al., J. Appl. Phys., 74, 7321 (1993). @footnote 2@Y.Wada, Trans. IEICEJ, OME 93-54, 31 (1994). @footnote 3@S.Heike, et al., Appl. Phys. Lett., 64, 1100 (1994). @footnote 4@S.Heike, et al., Japan. J. Appl. Phys., 34, L1061 (1995). @footnote 5@M.I.Lutwyche et al., Appl. Phys. Lett., 66, 2807 (1995). @footnote 6@T.Hashizume, et al., Japan. J. Appl. Phys., 35, L1085 (1996). @footnote 7@S.Watanabe, et al., Phys. Rev. B, 54, 17308 (1997).

9:40am **NS-TuM5 Self-Assembled Single Electron Tunneling Devices***, S.H.M. Persson, **L.K. Hedberg**, L.G.M. Olofsson, B. Kasemo,* Chalmers Univ. of Technology and Univ. of Gothenborg, Sweden

Single electron tunneling effects were studied in self-assembled devices, by contacting a nanoscale gold cluster to two gold electrodes. The size of the gold cluster was around 5 nm, which is controlled by the chemical synthesis. Coulomb blockade of tunnelling was observed at room temperature and Coulomb staircase at 4.2 K. With a third gate terminal it was possible to modulate the tunneling characteristic by electric field effect at 4.2 K. Nanoscale electronic devices can be made with refined lithographical techniques, e.g. using scanning probe instruments, but these methods are very slow and not practical for large scale fabrication. The electrodes were made by electron beam lithography and angled evaporation to control the gap between the electrodes to distances smaller than 10 nm. The surface of the gold electrodes were modified by a self-assembled monolayer of 1,8-octanedithiol and gold clusters were found to be captured in the electrode gap after immersion of the sample in a hexane solution of clusters. The characteristic feature of single electron tunneling can be seen in the current voltage characteristic as a number of steps, that is named the Coulomb staircase. The Coulomb blockade is observed at room temperature with a blockade voltage of the order 0.2 V. Recent theoretical results@footnote 1@ predict a new "electron shuttle" mechanism for systems similar to ours, where the middle electrode is softly coupled to the outer ones via organic molecules. The softness of the molecular links implies that charge transfer could give rise to deformation of these structures. Under certain conditions this would result in oscillation of the gold nanoparticle and a current through the structure that is proportional to the cluster vibration frequency. One aim of our work is to verify these predictions experimentally. @FootnoteText@ @footnote

1@L.Y.Gorelik, A.Isacsson, M.V.Voinova, B.Kasemo, R.I.Shekter and M.Jonson, Phys. Rev. Lett., 80 (1998), 4526

10:00am **NS-TuM6 Quantum Transport in Metallic Nanowires Fabricated by Electrochemical Deposition/Dissolution***, **N.J. Tao**, C.Z. Li, A. Bogozi, J. D'Agnese, B. Duong,* Florida International University

A non-mechanical method for fabricating a metallic narrow constriction between two electrodes using electrochemical deposition is described. The width of the constriction can be adjusted by slowly dissolving metal atoms away or re-depositing atoms onto the constriction which can be controlled flexibly by the electrodes' potentials. Well-defined plateaus near the integer numbers of the conductance quantum have been observed in these constrictions at room temperature. Since no mechanical movements are involved, nano-constrictions with long term stability have been fabricated. @FootnoteText@ Financial support is acknowledged through grants from AFSOR (F49620-96-1-0346) and NIH (GM-08205).

10:20am **NS-TuM7 Conductance of Molecular Junctions***, **M.A. Reed**,* Yale University **INVITED**

The charge transport and conductance measurement of a single atom or moiety, is an intriguing, experimentally challenging, and long sought goal. We have developed a number of techniques for the electrical measurement of single and/or few molecule systems. First, we have measured the electrical transport properties of a single molecule self-assembled onto the electrodes of a mechanically controllable break junction, allowing for direct observation of charge transport through the molecules. Current voltage I(V) measurements at room temperature demonstrate a highly reproducible apparent gap at about 0.7 V and a corresponding resistance of 22 MOhms. Second, we have developed a nanostructure device technique called a "nanopore" approach to measure the electronic transport of a class of stable self-assembled conjugated oligomers. This has allowed us to determine the barrier heights and transport mechanisms in these conjugated oligomer systems. We have also measured for the first time the molecular equivalent of a resonant tunneling device, and experimental results on a new molecular switching mechanism.

11:00am **NS-TuM9 Carbon Nanotubes: Manipulation, Properties and Functional Electronic Devices***, R. Martel, T. Hertel, T. Schmidt, H. Shea, **Ph. Avouris**,* IBM T.J. Watson Research Center

Carbon nanotubes (CNT) are materials with unique properties. Depending on their atomic structure, their electronic structure can be that of a metal or semiconductor, and this coupled with their extreme mechanical strength and high thermal conductivity makes them ideal candidates for novel nanoelectronic devices. While discussions of the CNT properties are usually confined to isolated perfectly symmetric tubes, CNT are supported on a solid substrate in actual applications. We will first explore the changes in atomic structure (axial and radial deformations) that result from the adhesion forces between the CNT and the substrate. For this we employee AFM measurements, molecular mechanics and electronic structure calculations. We will show that the deforma tions are significant and can have important consequences for the electrical transport properties of CNT. Next, we will demonstrate that by using the AFM we can manipulate not only the position but also the shape of individual CNTs and in this way fabricate model nano-electronic devices. We will demonstrate a field effect transistor based on a single nanotube (CNT-FET) connected via Schottky barriers to gold electrodes. The resulting band-bending can be controlled by a gate to change the source-drain current by four orders of magnitude at 300 K. Nanotube-based single electron transistors (CNT-SET) will also be demonstrated.

11:20am **NS-TuM10 Simultaneous Study of the Formation and Conductance of Single Wall Carbon Nanotube at STM Tunnelling Gap by Transmission Electron Microscopy***, **J. Yamashita**, H. Hirayama, Y. Oshima, K. Takayanagi,* Tokyo Institute of Technology, Japan

It is theoretically predicted that the single wall carbon nanotube (S WNT) has metallic and semiconducting property depending on its helicity, or diameter. Little experimental study has been done on the electric properties of the SWNT, although several works reported those of the carbon nanotubes. To study the structure and conductance of the SWNT simultaneously, we devised a miniaturized scanning tunnelling microscope (STM) in a UHV transmission elecron microscope (UHV-TEM). We observed formation process of SWNT and measured its conductance and I-V characteristics. The miniaturized STM had two tungsten tips, and graphitized carbon layers adhered to the surfaces of the both tips. The STM tip was touched to other tip and withdrawn from. At the moment of the touch and withdrawal, a SWNT with diameters 1~5nm was formed to bridge the both graphitized layers. The bridge of the SWNT grew and its conductance decreased as the withdrawal of the STM tip. The I-V characteristics were measured(-1.5~1.5V) in the course of the withdrawal of each SWNT. These I-V characteristics were found to fit with a formula, I=@alpha@V(1+ßV@super 2@). We calculated the resistivity for each SWNT by @pi@dt/l@alpha@. Here, l, d and t=0.17nm are the length, diameter, and thickness of each SWNT, which were measured from TEM images. The diameter is an average value for a SWNT, because each SWNT has shapes like coca-cola bottle. We found that the resistivities were from 0.0001 to 0.01(@OMEGA@cm). The magnitude of the resistivity is of high doped semiconductors. This result suggests that the coca-cola bottle like SWNT has metallic part and semiconducting part which are mixed alternately along the SWNT axis.

Organic Electronic Materials Topical Conference
Room 327 - Session OE+AS+EM-TuM

Organic Thin Film Interfaces

Moderator: J.L. Brédas, University of Mons-Hainaut, Belgium

8:20am **OE+AS+EM-TuM1 UV Photoemission Study of Interfacial Electronic Structures of Organic Materials***, **K. Seki**, E. Ito, H. Oji, K. Sugiyama, D. Yoshimura, Y. Ouchi, H. Ishii,* Nagoya University, Japan **INVITED**

The energy level alignment at organic/inorganic and organic/organic interfaces is a fundamental issue for understanding interfacial phenomena of organic-based electronic devices. Using UV photoemission spectroscopy (UPS), we have investigated the electronic structure and energy level alignment at the interfaces of various organic films on metal substrates prepared in ultrahigh vacuum (UHV). The observed results clearly demonstrated that the traditional picture which assumes vacuum level alignment at the interfaces is not valid: the vacuum level of organic layer is shifted from that of metal electrode. We report here our recent effort on the examination of the vacuum level shift at organic/metal, and organic/organic interfaces. At most organic/metal interfaces so far studied, downward shifts of vacuum level were observed (i.e. the vacuum level of organic layer is below that of the metal). At acceptor/metal interface, upward shift was often observed, depending on metal electrode. From the relation between the observed shift and the work function of the metal, we discuss the possible origins of the vacuum level shift such as the polarization of organic molecule by image effect, charge transfer, and mid-gap state. We will also present the results of 'sexiphenyl(6P) on metal' and 'metal on 6P' by UPS, X-ray photoemission (XPS), and metastable atom electron spectroscopy (MAES). At organic/organic interface such as Alq@sub 3@(tris(8-hydroxyquinolino)aluminum) /TPD(N-N'-diphenyl-N-N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine), the observed vacuum level shift was less than 0.1eV, leading to an apparent applicability of the traditional model. However, finite shift of 0.2 eV was observed at donor/acceptor interface such as TTN(tetrathianaphthacene)/TCNQ(tetracyanoquinodimethane) due to electron-transfer.

9:00am **OE+AS+EM-TuM3 Electronic Structure of Molecular Organic Semiconductor Metal Interfaces***, **A. Kahn**, I.G. Hill,* Princeton University

It is now well known that the traditional assumption of vacuum level alignment at metal-organic semiconductor interfaces is incorrect.@footnote 1,2@ Large interface dipoles shift the vacuum level at the interface by more than 1 eV in some cases. The electron injection barrier therefore cannot be reliably estimated as the difference between the metal work function and the organic electron affinity. Furthermore, it has been found that the magnitude of this barrier varies significantly with the metal work function on some organic materials, and not at all on others. To illustrate these properties, we present a comprehensive investigation of metal-organic semiconductor interfaces. Many of these interfaces have been studied both in the organic on metal and metal on organic systems, which in general are not equivalent. The metals studied range in work function from 3.7 eV (Mg) to 5.2 eV (Au). The organic materials studied include the hole transport materials, PTCDA and @alpha@-NPD, the electron transport material Alq@sub 3@, and the cathode interface material, CBP. Using ultraviolet photoelectron spectroscopy, we have measured the relative positions of the metal Fermi level and the organic HOMO, as well as the offset of the vacuum level at each interface. We show that the dependence of the barriers on the metal work function is very small with PTCDA and Alq@sub 3@, and increases with @alpha@-NPD and CBP. All of these organic-metal pairs exhibit substantial interface dipoles which compensate for the restricted range of interface Fermi level positions. Implications for contact performances are discussed. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295. @footnote 2@I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Submitted to Appl. Phys. Lett.

9:20am **OE+AS+EM-TuM4 Interface Dipoles and Band Bending in Organic Semiconductor Interfaces***, **R. Schlaf**, M.W. Nelson, P.G. Schroeder, B.A. Parkinson,* Colorado State University*; P.A. Lee, K.W. Nebesny, N.R. Armstrong,* University of Arizona

The fast paced development in the field of organic light emitting diodes (OLED) and thin film transistors (OTFT) has sparked intense efforts to determine the electronic structure at organic interfaces and to understand the rules governing it. Photoemission spectroscopy (PES) measurements offer direct information about the HOMO alignment, interface dipole and band bending at such interfaces. We performed multistep growth experiments with insitu PES characterization on a variety of organic/organic, organic/inorganic semiconductor and organic/conductor interfaces. We used combined X-ray and UV photoemission spectroscopies (XPS, UPS) which allow the separate determination of the band bending across the interface. This procedure, which is well established in the field of inorganic semiconductor heterojunctions, allows the measurement of HOMO alignment and interface dipoles with high precision. High precision results from avoiding the problem of the superposition of substrate and overlayer emissions in UP-spectra where elaborate curve fitting procedures are needed to distinguish between band bending and HOMO alignment. Our measurements indicate that band bending and interface dipoles play a significant role in the electronic structure at these interfaces similar to effects known from inorganic semiconductor interfaces. The interface dipoles are discussed in terms of quantum and structural dipoles caused by tunneling of charge carriers and permanent molecular dipoles at the interface.

9:40am **OE+AS+EM-TuM5 Molecular Level Offsets at Organic Semiconductor Heterojunctions***, **I.G. Hill**, A. Rajagopal, A. Kahn,* Princeton University

Organic light emitting devices typically consist of two or more organic layers between hole and electron injecting contacts. The interface between the two organics can provide a barrier to either holes or electrons, which may increase device efficiency by reducing the leakage current through the device (leakage current does not contribute to light production). Most of the exciton formation and subsequent light emission occurs near this interface because of the resulting high carrier densities. Knowledge of the relative positions of the organic highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular (LUMO) orbitals at the interface is required to predict the transport or blocking characteristics for holes and electrons, respectively. The assumption of vacuum level alignment at organic heterojunctions is usually used to predict the size of carrier injection barriers, but it has been shown that this model breaks down at organic-metal interfaces.@footnote 1@ We have addressed the validity of this assumption by performing the most comprehensive direct measurement of the HOMO-HOMO offsets at key organic-organic interfaces using ultraviolet photoelectron spectroscopy. Five molecular solids are considered: PTCDA, @alpha@-NPD, Alq@sub 3@, CBP and CuPc. In general, the assumption of a common vacuum level at the interface was found to be valid. A few heterojunctions, such as PTCDA/Alq@sub 3@ and @alpha@-NPD/Alq@sub 3@, do show substantial discontinuities of the vacuum level, however, indicating the formation of an interface dipole.@footnote 2@ The molecular level offsets are discussed in terms of the Fermi level positions observed at interfaces between these organics and various metals. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295. @footnote 2@A. Rajagopal, C. I. Wu and A. Kahn, J. Appl. Phys., 83, (1998) 2649.

10:00am **OE+AS+EM-TuM6 Interface Analysis of Naththyl-substituted Benzidine Derivative and tris-8(hydroxyquinoline) Aluminum Using Ultraviolet and X-Ray Photoemission Spectroscopy***, **E.W. Forsythe**, V.-E. Choong,* University of Rochester*; C.W. Tang,* Eastman Kodak Company*; Y. Gao,* University of Rochester

The interface energy level alignment is a decisive factor in producing highly efficient organic light emitting diodes (OLEDs). We have studied the interface between naththyl-substituted benzidine derivative (NPB) and tris-8-(hydroxyquinoline) aluminum (Alq), a prototypical system used in OLEDs. The combination of ultraviolet photoemission and x-ray photoemission spectroscopy (UPS, XPS) allows us to distinguish contributions from NPB and Alq and obtain a detailed picture of the interface formation. The NPB coverages were deposited onto a 150 Å thick Alq film prepared insitu at 1x10@super -9@ Torr. The Alq and NPB HOMO levels are -1.7 eV and -1.4 eV, relative to the Fermi level, respectively. From the UPS difference spectrum, the gradual modification of the HOMO levels of NPB and Alq are revealed. The Alq HOMO level increases from -1.7 eV in the bulk to -1.8 eV with 2 Å of NPB. Likewise, the NPB HOMO level increases from -1.1 eV for the 5 Å coverage to -1.4 eV with 55 Å of NPB. The increases observed for the Alq and NPB HOMO levels are consistent with the vacuum level shift as well as the observed core level shifts from XPS. Further, the XPS results show no chemical interactions at the interface. This observed local interface formation region may contribute additional traps and energy barriers for carrier transport across the Alq/NPB interface. This work was supported by DARPA DAAL01-96-K-0086 and NSF DMR-9612370.

10:20am **OE+AS+EM-TuM7 Vapor Deposition Polymerization of 4-fluorostyrene and Pentafluorostyrene***, **B. Bartlett**, L.J. Buckley, D.J. Godbey,* Naval Research Laboratory*; M.J. Schroeder,* U.S. Naval Academy

Solventless deposition of thin, uniform dielectric films is of considerable interest and importance in the microelectronics industry, due to increasing wafer sizes and environmental concerns. This work demonstrates a solvent-free method for atmospheric pressure chemical vapor deposition polymerization of thin dielectric films on a variety of substrates, including Si, Mo, Pt, and Cu. The films are characterized using transmission FTIR, and XPS. Depth profiling is performed using XPS, elipsometry, and step profilometry. Film growth is found to be independent of substrate, and proceeds with an activation energy of 15 kcal/mol between 450K and 500K. Films are shown by GPC (gel permeation chromatography) to consist of low molecular weight polymer and oligimer species (between 3 and 165 repeat units). AFM analysis indicates that the RMS thickness variation along the surface is < 0.2%, verifying film uniformity.

10:40am **OE+AS+EM-TuM8 Growth and Characterization of Polyaniline Thin Films on Metal Substrates***, K. Lee, R.V. Plank, **J.M. Vohs**,* University of Pennsylvania*; Y. Wei, N.J. DiNardo,* Drexel University

Polyaniline (PANI) thin films have potential for use as conductive layers in organic-based electronic devices. In a series of experiments, the near-surface sensitivity of High Resolution Electron Energy Loss Spectroscopy (HREELS) was used to probe interfacial and thin film properties of insulating and conducting forms of PANI grown on metal surfaces. PANI was deposited on Ag, Cu, and Au surfaces by evaporative-deposition in vacuum using an emeraldine source and from solution. The fully-resolved vibrational spectra and electronic excitation spectra of PANI films as a function of thickness and modes of preparation reveal clear trends regarding film quality and conductivity upon doping. Specific interface interactions observed in the vibrational spectra at the outset of growth of ultrathin vapor-deposited PANI correlate with increased ordering and an oxidation state similar to the starting emeraldine powder. A relatively high (microscopic) conductivity is indicated by the observation of a split-off far-IR plasmon loss upon HCl doping; this has been compared to the bulk (macroscopic) conductivity of similarly prepared films. In contrast, thicker vapor deposited and solution cast films exhibit a greater degree of branching and lower conductivities. Studying the evolution of polymer thin film properties from the polymer-substrate interaction to the polymer surface demonstrates a general approach with great potential, and the data suggests several aspects of preparation and modification to better control the properties of PANI films in particular.

11:00am **OE+AS+EM-TuM9 Tapping Mode Near-Field Scanning Optical Microscopy of Molecular Crystals and Thin Films***, **H. Stadniychuk**, A. Kosterin, C.D. Frisbie,* University of Minnesota

We describe near-field optical imaging experiments to probe fluorescence and birefringence in molecular crystals and polymeric thin films. These experiments utilize a near-field microscope that employs tapping mode feedback to scan the sample underneath a cantilevered optical fiber probe, facilitating imaging of soft organic samples. In one set of studies, we have focussed on fluorescence and transmission imaging of 30-400 nm thick crystals of tetracene grown by vacuum sublimation onto transparent substrates. These well-defined crystals are excellent samples for investigating quantitative aspects of near-field imaging, and we seek to determine the spatial extent of the near-field by quantifying the relationship between fluorescence intensity and crystallite thickness. A second set of studies exploits polarization modulation techniques to investigate birefringence from thin films of polymers, such as polyethylene oxide. A key aspect of these investigations is comparison of the near-field birefringence images with birefringence images obtained by confocal microscopy. This comparison facilitates understanding of contrast mechanisms in near-field characterization of organic thin films.

11:20am **OE+AS+EM-TuM10 Morphology and Relaxation Dynamics in Thin Organic Films Probed by Femtosecond Time-Resolved Photoemission Spectroscopy*, A.J. Makinen*,** *S. Xu, S. Diol, A.R. Melnyk, D.A. Mantell, M.G. Mason, A.A. Muenter, Y. Gao,* University of Rochester

We have studied for the first time the lifetimes of the excited electron states of thin N,N'-bis(phenethyl)-perylene-3,4:9,10-bis(dicarboximide) (DiPe)films, prepared in situ, using femtosecond time-resolved photoemission spectroscopy. DiPe is an organic compound similar to photoreceptor materials widely used in many imaging applications. By controlling the evaporation conditions, we have been able to grow films of different morphologies, and found that the relaxation dynamics depends on the morphology. We have investigated two distinct films characterized by very different absorption spectra. We have found that for the film with absorption maximum at 500 nm, a typical lifetime is 45 fs at 2.1 eV above the molecular HOMO level. For the other film with absorption maximum at 630 nm, the relaxation rate is almost twice as fast, resulting a lifetime of 25 fs at the same energy. We attribute the extremely short lifetimes to a rapid charge transfer reaction from the high energy sites to the low energy sites. This mechanism is further enhanced by the presence of disorder, which prevents the conservation of crystal momentum in the films. The dependence of the lifetimes on the morphology can be explained by the difference of crytallinity of the films, which affects the density of states and the localization of the excited electrons.

11:40am **OE+AS+EM-TuM11 XPS and ISS Studies of Cu Deposited onto Acid-terminated Self-Assembled Monolayers*, L.S. Dake*,** *D.E. King, A.W. Czanderna,* National Renewable Energy Laboratory

Metal/self-assembled monolayer (SAM) systems serve as models for more complex metalized polymers. Often the adhesion of metals to polymers is a problem, and the metal/polymer interface can be the critical weak link in such a system. We have studied the interactions of Cu deposited onto an acid-functionalized (COOH) SAM surface to improve our understanding of the fundamental metal/organic interactions. We are interested in the chemical interactions of the Cu with the SAM surface, the growth mode of the deposited metals, and the penetration of the metal. Copper deposited onto SAMs with different organic functional endgroups exhibits a wide range of behavior ranging from no surface interaction and rapid penetration (for methyl-terminated SAMs) to weak interactions followed by slow penetration (for methyl-ester terminated SAMs). In this work, we have characterized the interactions of Cu with a carboxylic acid-functionalized alkanethiol SAM, using XPS to examine the chemical interactions, and a combination of XPS and ISS to deduce the growth mode and penetration rate of the deposited Cu. Of particular interest is whether a chemical reaction with the acid surface suppresses penetration, and if there is a limit to the amount of Cu that penetrates the SAM. We find that small amounts of Cu react with the acid surface group, whereas the rest of the Cu penetrates beneath the SAM. Considerable amounts of Cu (10 nm or more) will diffuse beneath the SAM layer, despite the presence of small amounts of reacted Cu at the surface. The penetration rate depends strongly on the deposition rate, with much more rapid penetration occurring at deposition rates of 0.1 nm/min or less. Cooling the sample during Cu deposition, and more rapid Cu deposition rates result in slower or even completely suppressed penetration of the Cu through the SAM layer. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selinsgrove, PA 17870-1001

Plasma Science and Technology Division
Room 314/315 - Session PS1-TuM

Pulsed Plasmas

Moderator: N. Hershkowitz, University of Wisconsin, Madison

8:20am **PS1-TuM1 Simulation of a Pulsed-Power Inductively Coupled Chlorine Plasma*, V. Midha*[1],** *D.J. Economou,* University of Houston

Low pressure high density plasmas are widely used for the fabrication of sub-micron semiconductor devices. Recently, pulsed power operation has emerged as a promising technique for reducing charge induced damage and etch profile distortion (e.g., notching) associated with conventional continuous wave discharges. This paper reports results of a fluid simulation of a pulsed-power inductively-coupled chlorine plasma. The mass, energy, and full momentum equations for the charged species are solved simultaneously with the Poisson equation and the Helmholtz equation for the electromagnetic power deposition profiles. A p-version, least-squares finite-element formulation of the glow discharge equations was developed which is capable of capturing sharp fronts in the sheath region without numerical diffusion. Also, this method is unconditionally stable circumventing the extremely short dielectric relaxation time constant of the system. Simulation results show spontaneous separation of the plasma into an ion-ion core and an electron-ion periphery, depending on the negative ion to electron density ratio. These results are in agreement with a semi-analytic model of the system. The influence of the rf bias frequency on the sheath dynamics and the ion flux and energy to the driven electrode during the afterglow was also examined. Significant oscillations of the ion flux were observed when the ion transit time through the sheath was about equal to the period of the applied field. Finally, the transition to a fully developed ion-ion plasma state and the dynamics of this new kind of plasma were studied.

8:40am **PS1-TuM2 Fluorocarbon Film Composition and Reactor Effluent from Pulsed PECVD of Difluoromethane, 1,1,2,2-Tetrafluoroethane, and Hexafluoropropylene Oxide*, C.B. Labelle*[2],** *K.K. Gleason,* Massachusetts Institute of Technology

Low dielectric constant (< 2.5) fluorocarbon thin films were deposited from three precursors with relatively low global warming potentials: difluoromethane (CH@sub 2@F@sub 2@), 1,1,2,2-tetrafluoroethane (C@sub 2@H@sub 2@F@sub 4@), and hexafluoropropylene oxide (HFPO, C@sub 3@F@sub 6@O). For each feed gas, reactor effluent and film composition were determined as a function of pulsed plasma excitation on and off timing cycles. Fourier Transform Infrared Spectroscopy (FTIR) confirms only partial decomposition of the feed gas occurs in pulsed PECVD, and only a relatively small number of additional gas-phase effluent species are produced in significant concentration. A minimum reaction set has been proposed for each precursor to account for the major effluent species. Most notable for CH@sub 2@F@sub 2@ and C@sub 2@H@sub 2@F@sub 4@ pulsed plasmas is the competition between CF@sub 2@-producing reactions and HF elimination reactions. HFPO pulsed plasmas, due their lack of H, do not have this competition, but the presence of oxygen in the precursor is significant. Support for these reaction sets is also found from a comparison of film composition. In each case, the CF@sub x@ distribution, as well as the presence or absence of hydrogen in the film, can be explained by the proposed reaction sets. Most notably, the role of the competition between CF@sub 2@-producing reactions and HF elimination reactions is reflected in the CF@sub 2@ vs. quaternary carbon concentrations as determined by carbon-1s x-ray photoelectron spectroscopy. Precursors with dominant CF@sub 2@-producing reactions lead to films with larger CF@sub 2@ concentrations, whereas precursors with dominant HF elimination reactions lead to films with larger quaternary carbon concentrations. In the case of the HFPO films, the high CF@sub 2@ fractions are easily explained by the dominant decomposition of HFPO into CF@sub 2@ and trifluoroacetyl fluoride (CFOCF@sub 3@). More significantly, however, the absence of significant oxygen in the films can be traced to the formation of several very stable oxygen species in the pulsed plasma which exit the reactor without being further broken apart and incorporated into the film. Finally, the global warming impact of the pulsed plasma effluents, and thus, of each film deposition process, has been determined.

9:00am **PS1-TuM3 Surface Composition and Reactivities of Fluorocarbon Radicals from Pulsed Fluorocarbon Plasmas**, *N.M. Mackie,* Colorado State University*; J. Bard,* Butler University*; N.E. Capps,* ***E.R. Fisher,*** Colorado State University

Pulsed fluorocarbon plasmas are becoming an increasingly popular method to deposit materials with high fluorine content for a variety of thin film applications and to reduce the adverse charging effects during dry etching. Despite the enormous bod y of work on continuous wave (CW) fluorocarbon plasmas, the underlying deposition and etching mechanisms in pulsed and CW plasmas are still controversial. Pulsed hexafluoropropylene oxide (HFPO) plasmas have been postulated to deposit films from surface reactions of CF@sub 2@ radicals even though the sticking coefficient of CF@sub 2@ is known to be low. We have performed a critical comparison of fluorocarbon films deposited from variable duty cycle pulsed and equivalently powered CW HFPO plasmas. We have determined the duty cycle dependence of CF@sub 2@ reactivities

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

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

and relative gas phase densities from CW and pulsed HFPO plasmas using our Imaging of Radicals Interacting with Surfaces (IRIS) method, which combines spatially resolved laser-induced fluore scence (LIF) with molecular beam techniques.. Preliminary results show that CF@sub 2@ radicals indeed have a low reactivity in a 5% pulsed HFPO plasma with R = -0.1 ± 0.07 and that there is some surface production of CF@sub 2@ during pulsed plasma processing. In addition, time resolved optical emision spectroscopy (OES) has been used to track excited state atoms and radicals throughout the pulse cycle. Insights into the deposition mechanism of HFPO pulsed and CW plasmas will be discussed.

9:20am **PS1-TuM4 Pitting-Free Gate Etching by Lowering Bias Frequency in Pulsed ECR Plasma with a Divergent Magnetic Field***, **H. Morioka,** A. Hasegawa, D. Matsunaga, N. Abe,* Fujitsu Ltd., Japan

In the fabrication of ULSI beyond quarter micron design rule, very high selectivity to gate oxide is one of the essential issues for gate electrode etch process such as poly-Si etching. The reason for this is not only that the gate oxide is getting thinner as the device generation changes, but also that the gate oxide along gate electrodes in a dense pattern region is easily pitted like spikes during overetch (microtrenching), even though the selectivity to the oxide is high enough in the open space. Therefore, excessively high selectivity is required to suppress the pitting in most cases. There are roughly two approaches to achieve high selectivity. one is lowering ion energy by decreasing bias power, and the other is changing chemistry. However, these approaches have disadvantages, that is, lowering ion energy often causes profile distortion such as notching, and the chemistry of high selectivity is sometimes followed by etching residue, strong proximity effect, and "particle" problem because this kind of chemistry tends to enhance polymer deposition on the wafer and chamber wall. Therefore, we have studied effects of bias frequency and pulsed plasma, to suppress the pitting in an alternative way. Our experiments were performed on an ECR plasma etch tool with a divergent magnetic field. Several bias frequencies between 13.56 MHz and 400 KHz with CW and pulsed ECR plasma sources were used to examine their effect to µ-loading of the selectivity and sub-trench depth of half-etch profile. In this experiment, by using pulsed plasma, having a cycle of 100 µs and 25% - 50% duty, and lower bias frequency than 2 MHz, we found that the selectivity µ-loading and the sub-trench depth were decreased, and consequently, we have achieved vertical etched profile without the pitting of the thin gate oxide (2.5 nm). These results imply that the lowering bias frequency (and pulsed plasma) has the efficiency to suppress topography dependent variation of selectivity and etched profile.

9:40am **PS1-TuM5 Pulse-Power Hollow Cathode***, A. Belkind, **J. Cai,*** Stevens Institute of Technology*; R. Scholl,* Advanced Energy Industries

An oxygen plasma generated by a linear multiorifice hollow cathode (LMHC) is used for oil removal from metal strips. To operate the source with a DC power the cathode is constructed from stainless steel. The source has a power limit that determined by cathode overheating and consequential appearance of arcs that destroy the cathode. Stainless steel replacement by aluminum would substantially improve cathode cooling and increase the power limit. Unfortunately DC discharge in oxygen with an aluminum cathode is accompanied with arcing. One way to avoid arcing in to use pulse-power. In this work, pulse-power hollow cathode discharge is investigated. Pulse durations and frequency influences on an oxygen plasma generated in various hollow cathodes are studied. Implementation of pulse-powered aluminum hollow cathode for oil removal is discussed.

10:00am **PS1-TuM6 Diagnostics of Pulsed Plasmas, and the Use of Pulsed Plasmas as a Diagnostic Tool***, **M.V. Malyshev,** V.M. Donnelly,* Bell Laboratories, Lucent Technologies

Pulsed plasma (PP) experiments were carried out in a transformer coupled plasma (TCP) reactor in argon and chlorine plasmas. Time resolved electron temperatures (T@sub e@), electron energy distribution functions (EEDF), electron densities (n@sub e@), positive ion densities (n@sub i@ @super +@), and negative ion densities ~(n@sub i@ @super +@ - n@sub e@) were measured with combinations of trace rare gases optical emission spectroscopy (TRG-OES), Langmuir probe, and microwave interferometry (MWI). These plasma parameters were studied as a function of pressure and power and compared with CW plasma operation. Time resolved number densities of metastable states of rare gases (1s@sub 3@ and 1s@sub 5@) were determined from a model that computes TRG-OES intensities. As the RF power is switched on at the beginning of the 100 us pulse period in a 10 mTorr Cl@sub 2@ plasma, n@sub e@ is near zero and starts increasing slowly, while T@sub e@ rises rapidly to 8 eV and falls to 4 eV in 5 us and to 1.9 eV in 20 us. We also designed a series of PP experiments to circumvent an impediment (the lack and inconsistency of published cross sections for electron impact excitation out of metastable states) in our TRG-OES model. Time resolved OES signals and n@sub e@ (from MWI) were recorded and compared. The rise of optical emission excited from the ground state (e.g. Ar 750.4 nm) coincides with the rise of n@sub e@ during the plasma-ON period, while the emission that comes mainly from excitation out of metastables (e.g. Xe 881.9 nm) increases more rapidly. Assuming the ground state cross sections are correct, we used this comparison to scale cross sections for excitation out of the metastables. Recent theoretical calculations agree with our pulsed-plasma-corrected cross sections.

10:20am **PS1-TuM7 Pulsed Plasma Processing with Helicons***, **C. Charles,*** Australian National University, Australia **INVITED**

High density, low pressure plasma sources utilizing modulated power have been attracting much attention recently. By modulating the power it is possible to further optimize and control the performance of processing plasmas by changing the pulse frequency and the duty ratio. Pulsing is also of interest for studies of basic plasma physics and pulsed argon discharges are useful benchmarks for a better understanding of the more complex mechanisms involved in pulsed plasma processing with electronegative discharges. Experimental and analytical analyses of helicon discharges in continuous and pulsed excitation using various gases (argon, oxygen) are used to present the main features of pulsed plasma processing. Three phases can be distinguished in a pulsed discharge, the breakdown phase, the steady-state phase and the post-discharge, which affect the processing in various ways as a result of temporal changes in the ion energy distribution function, plasma potential, plasma density and electron temperature. Details on the pulsed deposition of silicon dioxide using silane/oxygen mixtures are given to illustrate the effect of those temporal changes on the quality of the deposited films.

11:00am **PS1-TuM9 Very High Density Helicon Mode Operation in WOMBAT***, **R.W. Boswell,** A. Degeling,* Australian National University, Australia

A Helicon Wave mode which exhibits a peak downstream density of greater than 10@super 12@ cm@super -3@ in argon (so called the "blue mode" because of bright ArII emission along the axis) has been oberved. The experimental conditions are : argon gas pressure of 3 mtorr, dc magnetic field of 100g and rf power input of 2 to 3 kW at 13.56MHz into a source region of 18 cm radius and 50 cm length using a double half - turn antenna. The nominal plasma density is about 10@super 11@cm@super -3@ when tuned for the normal Helicon wave mode under these conditions, and the blue mode appears sporadically for intervals of about 2 ms every few seconds. By pulsing the rf power for a duration of a few milliseconds it was found that the blue mode could be tuned to and operated more consistently, however the duration of the mode never exceeded a few milliseconds until the power level was increased above 4kW (where the blue mode operated continuously). B-dot probe measurements indicate that the wave phase velocity while the blue mode operates is about 3x10@super 6@ m/s, which has been shown previously to be the optimum velocity for resonant wave heating of plasma electrons to increase the ionisation rate.The instability of the mode on time scales of a few milliseconds may be due to a neutral pressure decrease in the source caused by ion pumping while the blue mode is operating. Once the blue mode is quenched the ion pumping stops and the pressure increases in the source, allowing the blue mode to return in a few milliseconds.

11:20am **PS1-TuM10 An Overview of Ion-Ion Plasmas for Semiconductor Processing@footnote 1@***, **L.J. Overzet,*** University of Texas, Dallas*; D.J. Economou,* University of Houston*; J.L. Kleber, S.K. Kanakasabapathy,* University of Texas, Dallas*; B.A. Smith,* Texas Instruments Inc. **INVITED**

Negative ions form in almost all discharges used in semiconductor etching and deposition. In addition, the presence of negative ions can impact nearly every aspect of the discharge: from the discharge chemistry and the formation of particulates to the discharge structure and the transfer of energy from the source to electrons. The presence of negative ions forces the question: Can negative ions be used effectively in plasma processing? Recently, several groups have been investigating whether or not negative ions can be used to process semiconductors and the results thus far have been encouraging. We have found that time resolved measurements of pulsed discharges can provide information on how negative ions can be used for surface processing. Negative ions are ordinarily trapped inside the plasma volume, but, pulsed plasmas allow for efficient negative ion extraction during the afterglow period because the negative ion to electron concentration ratio (electronegativity) can increase dramatically. Plasmas with very large electronegativities are often called "ion-ion plasmas." Ion-ion plasmas have such small electron densities, that the sheaths one ordinarily expects to form no longer form in the same fashion and negative ions can more freely reach processing surfaces. This change in the sheath structure during the transition to an ion-ion plasma should be detectable and a proposed "plasma four point probe" for detecting this transition will be presented as well. Finally, high density plasmas can facilitate negative ion extraction because the high densities make the sheaths thin and the plasma source is sometimes positioned far from the processing wafer allowing the electron average energy to be smaller near the wafer. @FootnoteText@ @footnote 1@ This material is based upon work supported by the National Science Foundation under Grant Nos. ECS-9257383 and CTS-9713262 and by the State of Texas Advanced Research Program under Grant No. 009741-043.

Plasma Science and Technology Division
Room 318/319/320 - Session PS2-TuM
Oxide Etching

Moderator: M.D. Armacost, IBM Microelectronics

8:20am **PS2-TuM1 Very Uniform and High Aspect Ratio Anisotropy SiO@sub2@ Etching Process in Magnetic Neutral Loop Discharge Plasma***, **W. Chen**, T. Hayashi, M. Itoh, Y. Morikawa,* ULVAC Japan Ltd., Japan*; K. Sugita, H. Shindo,* Tokai University, Japan*; T. Uchida,* ULVAC Japan Ltd., Japan

Magnetic Neutral Loop Discharge (NLD) plasma@footnote 1@ is a new plasma source for dry etching process, and characterized by a well coupling of the input electric field to the electron motion near the Magnetic Neutral Loop (NL) region. Therefore a dense plasma can be produced and controlled spatially by changing the position of the NL.@footnote 2@] As an evidence, uniform SiO@sub 2@ etching was successfully carried out in several kind of gases and/or those mixture by setting the suitable NL positions.@footnote 3@ Three topics are reported here, which are very uniform etching process by temporal and spatial NL control, high aspect ratio etching for nano-scale pattern in a CHF@sub 2@@super +@ rich plasma and effect of a simple parallel antenna structure for NLD plasma production. In the uniformity control, the deviation of SiO@sub 2@ etch rate was obtained within 3.0% (3 @sigma@) on 200mm diameter wafer, by changing the radius of NL temporally during the etching where the magnetic coil current was varied sinusoidally from a constant value with the repetition frequency of 0.1Hz. Meanwhile the etched profiles of the 0.4 micrometer hole pattern with about 2 micrometer in depth were almost vertical (about 89-90 degrees) at the wafer center and edge. In nano-scale pattern etching process, we found that CHF2+ ions played an important role in a very high aspect ratio profile etching. In a CHF@sub 2@@super +@ ion rich plasma ZEP photo-resist patterned 20nm space was successfully etched with 800nm in depth at the pressure of about 0.3Pa, where CH@sub 2@F@sub 2@, C@sub 4@F@sub 8@, O@sub 2@ gases were used. For plasma production, we proposed a parallel turn antenna, which is characterized in low inductance and larger volume plasma heating in comparison with a conventional single turn antenna. Therefore a high density, low electron temperature plasma with a large diameter of about 0.5m can be produced by 13.56MHz as well as 27MHz power supplies. @FootnoteText@ @Footnote 1@T. Uchida, Jpn. J. Appl. Phys., 33 (1994) L43 @Footnote 2@T. Uchida, AVS 44th National Meeting (1997) ID#98, Conf. Paper #PS1-TuM1 @Footnote 3@W. Chen, M. Itoh, T. Hayashi and T. Uchida, ibid ID#207, Conf. Paper #PS2-WeM1

8:40am **PS2-TuM2 Microloading Effect in Ultra-Fine SiO@sub 2@ Hole/Trench Etching***, Y. Chinzei, T. Kikuchi, M. Ozawa, M. Ogata,* ***Y. Feurprier****, T. Ichiki,* Toyo University, Japan*; H. Shindo,* Tokai University, Japan*; Y. Horiike,* Toyo University, Japan

The 10% trimethylsilane (TMS) added CF@sub 3@-O-CHF-CF@sub 3@ (HFE227)@footnote 1@ and CF@sub 3@-CO-CF@sub 3@ gas chemistries were found to provide high aspect ratio SiO@sub 2@ contact hole using Neutral Loop Discharge plasma. No microloading effect was found down to 0.15µm contact holes provided the bias voltage is high enough (500 V). A new XPS method was employed to analyse the SiO@sub 2@ bottom contact hole surface (aspect ratio about 2) in the course of etching. Prior to XPS analysis a very thin Al film is deposited to cover the resist layer. Then negatively biasing the substrate allowed the discrimination of the SiO@sub 2@ bottom contact hole surface from the top surface contribution. Playing an important role in the occurrence of microloading the bias voltage influence on the bottom SiO@sub 2@ surface composition was investigated for 0.45µm contact hole in the 200 V to 600 V range. The C1s distribution demonstrated C-rich polymer film as evidenced by the C-C component as the major contribution. The total amount of carbon was observed to decrease with increasing the bias voltage while that of F did not change significantly. This strongly suggested that increased bias voltages effectively decrease the polymer film thickness. Futhermore in order to clarify the limits of the HFE227-based chemistry a newly developped 75 keV EB lithography system was used to define line and space patterns of 40 nm to 250 nm using calixarene resist. The percentage of added TMS was slightly varied between 5% to 13%. High TMS addition to the fluorocarbon gas resulted in the occurrence of microloading. For example in the HFE227-based chemistry the microloading appeared for trench width below 50 nm and 110 nm for 10% and 13% TMS respectively. The space width measured at the top of the feature takes into account the increasing resist width due to the film deposition on the sidewalls. Finally no microloading was observed for the addition of 5% TMS then allowing the fabrication of 30 nm trenches. The fine effects of the TMS addition are not yet fully understood due to the complicated plasma and surface reactions involved. EB patterned fine hole array were also fabricated to further evaluate the microloading limits of this fluorocarbon gas chemistry. @FootnoteText@ @footnote 1@Y. Chinzei, M. Ogata, J. Takekawa, N. Hirashita, T. Hayashi, H.Shindo, T. Ichiki and Y. Horiike, PS-WeA10 AVS44th.

9:00am **PS2-TuM3 Selective Oxide Etching in a High-Density Plasma Reactor: Gas Phase Chemistry***, **J.L. Cecchi**, T.M. Bauer, A. Inoue, M.E. Littau, M.J. Sowa,* University of New Mexico **INVITED**

Achieving a stable, reproducible selective oxide etch process in high-density plasma reactors continues to prove problematic, owing in large part to the complex chemistry on the wafer surface. The process relies upon polymerizing hydrofluorocarbon (HFC) feedstocks that produce simultaneous deposition and etching, which must be balanced to provide selectivity while avoiding etch stop. The process is further complicated by a preponderance of reactions occurring on internal surfaces, the composition and temperature of which may change in time. Much of this complexity is revealed in the gas phase chemistry that accompanies the selective oxide etch process, and in this paper, we explore the relationship between the gas phase chemistry and the etching characteristics. We measure the concentration of fluorocarbon precursors, including CF@sub 3@, CF@sub 2@, and CF, with wavelength-modulated diode laser spectroscopy. Atomic species concentrations are measured by optical emission spectroscopy and ion current is measured with a Langmuir probe. These measurements have been made in inductively coupled plasma (ICP) reactors using a variety of HFC feedstocks over a pressure range of 5 to 60 mTorr, ICP powers of 300 to 2500 W, wafer bias of 0 to 400 W, residence times from 0.1 to 1 s, and with varying distance between the ICP coil and the wafer. By exercising the reactor over this large range of parameter space, we are able to vary the concentrations of most gas phase species by over two orders of magnitude. We have analyzed our data with models which relate the polymer growth rate, oxide etch rate, and resist etch rate to the gas phase species concentrations. From this we are able to infer the role of the gas phase precursors, as well as extract kinetic parameters for the processes.

9:40am **PS2-TuM5 Analysis of C@sub 4@F@sub 8@/Ar/O@sub 2@ Plasma for High-aspect Contact Hole Etching using Narrow-gap RIE***, **T. Tatsumi**, H. Hayashi, S. Morishita, S. Noda, Y. Hikosaka, M. Okigawa, M. Inoue, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan **INVITED**

Plasma characteristics and radical species in a dual-frequency (27/0.8MHz) parallel plate system were measured using various in-situ measurement tools, such as infrared laser absorption spectroscopy (IRLAS), appearance mass spectroscopy (AMS), and optical emission spectroscopy (OES). In particular, the densities of key radical species, C@sub x@F@sub y@, CF@sub x@, F, C, SiF@sub x@ and O were analyzed in conjunction with SiO@sub 2@ etch performance. We found that the radical composition could be controlled by limiting the number of collisions with electrons and the interaction with the wall materials, besides the composition of the inlet gases. The number of collisions with electrons can be described as @tau@N@sub e@<@sigma@v>, where @tau@ is residence time, N@sub e@ is electron density, @sigma@ is collision cross section of dissociation, and v is electron velocity. <@sigma@v> means integrated value of @sigma@v multiplied by normalized electron energy distribution function.@footnote 1@ When @tau@N@sub e@<@sigma@v> was large, C@sub 4@F@sub 8@ was dissociated excessively and the relative density of F radical increased. Under long-residence-time conditions, large molecules, such as C@sub x@F@sub y@ and SiF@sub x@, were also observed that were released from the top electrode surface made of Si.

The etch rate and the selectivities to photoresist and underlying Si were affected by not only the [F]/[CF@sub x@] (x=1,2,3) ratio but also these depositive species, i.e., the large molecules. It was possible to suppress both the excessive dissociation of C@sub 4@F@sub 8@ and the excessive deposition of the large species under the short-residence-time condition. We achieved a 0.09 µm@phi@ contact hole with an aspect ratio of 11, under low [F]/[CF@sub x@] ratio plasma conditions established by a short residence time (6 ms), and under an optimized radical/ion flux ratio controlled by the Ar diluted process. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998); to be published.

10:20am **PS2-TuM7 Plasma Kinetics of Silicon Dioxide Etching with Fluorocarbon***, **H. Chae**, H. Sawin,* Massachusetts Institute of Technology*; M.T. Mocella,* DuPont Fluoroproducts

Plasma kinetics of silicon dioxide etching was studied in various conditions: i) oxide cleaning after PECVD(plasma enhanced chemical vapor deposition) ii) oxide etching in an inductively coupled plasma. Chamber cleaning after PECVD of silicon dioxide is known to be one of the major emission sources of perfluorocompounds (PFCs) which have high global warming potentials and very long atmospheric lifetimes. Silicon dioxide etching mechanism in the cleaning condition was studied in this work with various kinds of fluorine containing compounds such as C@sub 2@F@sub 6@, CF@sub 3@CF@sub 2@OCF=CF@sub 2@ (PEVE), NF@sub 3@, F@sub 2@. Silicon dioxide was etched in high temperature of 400@degree@C in parallel plate plasma reactor after TEOS (tetraethyl-orthosilicate) oxide deposited by PECVD. The kinetic study using actinometry measurement of atomic F shows linear correlation between silicon dioxide etching rate and F atom concentration. Arrhenius plots show low activation energies about 0.05 eV below 100 @degree@C and about 0.16 eV above 200@degree@C. The activation energy measurement indicates that ion-enhanced etching is dominant mechanism below 100@degree@C and F atom spontaneous chemical etching is dominant above 200@degree@C. Silicon dioxide etching in high-density plasma can provide high etching rate and good directionality without device damage. However, there are a lot of concerns about RIE(reactive ion etching) lag, inverse RIE lag, etch stop and low photoresist selectivity. Profile evolution modeling can reveal the mechanism of the concerns mentioned above as well as other detail feature profiles like bowing, trenching and faceting. However, parameters for the profile modeling are not available. In this study an inductively couple plasma reactor was built with diagnostic capabilities of mass spectrometer and quartz crystal microbalance. Oxide etching and fluorocarbon deposition rate dependence on ion energy, ion-to-neutral flux ratio, ion impingement angle, and surface temperature were measured. At the same time, ion composition was measured with mass spectrometer.

10:40am **PS2-TuM8 Effect of Ion Bombarding Energies in Silicon Dioxide Etching***, **Y. Hikosaka**, H. Hayashi, K. Kinoshita, S. Noda,* Association of Super-Advanced Electronics Technologies (ASET), Japan*; H. Tshuboi, M. Endo, N. Mizutani, Y. Nagata,* ULVAC Ltd., Japan*; M. Sekine,* ASET, Japan

Ion energy is one of the key parameters in the fabrication of high-aspect-ratio contact holes. Ions incident to the wafer have both high- and low-energy components that depend on the bias frequency and the ion transit time across the rf sheath. However, the relationship between ion energies and etching characteristics such as rate, selectivity, profile and RIE-lag have not been well understood. Our goal is to clarify the role of high- and low-energy ions in SiO@sub 2@ etching. We used a planar-type NLD plasma source operating at 13.56 MHz. An rf-floating ion energy analyzer with a mass spectrometer was equipped inside the rf-biased electrode to measure IEDs (ion energy distributions) and ion fluxes at the rf-driven electrode. First, IED measurements were made for Ar/C@sub 4@F@sub 8@/O@sub 2@ plasma at rf biases of 2 and 13.56 MHz. The CF@sub 1@@super +@ ion is the dominant species for both bias frequencies. The ion energies of CF@sub 1@@super +@ were distributed from 89 to 715 eV at 2 MHz, wider than at 13.56 MHz. Next, we measured SiO@sub 2@ etch rates, self-bias voltages and IEDs as a function of bias rf power for both frequencies. We found that the etch rates were defined by the energy and flux of ions mainly at the higher peak region of the IED, whereas the each energy-splitting width of the IEDs and the self-bias voltage at 2 MHz were different from those at 13.56 MHz. Next, we estimated the energy dependence of the etch yield under actual etching condition, using the obtained IEDs and etch rates. We found that the etch yield of SiO@sub 2@ increased monotonically with increase in ion energy and tended to saturate at a value of 1.5 molecules/ion at energy levels exceeding 800 eV. This energy dependence of the etch yield led to a 65 % contribution of high-energy ions to the etch rate. @FootnoteText@ This work was supported by NEDO.

11:00am **PS2-TuM9 Studies of High Density Oxide Etch Mechanisms with a Physically-based Profile Simulator***, **V. Vahedi**, D.J. Cooperberg, J.M. Cook, L. Marquez, E. Hudson, J. Winniczek,* Lam Research Corporation

Dielectric etching accounts for about forty-five percent of the etch steps in a semiconductor fabrication process, and with emerging device integration technologies this percentage will soon increase. In contrast to other etch processes, highly selective dielectric etching using high density fluorocarbon plasmas results in simultaneous etching and deposition. In order to implement dielectric etching successfully in a production environment, it is critical to understand how to balance the etching and deposition components. The required balance will be a strong function of the properties of the microstructures being produced as well as the aspect ratio of the features. While there are many proposed mechanisms to explain the dependence of this balance on aspect ratio, it is not clear which mechanisms are the dominant ones under a given set of process conditions. We are using our semi-empirical profile simulator to investigate the relative importance of various mechanisms leading to aspect ratio dependent etching (ARDE) in dielectric etching. Our dielectric etch model includes ion-enhanced etching, physical sputtering and polymer deposition as well as realistic ion energy distribution functions. We will present the results of our polymer deposition experiments which were performed to determine polymer sticking coefficients and study the role of ion-assisted deposition in sub 0.5µm features. We will also present results from sputtering experiments which were designed to measure carefully the angular and energy dependence of sputter yield of photoresist and oxide. The rest of the parameters were set using our calibration scheme which leads to optimal agreement between simulation and digitized SEM data. We will also present typical profiles under various process conditions.

11:20am **PS2-TuM10 The Challenge of Predictive Profile Simulators for Dielectric Etch***, G.S. Hwang, **J. Kenney**, K.P. Giapis,* California Institute of Technology

Current ULSI technology requires extensive plasma etching of dielectric materials, a need that will further increase with the anticipated move to copper interconnects and low-k dielectrics. The increased importance of dielectric etch, when combined with tighter tolerances for profile control at larger aspect ratios, presents a unique opportunity for fundamental research to assist in the development of etch processes in a timely and cost-effective manner. To be sure, understanding plasma etching of dielectric materials poses a challenge, considerably taller than that of metal or polysilicon etch for two reasons: a) Etching of dielectrics proceeds by more complex surface chemistry, involving simultaneous deposition and etch processes, and b) Differential surface charging is significant. These differences can lead to etch rate dependencies and profile irregularities that are unique to dielectric etching. Direct Simulation Monte Carlo techniques are used to study dielectric etch in high density plasmas. The simulations include sheath theory, microstructure charging, surface currents, and etching by a simple sputtering model. We explicitly investigate the etch rate dependence as a function of etch depth on plasma parameters and dielectric quality (as judged by a surface discharge threshold). The results suggest that ion shadowing (aspect ratio dependent) and surface currents (absolute depth dependent) play a crucial role in dielectric etch. Based on the simulations, we develop an empirical relationship to capture the etch rate dependencies on etch time, ion temperature, ion energy, surface discharge threshold, aspect ratio, and etch depth. The relationship describes well published etch rate data and reported parameter dependencies for various oxide etch chemistries and can be used to predict the etch stop occurrence. Furthermore, profile evolution simulations are performed to investigate the rigin of two profile peculiarities in oxide etch: microtrenching and sidewall bowing. The results indicate that ion scattering is not the dominant mechanism by which these irregularities form. Rather, charging effects at the trench bottom and mask sidewalls appear to be mainly responsible as asserted by a comparison of predicted with experimental profiles.

11:40am **PS2-TuM11 Control of Profile in High Aspect Ratio Contact and Via Etch***, **C.H. Bjorkman**, K. Doan, J. Wang, B. Pu, H. Shan,* Applied Materials, Inc.*; N. Kuo, P. Chang,* Applied Materials, Taiwan

The purpose of this study was to investigate which parameters control the profile in high aspect ratio (HAR) dielectric etch. Holes with aspect ratios in the range 6:1 - 10:1 were etched in a low-to-medium density MERIE etch chamber. A common observation among the fluorocarbon chemistries we investigated was the variation in profile angle from the top to the bottom of the hole. For example, the profile of a close to optimized single step chemistry starts off with a taper angle of 86-87°. After reaching an aspect ratio of approximately 3:1, the profile starts to straighten out. However, this trend is reversed as endpoint is approached. Typically, the taper angle at the bottom of the hole is approximately the same as what we observe at the top of the hole. This tapered bottom profile tends to decrease the CD (critical dimension) with a resulting increase in contact resistance. We divided the profiles into three components in order to quantitatively analyze our results: (1) any flaring and/or necking observed in top portion of the hole, (2) bowing or taper in the center portion and (3) excessive tapering and/or rounding of the bottom of the hole. We found that any initial tapering will remain and thus give rise to flaring at the top of hole. This can be prevented by minimizing polymer deposition on the sidewalls during the first third of the etch. We achieved this by making the chemistry leaner, raising the pressure and raising the wafer temperature. Controlling the profile during the second portion of the etch turns out to be a compromise between preventing bowing and maintaining a large bottom CD. The main parameter controlling this portion of the etch was determined to be the pressure. As for the last portion of the etch, the tendency to taper and thus reduce bottom CD was found to be controlled by the DC-bias. We obtained a straighter profile by decreasing both pressure and B-field and thus increasing the DC-bias.

Surface Science Division
Room 308 - Session SS1-TuM
Semiconductor Surface Structure

Moderator: L.J. Whitman, Naval Research Laboratory

8:20am **SS1-TuM1 Effect of Tensile Strain on B-type Step Energy on Si(001)-(2x1) Surfaces Determined by Switch-Kink Counting*, E. Heller*,** *J.P. Pelz,* Ohio State University*; D.E. Jones, Y.H. Xie, P.J. Silverman,* Company

Several years ago Xie et al.@footnote 1@ suggested that applied strain could strongly influence the creation energy of so-called S@sub B@ steps on Si(001)-(2x1) surfaces, which could dramatically affect surface roughening during strain-layer growth. Swarzentruber et al.@footnote 2@ and then later Zandvliet et al.@footnote 3@ showed that step energies on unstrained Si(001)-(2x1) surfaces could be estimated by counting kinks (a kink being a small perpendicular jump in a surface step edge) on samples annealed at elevated temperatures. In order to directly test the proposal of Xie et al., we have used kink-counting in STM images of strained Si(001) surfaces to quantify the effect of strain of the S@sub B@ step energy. For this purpose, we have developed a new kink-counting method (called switch-kink counting), which is more accurate than previous methods when the azimuthal miscut angle changes across the surface. This can be problematic when there is macroscopic surface roughness, due to cross-hatch or imperfect surface preparation. I will describe both the method used by Zandvliet et al. and our new method as well as why it is more accurate for non-constant azimuthal miscut angle. I will then give an analysis of data using both of these methods on a large data set we have collected from STM images. We find an energy for these kinks that is significantly higher than that found by Zandvliet et al. for unstrained silicon, and appears to increase with increasing tensile strain, although possibly not as fast as Xie et al. predict. @FootnoteText@ @footnote 1@Xie et al., Phys. Rev. Lett. 73, 3006 (1994). @footnote 2@B. S. Swartzentruber, Y.-W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. 65, 1913 (1990). @footnote 3@H. J. W. Zandvliet, H. B. Elswijk, E. J. van Loenen, and D. Dijkkamp, Phys. Rev. B, 45, 5965 (1992).

8:40am **SS1-TuM2 Geometry, Energetics, and Electronic Structure of the Dimer Reconstruction on the Carbon, Silicon and Germanium (100) Surfaces*, H.C. Kang*,** *C. Yang,* National University of Singapore, Singapore

The ground state geometry of dimers on the C(100), Si(100) and Ge(100) surfaces have been the subject of much study and controversy, particularly in the case of the silicon surface. There are at least two issues which have not been resolved. First, theoretical calculations for Si(100) have favored both the buckled and unbuckled dimer geometry as the ground state. The most recent cluster calculations favor an unbuckled ground state while the most recent slab calculations favor a buckled ground state. Second, the driving force for dimer buckling is still not well understood. There have been suggestions that slab calculations predict the unbuckled ground state for Si(100) because of the inadequate treatment of electron correlation. We performed density functional cluster calculations for all three surfaces in an attempt to resolve these issues. We find that a number of previous cluster calculations have not dealt satisfactorily with the geometric constraints applied during geometry optimization. Our calculations resolve the differences in ground state geometry, dimer bond length and energetics between cluster and slab calculations. We also find that buckling is driven by a kinetic energy decrease, and that for silicon and germanium this dominates the increase in potential energy with buckling. For carbon the decrease in kinetic energy with buckling is less than the increase in potential energy and, hence, buckling is energetically unfavorable. We can trace this difference in behavior to the small core size of the carbon atom compared to silicon and germanium.

9:00am **SS1-TuM3 An Atom-Resolved Dynamical Study of Hydrogen Diffusion on the Si(100) Surface*, J.J. Boland*,** University of North Carolina, Chapel Hill **INVITED**

A detailed knowledge of the dynamical processes that occurs on surfaces has important implications for materials growth and processing. In the case of low temperature silcon growth hydrogen surface diffusion and desorption are key processes. However, little is known about the behavior of hydrogen on silicon surfaces at high temperatures. In this work we describe in detail the dynamical behavior of hydrogen on the Si(100) surface at temperatures between 600K and 750K. Our starting point for all these studies is a Si(100) surface that is completely terminated with hydrogen. At high temperatures H2 desorption occurs and the dangling bonds that result are initially localized on the same dimer unit. Even though this paired arrangement is stabilized by a weak pi interaction it soon dissociates due hopping of neighborng H atoms into these vacancy sites. Dangling bond motion is largely confined along the dimer row direction but steps act as turning points for this motion. We observe that dangling bonds recombine with surprising efficiency. A statistical analysis indicates that there are configurations other than the paired configuration that are stabilizing and that these promote dangling bond recombination. Missing dimer defects also act a recombination centers and effectively localize dangling bonds about them. Moreover, the residence times of dangling bonds at different surface locations provides a direct measure of the relative energies of the different sites on the Si(100)-2x1 surface.

9:40am **SS1-TuM5 Ultra-high B and As Doping during Si(001) Gas-Source Molecular Beam Epitaxy: Growth Kinetics, Dopant-Incorporation, and Electrical Activation*, G. Glass*,** *H. Kim, A. Vailionis, J. Soares, P. Desjardins, J.E. Greene,* University of Illinois, Urbana-Champaign

Si(001) layers doped with B or As were grown on Si(001)2x1 substrates by gas-source molecular-beam epitaxy using Si@sub 2@H@sub 6@, B@sub 2@H@sub 6@, and AsH@sub 3@ at temperatures T@sub s@ = 500-850 °C. Dopant concentrations ranged from 1x10@super 16@ to 1.2x10@super 22@ cm@super -3@ for B and 1x10@super 16@ to 1x10@super 18@ cm@super -3@ for As. B incorporation was linear with incident B@sub 2@H@sub 6@/Si@sub 2@H@sub 6@ flux ratio for B concentrations C@sub B@ @<=@ 2.5x10@super 20@ cm@super -3@, and increased with higher flux ratios. As incorporation was linear to 3x10@super 17@ cm@super -3@, and subsequently was sub-linear. At T@sub s@ = 550 and 600 °C, B was incorporated into substitutional electrically-active sites for C@sub B@ up to 2.5x10@super 20@ cm@super -3@. At higher B concentrations, there is a large and discontinuous decrease in the electrically active fraction of B, although the total activated B concentration continues to increase. Hall-effect measurements show the As to be fully electrically active for all films in the study. All films were fully strained. TEM investigations revealed that B doped films grown at T@sub s@ @<=@ 600 °C, and all As doped films were highly perfect with no indication of precipitates or dislocations. Deuterium temperature-programmed desorption measurements as a function of increasing C@sub B@ and C@sub As@ show strong surface segregation. The B deactivation behavior can be explained on the basis of a model which accounts for strong B segregation to the second-layer, and the surface formation and subsequent incorporation of electrically inactive B-dimers at higher C@sub B@ values. In contrast, As acts to passivate the surface, resulting in arrested growth as the As coverage approaches 1 ML. The combination of HR-XRD, SIMS and Hall-effect measurements, show that the Si-B bond length due to B-dimers is 1.99 Å, compared to 2.04 Å for substitutional B atoms.

10:00am **SS1-TuM6 Scanning Tunneling Microscopy of B/Si(001)*, J.F. Nielsen*,** *H.-J. Im, J.P. Pelz,* Ohio State University*; M. Krueger, B. Borovsky, E. Ganz,* University of Minnesota

Previous work has shown that annealing of heavily B-doped Si(001)-(2x1) surfaces produces spontaneous formations of S@sub A@ steps into periodic "striped" patterns,@footnote 1@ consistent with stress relaxation effects considered by Marchenko@footnote 2@ and Alerhand et al.@footnote 3@ However, the exact role of boron in the step formation, as well as the cause for the observed increase in step density with decreasing annealing temperature, are still under investigation. Using detailed bias-dependent STM measurements of various B-induced surface structures, we have (1) determined that the density of B-induced surface structures does NOT change significantly with annealing temperature, leaving unresolved the strong temperature dependence of the step formation, (2) observed direct evidence of boron accumulation at step edges, providing a possible mechanism for boron-induced lowering of S@sub A@-step creation energy, and (3) identified characteristic structural and electronic features of a number of distinct B-induced structures, which indicate a need to reclassify previously reported B-related structures.@footnote 4@ We are currently introducing surface B in a controlled way by decomposing B@sub 2@H@sub 6@ on lightly P-doped Si(001). Initial observations indicate that deposition parameters determine whether B induces the formation of reconstructed islands@footnote 5@ or whether B forms isolated structures equivalent to those observed on bulk-doped samples. Employed as a semiconductor processing step, this process could allow for the controlled production of periodic arrays of nanoscale step structures. @FootnoteText@ @footnote 1@D.E. Jones et al., Phys. Rev. Lett. 77, 330 (1996) @footnote 2@O.L. Alerhand et al, Phys. Rev. Lett. 61, 1973 (1988) @footnote 3@V.I. Marchenko, JETP Lett. 33, 381 (1981) @footnote 4@Z. Zhang et al, J. Vac. Sci. Technol. 14, 2684 (1996) @footnote 5@Y. Wang et al., Phys. Rev. Lett. 74, 403 (1995)

10:20am **SS1-TuM7 Halogens Adsorbed on the Ga-rich c(8x2) GaAs(001) Surface: Adsorbtion Sites, Mobility and Overlayer Structure***, **J.G. McLean,** P. Kruse, A.C. Kummel,* University of California, San Diego

Chlorine is commonly used to etch the As-rich c(2x8) Gallium Arsenide (001) surface. However, on the well-ordered Ga-rich c(8x2) reconstruction of GaAs(001) at 300 K, Cl@sub 2@ has been found to form an overlayer which passivates the surface against attack by atmospheric gases. Although the clean surface always reconstructs, the Cl@sub 2@ passivated surface yields a sharp (1x1) LEED pattern. A more complete understanding of the Cl chemisorption is desirable both for better control of the etching process and to understand the properties of the passivating overlayer. We have used scanning tunneling microscopy to study the adsorption sites of Cl@sub 2@ on the Ga-rich c(8x2) surface of GaAs(001). The Cl bonds exclusively to the Ga atoms, consistent with expectations based on molecular bonding theory. At low coverage the Cl is mobile along the Ga rows, which is surprising given the strength of the Ga-Cl bond. We have also investigated the overlayer at high coverages, for which STM revealed both c(2x6) and (1x1) structures. In both cases, the structures are inconsistent with the Ga/As ratio of the initial clean c(8x2) reconstruction. This shows that long-range rearrangement of surface atoms has taken place, allowing a bulk terminated surface to form in the case of the (1x1) structure. Tunneling spectroscopy will be used to determine whether this surface rearrangement results in a modified electronic structure, allowing electronic as well as chemical passivation.

10:40am **SS1-TuM8 The Role of Dimer-Stacking-Fault Structures in Si(111) Etching***, **M. Fouchier,** J.J. Boland,* University of North Carolina, Chapel Hill

Etching of semiconductors continues to be important from both a fundamental and applied prospective. In this work, we investigated the etching of Si(111) by halogens using Scanning Tunneling Microscopy. It is known that Si(111) etching occurs preferably at steps but also within terraces. We showed that Dimer-Stacking-fault (DS) structures are formed during etching by Bromine at 900K. These structures result from the coalescence of vacancies on the surface.@footnote 1@ These vacancies are produced either thermally or by isolate etching events. These results suggest that DS structures are intermediates in the terrace etching process and that the dimer-rows bounding these structures serve as etch sites. @FootnoteText@ @footnote 1@Marc Fouchier and John J. Boland, Phys. Rev. B 57, 8997 (1998).

11:00am **SS1-TuM9 The Structure of Ge Surfaces from (001) to (111)***, **A. Laracuente**, S.C. Erwin, L.J. Whitman,* Naval Research Laboratory

We are studying the structure of Ge surfaces oriented between (001) and (111) using STM and first-principles electronic structure calculations (LDA). Similar to Si,@footnote 1@ Ge surfaces oriented within ~12° of (001) and (111) consist of low-index terraces and steps. Between this range, it appears that only (113) and ~(559) are planar surfaces on Ge, in contrast to Si where (114), (113), and (5 5 12) are planar. Because (113) is the only planar high-index surface common to Si and Ge in this range, its structure is of particular interest. At room temperature, Si(113) has a (3x2) reconstruction that incorporates a highly unusual six-fold-coordinated surface interstitial. The "self-interstitials" occur within every other tetramer (a dimer plus nonrebonded double-layer step), making the otherwise (3x1) surface (3x2). At room temperature the Ge(113) surface consists of an equilibrium mixture of (3x1) domains (~80%) and Si-like (3x2) domains (~20%). In contrast to previously reports, we find that the (3x1) domains have the same structure as Si(113)-(3x2), with the exception that every tetramer includes an interstitial. Extensive LDA calculations confirm that the "self-interstitials" dramatically lower the surface energy on Ge(113). Whereas on Si the (3x1) structure is 2 meV/ Å@super 2@ higher in surface energy than the (3x2), it is approximately degenerate on Ge (in agreement with experiment). Furthermore, calculations of the stability of interstitials at various sub-surface sites indicate that they do not migrate to the surface from the bulk, as previously suggested, but rather originate from surface adatoms (perhaps in a lattice gas). @FootnoteText@ @footnote 1@Baski, Erwin, and Whitman, Surf. Sci. 392, 69 (1997).

11:20am **SS1-TuM10 Structure of Arsenic-Passivated Germanium (100)***, **S. Gan**, L. Li, M.J. Begarney, D. Law, C. Li,* University of California, Los Angeles*; B.-K. Han,* University of California, Los Angeles, US*; R.F. Hicks,* University of California, Los Angeles

Arsenic passivation is an important first step in the heteroepitaxy of GaAs on Ge (100). Using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy and low energy electron diffraction, we have identified the atomic structure of arsenic-terminated Ge (100) surfaces. The germanium substrates were exposed to arsenic in two different ways: (1) by dosing with 500 L arsine in ultrahigh vacuum, and (2) by exposure to 2.0 Torr tertiarybutylarsine and 97.0 Torr hydrogen at 650°C in a CVD reactor. During AsH3 dosing at 25 to 300°C, the As coverage is approximately constant at 0.3 ML. Upon increasing the dosing temperature further, the coverage attains a maximum of 1.0 ML at 425°C, then gradually declines to zero at 600°C. Scanning tunneling micrographs obtained at 1 ML coverage show that the surface has been transformed into a series of flat islands, one atomic layer in height, that are terminated with arsenic dimers. Also, B-type steps are preferred over A-type steps, causing the islands to exhibit narrow rectangular shapes with long straight edges. By contrast, when the surface is treated with tertiarybutylarsine in the CVD reactor, the initial coverage of arsenic is 2.0 ML. Upon annealing these samples in vacuum, the coverage remains constant up to 300°C, then slowly drops to zero as the temperature is raised to 600°C. At more than 1.5 ML of arsenic, the As:Ge (100) surface exhibits an unusual "waffle" pattern, with ridges about 20-50 Å in width crisscrossing the surface in the [110] and [-110] directions. Heating to 425°C, decreases the coverage to 1.0 ML. In this case, the surface is terminated with a series of square, flat islands that are separated by straight step edges one to three atomic layers in height. These surfaces are completely terminated with As dimers. Further heating to desorb the arsenic, causes the Ge (100) surface to transform back into a series of large terraces with their edges composed of equal amounts of A and B steps. The unusual morphology observed after exposure to tertiarybutylarsine in the CVD reactor is attributed to hydrogen-atom etching of the germanium surface.

11:40am **SS1-TuM11 STM of Tl Overlayers on Si(111): Structures of a "New" Group III Element***, L. Vitali, M.G. Ramsey, **F.P. Netzer,*** Karl-Franzens-Universität Graz, Austria

Thallium is an unusual group III element because it can adopt a monovalent state in addition to the more conventional trivalent state of the other elements of this group. In this study we investigate for the first time the growth and the structure of Tl overlayers on Si(111)7x7 surfaces from room temperature (RT) to 500°C, using STM and STS in conjunction with LEED and AES. At low coverages Tl adatoms adsorb preferentially on the faulted half of the unit cell, covering the surface with an array of triangular adsorbate islands maintaining the (7x7) periodicity. The Tl adatoms are highly mobile at RT as recognised in consecutive STM images. On completion of the first monolayer a low corrugation surface develops at RT, but at 350°C a well ordered (1x1) structure is observed in LEED and with atomic resolution in the STM. This layer shows a metallic state with a prominent feature at -0.5 eV in STS. Depending on the substrate temperature remarkable contrast phenomena are seen in the STM for the first and the second monolayer of Tl. From RT to 200°C the Si(7x7) substrate arrangement determines the structure of the overlayer, with a network of contrast lines reflecting, presumably, the (electronic?) influence of the (7x7) substrate mesh. Atomic resolution along the lines displays a different distribution of occupied and unoccupied states. From 300-450°C a (6x6) array of broad second layer maxima (~17Å diameter, corrugation ~1Å) on a (1x1) monolayer signals a structural transformation of the overlayer. Tl overlayers on Si(111) thus display a very different structural behaviour to the other group III elements and possible reasons are discussed in terms of valency, bonding geometry and size effects.

Surface Science Division

Room 309 - Session SS2-TuM

Noble Metal Catalysis

Moderator: G.B. Fisher, General Motors R & D Center

8:20am **SS2-TuM1 Microfabrication and Evaluation of Supported Model Catalysts**, ***B. Kasemo***, Chalmers University of Technology, Sweden **INVITED**

Supported catalyst particles and single crystals exhibit differences in catalytic properties which are referred to as the structure gap in catalysis. Experimentally this is addressed by systematic studies of the influence of e.g. particle size and structure, and type of support on the catalytic properties. Modern microfabrication adds new opportunities, complementing the existing ones, to systematically manufacture and evaluate supported model catalysts. In this presentation the advantages and limitations of different microfabrication techniques are briefly reviewed. The use of electron beam lithography (EBL) applied to model catalyst production is described in detail. Specific examples are given of EBL manufactured noble metal catalysts on different supports. Evaluation of these catalysts in catalytic reactions involve (i) studies of morphological changes of the native structures caused by the reaction conditions and (ii) evaluation of the kinetics.

9:00am **SS2-TuM3 Chemisorption and Kinetic Studies of Model Low-Temperature CO Oxidation Catalysts: Au/TiO@sub 2@(110)**, ***V.A. Bondzie***, *S.C. Parker, C.T. Campbell,* University of Washington

As a room-temperature CO oxidation catalyst, Au/TiO@sub 2@ shows exciting potential in automotive applications. Oxygen does not dissociatively adsorb on bulk Au, although one of the elementary steps in the proposed mechanism for this reaction is the activation of O@sub 2@ at the Au/TiO@sub 2@ interface. No such adsorption sites that react with molecular O@sub 2@ have so far been identified spectroscopically. In order to understand this reaction at the molecular level, O@sub 2@ chemisorption and CO titration over O-covered 2D and 3D Au islands, grown on TiO@sub 2@(110) have been studied. Techniques used included TPD, LEED, XPS and LEIS. A hot filament was used to deposit O adatoms. Subsequent TPD shows O@sub 2@ desorption with a peak maximum shifting from ~650 K (for 2-atom thick Au islands) to ~550 K (for bulk Au). No O@sub 2@ desorption is seen from 2D (i.e., 1-atom thick) Au islands below 770 K. This indicates that as the thickness of the Au islands decreases, the O adatoms bind increasingly strongly to the Au. The kinetics of the titration of oxygen adatoms with CO (CO@sub g@+O@sub a@ ? CO@sub 2,g@) were also measured from O-covered Au particles on TiO@sub 2@(110). The reaction rate on 2D Au islands is slower than on the 3D Au islands, even though CO bonds slightly more strongly on the former. This reflects a higher activation barrier on the 2D Au islands than on the 3D Au islands for the Langmuir-Hinshelwood step (i.e., CO@sub a@+O@sub a@ ? CO@sub 2,g@). This is due to the stronger O-Au chemisorption bond strength on 2D Au islands than on 3D islands. This stronger bond should promote dissociative O@sub 2@ adsorption, which we postulate as the rate-determining step in catalysis.

9:20am **SS2-TuM4 Monte Carlo Simulations of Catalytic Reactions on Nanometer-sized Particles**, ***H. Persson***, *P. Thormählen, V.P. Zhdanov, B. Kasemo,* Chalmers University of Technology, Sweden

Using a Monte Carlo algorithm, we have investigated the 2A+B@sub 2@ @>=@ 2AB reaction both on a nanometer-sized catalyst particle, with interacting facets, and also on an infinite surface, which represents a macroscopic catalyst surface. The reaction mimics practically important catalytic processes such as CO oxidation on Pt, Rh or Pd. In the present work we have studied the role of diffusion between different facets, different reaction to diffusion rates and the effect of desorption in these systems. Our results indicate that the kinetics on nanometer-sized particles can be remarkably different compared to the kinetics on a macroscopic catalyst surface.

9:40am **SS2-TuM5 Ab Initio Density-Functional Theory Study of CO Oxidation Over Ru(0001)**, ***C. Stampfl***, *M. Scheffler,* Fritz-Haber-Institut der MPG, Germany

Under "Realistic conditions'' the rate of oxidizing catalytic reactions is very much higher at ruthenium than at any other transition metal, and the dependence on the oxygen partial pressure is qualitatively different.@footnote 1@ Yet, under ultra high vacuum (UHV) conditions Ru is by far the worst catalyst, and the question was frequently raised concerning the relevance of Surface Science studies for real catalysis. Using density-functional theory we show in this contribution that the above noted "pressure gap'' phenomenon is only apparent. Thus, if understood, it can be circumvented. In particular, we investigate both a scattering reaction of CO at the O-covered surface [Eley-Rideal mechanism (E-R)]@footnote 2@ and the Langmuir-Hinshelwood (L-H) reaction. In each case the transition state corresponds to a bent CO@sub 2@-complex with an associated bond angle of 131° (E-R) and 125° (L-H). The metastability of a carbonate species is also identified which could act as an intermediory species for CO@sub 2@ production. We attribute the enhanced CO@sub 2@ formation rate at elevated gas pressures (and high coverage) to be due to the notably weaker O-Ru bond strength compared to that at lower O-coverages as are present under UHV conditions. In this respect we also report results investigating the affect of subsurface oxygen on the energetics of the reaction. Subsurface O has been proposed to be responsible for the very recently reported CO@sub 2@ reaction rates@footnote 3@ that are two orders of magnitude higher than those measured in Ref. 1. @FootnoteText@ @footnote 1@C. H. F. Peden and D. W. Goodman, J. Phys. Chem. 90, 1360 (1986). @footnote 2@C. Stampfl and M. Scheffler, Phys. Rev. Lett. 78, 1500 (1997). @footnote 3@A. Böttcher, H. Niehus, S. Schwegmann, H. Over, and G. Ertl, J. Phys. Chem. 101, 11185 (1997).

10:00am **SS2-TuM6 The Effect of Strain on the Reactivity of Metal Surfaces**, ***M. Mavrikakis***, Technical University of Denmark, DENMARK; *B. Hammer,* Aalborg University, Denmark; *J.K. Norskov,* Technical University of Denmark, DENMARK

Self-consistent density functional calculations for the adsorption of O and CO, and the barrier to CO dissociation on strained and unstrained Ru(0001) surfaces are used to illustrate the general phenomenon of strained metal surfaces having chemical properties drastically different from those of unstrained surfaces. Surface reactivity increases with lattice expansion, following a concurrent upshift of the metal d-states. Consequences for the catalytic activity of thin metal overlayers are discussed.

10:20am **SS2-TuM7 In-situ Investigation of the Catalytic Reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@O on Pt(111) with Second Harmonic Generation**, ***F. Gudmundson***, Chalmers University of Technology, Sweden; *F. Eisert,* University of Heidelberg, Germany; *A. Rosén,* Chalmers University of Technology, Sweden

Most knowledge about catalytic reactions is obtained by the use of surface analytical tools, which are restricted to ultrahigh vacuum conditions. The extrapolation to real reaction conditions at ambient pressure however is connected with a relatively high uncertainty. Nonlinear optical techniques like Second Harmonic Generation (SHG) combine the capability of in-situ investigations with an inherent surface sensitivity. We present in-situ SHG investigations of the catalytic reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@ O on Pt(111) in the pressure range between 200 mtorr and 10 torr at a catalyst temperature of T=700 K. With SHG the oxygen coverage is determined as function of the hydrogen partial pressure. In the pressure range investigated, the gas flow changes from molecular flow to laminar flow. This transition has a profound influence on the experimental observed oxygen coverages. However, using a kinetic reaction model of the hydrogen oxidation developed by Hellsing, Kasemo and Zhdanov the experimental results can readily be interpreted, if the transition of the gas flow conditions from molecular to laminar flow is taken into account.

10:40am **SS2-TuM8 Suppression of Water Formation by Adsorbed Gold on Pt(335)**, ***D.C. Skelton***, Michigan State University/General Motors R & D Center; *R.G. Tobin,* Tufts University; *D.K. Lambert, C.L. DiMaggio, G.B. Fisher,* General Motors R & D Center

Platinum, an excellent catalyst for water formation, has its catalytic activity significantly reduced by a submonolayer coverage of gold. As part of a larger study on surface reactions on modified electrodes for chemical gas sensors, temperature programmed reaction on a stepped platinum surface, Pt(335), at three gold coverages was studied. Reactive surfaces were prepared in UHV with systematic doses of hydrogen and oxygen to obtain submonolayer coverages of adsorbed atomic hydrogen and oxygen. Gold coverage was measured by comparing the relative intensities of the 64 and 69 eV Auger peaks of platinum and gold, respectively. At low coverages gold adsorbs into the step sites on Pt(335) [4(111) × (100) in terrace step notation] and fills in to form islands which merge into a semi-continuous surface with openings to the platinum approximately 50 to 100 @Ao@ in diameter at 0.7 monolayers. This presumably leaves 30% of the surface platinum atoms available for chemisorption. However, hydrogen and oxygen in adsorption are reduced to 15% and 9% of their values on bare Pt(335), respectively, and bonding in step sites is reduced to 3% and 6%, respectively. Neither molecule bonds to the gold covered areas. The temperature-programmed reaction data for both Pt(335) and 0.7Au/Pt(335) show that this reduction in reactant coverage accounts for only part of the reduction in water production. Blockage of step sites by gold eliminates a major low-temperature reaction pathway seen on Pt(335) and a slight reduction in the desorption temperature of terrace hydrogen shifts hydrogen desorption into the same temperature range as water formation. At intermediate coverages (40% of the maximum hydrogen coverage and 50% of the maximum oxygen coverage) on each surface, the resulting competition between desorption and reaction lowers the reaction probability per hydrogen atom from 0.6 on Pt(335) to 0.2 on 0.7Au/Pt(335).

11:00am **SS2-TuM9 Isothermal Kinetic Study of the Catalytic Reduction of Nitric Oxide over Rh(111) Surfaces***, G. Chinnakonda, **F. Zaera**,* University of California, Riverside

The kinetics of the thermal decomposition of NO and of its catalytic reduction to molecular nitrogen on Rh(111) surfaces was probed by isothermal measurements using an extension of the so-called King and Wells collimated beam method. Initial NO TPD studies corroborated previously reported results, including the development of two distinct molecular nitrogen desorption peaks at 460 and above 500 K, the first of which displays apparent first-order kinetics. In the isothermal experiments the rate of molecular nitrogen production was found to be significant above 450 K, and to be controlled by the recombination of atomic nitrogen below 600 K. In addition, the adsorption of NO was found to not be affected significantly by the presence of coadsorbed nitrogen and/or oxygen atoms at any temperature below 900 K. There is an induction period during which the surface concentrations of nitrogen and oxygen atoms build up before the recombination reaction starts. When performing the experiments with NO alone oxygen deposition on the surface eventually poisons the system and stops the reaction, but when using CO + NO mixed beams that oxygen is removed and a steady-state catalytic regime is reached. In any case, the experimental data could not be reproduced in a satisfactory manner by any empirical rate law unless the order in nitrogen coverage was set to less than unity, an observation that is interpreted here as being the result of the slow diffusion of nitrogen atoms across the surface prior to their recombination. A strong additional effect due to lateral repulsions between nitrogen and/or oxygen atoms was also observed.

11:20am **SS2-TuM10 Surface Species and Desorption Products from NO Exposure on Clean and (Rh,Pt) Loaded Surfaces of Highly Oriented CeO@sub 2@ Characterized by SXPS and TPD***, **S.H. Overbury**, D.R. Mullins, D.R. Huntley,* Oak Ridge National Laboratory

Adsorption and reaction of NO on ceria, both with and without Rh or Pt additions, was studied by soft x-ray photoelectron spectroscopy and temperature programmed desorption. The results demonstrate the complexities and interactions which may occur in supported catalysts involving reducible substrates. Growth in UHV of thin films of CeO@sub 2@ on a Ru(0001) substrate allowed creation of oriented films with variable oxidation state, quantitatively determined by valence band and Ce 4d photoemission. Following NO exposure various N containing surface species were observed by N 1s photoemission, and their distribution depended upon surface oxidation state, exposure and adsorption temperature. These species included N@sub 2@O, NO, NO@super +@ and three states believed to be associated with NO@super -@ or atomic forms of N. Occurrence of adsorbed N@sub 2@O at 100 K indicates that NO dissociation and reaction occurs readily at low temperature. N@sub 2@ is evolved during adsorption from above 100 K to at least 600 K indicating that some NO direct decomposition occurs over a wide range of temperatures and coverages. Adsorption of NO at 150 K is predominantly molecular while exposure to NO at 400 K leads to a low binding energy atomic state which desorbs at temperatures above 500 K. NO adsorbed on oxidized ceria yields a molecular state at a higher binding energy than on reduced ceria and thus is associated with NO@super +@. Adsorption of NO on reduced ceria is oxidative resulting in strongly non-Langmuirian adsorption behavior. Deposition of Rh or Pt on these surfaces alters the observed NO chemistry, and the extent of reduction of the ceria in turn modulates the activity of the noble metal for NO dissociation. Greater dissociation probability of NO and increased stability of the resulting N atoms is observed for the noble metal deposited on a reduced compared to a fully oxidized support. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy

11:40am **SS2-TuM11 An Investigation of the NO@sub x@ Storage Mechanism***, **M. Skoglundh**, H. Persson, E. Fridell, P. Engström, S. Ljungström,* Chalmers University of Technology, Sweden

In order to reduce nitrogen oxides (NO@sub x@) from lean burn vehicles, NO@sub x@ storage catalysts are used. The key idea is to first store NO@sub x@ in the catalysts during lean conditions (oxygen in excess) and then the NO@sub x@ is released and reduced during short periods of fuel rich conditions. In the present study we systematically investigate the sequence of mechanistic elementary steps in the NOx storage cycle, by using different experimental techniques in combination with theoretical modelling. As a model system we have used a NO@sub x@ storage catalyst containing Pt, @gamma@-Al@sub 2@O@sub 3@ and BaO as the storage component. Our results suggest that an intermediate peroxide step (BaO@sub 2@) is essential for storing NO@sub x@ as Ba(NO@sub 3@)@sub 2@. Furthermore, the relative importance of direct NO@sub x@ storage via gas phase or NO@sub x@ storage via Pt spillover is discussed.

Thin Films Division
Room 310 - Session TF-TuM

Thin Films for Sensing and Data Storage

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am **TF-TuM1 Thin Film Media Requirements in Ultrahigh Density Magnetic Recording***, **D. Weller**, A. Moser,* IBM Almaden Research Center **INVITED**

Rapidly increasing areal densities and data rates in hard disk magnetic recording impose stringent requirements on media and head materials. An imminent problem is media instability, which results from superparamagnetic effects. These effects become measurable in thin film granular magnetic recording media in the thickness range of about 10 nm and below. They lead to sizeable magnetic viscosity (logarithmic magnetization decay as function of measurement time) and to a write pulse width dependent coercivity. Examples of the latter measurements over 10 magnitudes in time (5 ns to 50 s) will be presented for typical CoPtCr magnetic recording media of variable thickness and at variable temperatures. The results will be discussed in the context of Neel-Arrhennius based decay models and recent micromagnetic modeling calculations. The thermal stability problem has led to a surge in interest in novel materials and media schemes. These include conventional but higher anisotropy media, perpendicular media, self assembled particle arrays and patterned media. We will discuss these various approaches in the context of ultimately achievable areal densities.

9:00am **TF-TuM3 Molecular Dynamics Analysis of Energy Modulated Deposition of Model GMR Materials***, **H.N.G. Wadley**, X.W. Zhou,* University of Virginia

Vapor deposited multilayers consisting of low electrical resistivity conductors sandwiched between ferromagnetic metals exhibit giant magnetoresistance (GMR). The best GMR properties are obtained from materials with flat interfaces and low intermixing between adjacent layers. Interfacial roughness and intermixing are sensitive to the deposition method and process conditions. A three dimensional molecular dynamics model has been developed and used to establish the relationship between the multilayer nanostructure and vapor deposition conditions, including incident atom angle, incident atom energy and substrate rotation. The results indicate that at low incident energies (e.g., 1 eV or below), an increase in the incident angle leads to a significant increase in the interfacial roughness (and even to void formation) due to a shadowing effect. The development of interfacial roughness was also found to be accompanied by an increase in intermixing. The high interfacial roughness formed during oblique, low energy deposition can be significantly reduced by substrate rotation. High incident atom energies were found to result in a lower interfacial roughness, but at the expense of increased intermixing caused by an atomic exchange mechanism. Under normal incidence conditions, an intermediate incident energy of between 1 and 2 eV resulted both in a low interfacial roughness and intermixing. The simulation methodology was used to explore the benefits of modulated incident energy deposition strategies. When thermal energy adatoms were used to deposit the first few monolayers of each new metal layer, intermixing by the exchange mechanism during subsequent hyperthermal energy deposition could be eliminated, and films with almost no interfacial roughness or intermixing could be grown over a wide incident angle range.

9:20am **TF-TuM4 Obtaining Optical Constants of Thin Ge@sub x@Sb@sub y@Te@sub z@ Films from Measurements of Reflectance and Transmittance***, **D.V. Tsu**,* Energy Conversion Devices

Chalcogenide thin films are currently used in Phase Change Rewritable Optical Recording media such as CD-RW and PD. These media have storage capacities 650 Mbytes, and can be rewritten over 1000 and over 100,000 times respectively. The second generation of Phase Change Rewritable media, using the DVD format, will extend that capacity to 4.7 GBytes/side. At the heart of this technology is the Chalcogenide layer, which undergoes a reversible change between amorphous and crystalline structures upon absorption of appropriate laser energy. The accompanying change in the optical constants [n,k] of the chalcogenide layer results in large reflectivity differences of the multi-layer media. Design of Phase Change optical media requires precise determination of [n,k] for both structures of the alloy over a wide spectral range. We have accomplished this task from measurements of [R,T] using the [air/film/substrate/air] configuration for films < 50 nm thick. The film's [n,k] are obtained by direct numerical inversion of the appropriate [a/f/s/a] expressions relating [n,k] to the measured [R,T]. Since R and T are highly non-linear in [n,k], calculating [n,k] provides multiple solutions at each wave length including the physical solution and also other mathematically relevant solutions. The other solutions can be used to determine the film's average thickness to an accuracy of ~ 1% or better. Using this technique we show that when as-deposited amorphous Chalcogenide films crystallize upon annealing they typically undergo a reduction in thickness of ~ 10%. We have developed software which can calculate [n,k] at 1800 wavelength points in less than 30 seconds. Attaining the correct film thickness requires only a few iterations. The calculation methodology does not include any assumption regarding the dispersion relation of the unknown film. This is critically important when multi-layered media structures are developed using new alloys.

9:40am **TF-TuM5 Process Monitoring of Hemispherical-Grained Polysilicon Thin Films for DRAM Applications***, C. Hayzelden, **A. Bivas**, C.L. Ygartua, K.C. Chan,* KLA-Tencor Corporation

The fabrication of hemispherical-grained (HSG) polycrystalline silicon was developed to increase the surface area (and storage capacitance) of Dynamic Random Access Memory (DRAM) devices. The increase in surface area (typically 2.4 x) is extremely sensitive to processing conditions. Therefore, to obtain high yields, process monitoring is of great importance. The use of spectroreflectometry and spectroscopic ellipsometry, described in this paper, provides a non-destructive method to monitor film fabrication. Using these two measurement technologies, the intensity and polarization state of the light reflected from the wafer surface is measured and analyzed over the wavelength range 220 to 800 nm. In the measurement analysis, a polysilicon layer is frequently modeled as a mixture of several materials, using the Effective Medium Approximation (EMA). Using the EMA model, with a composition of crystalline silicon, amorphous silicon, and a percentage of "voids", the analysis of measurement data yields values of the optical parameters (refractive index, extinction coefficient) and effective thickness of the HSG layer. In this paper, we present capacitance data from a series of HSG-processed wafers and report the observed correlation with the measured variables: percentage of "voids", effective thickness and optical parameters. The most appropriate variables to report for accurate process control will be discussed.

10:00am **TF-TuM6 Atomistic Scale Modeling of Ion Assisted Deposition of GMR Multilayers***, **X.W. Zhou**, H.N.G. Wadley,* University of Virginia

Giant magnetoresistance (GMR) is found in many ferromagnetic metal multilayers separated by thin copper films. Low interfacial roughness and intermixing are critical for obtaining the high giant magnetoresistance ratio needed for magnetic random access memories. A three dimensional molecular dynamics physical vapor deposition model has been developed and used to explore the effects of Ar- and Xe- ion assisted deposition of model Ni/Cu/Ni multilayers. The results indicate that the interfaces can be significantly flattened by ion assisted deposition provided the ratio of ion to metal atoms exceeds about 2.0. However, we found that as the assisting ion energy is increased, interfacial roughness decreases, but intermixing of the layers increases. A modulated ion energy / flux strategy for ion assisted deposition has then been investigated in which the ion beam energy / current was reduced while depositing the first few monolayers of each new metal layer. This strategy was found to successfully reduce both interfacial roughness and intermixing. The optimal ion to metal atom ratio and ion incident energy were identified.

10:20am **TF-TuM7 Thin Film Gas Sensors Based on Metal Oxides***, **H. Meixner**, M. Fleischer,* Siemens AG, Germany **INVITED**

Recently, research into the characteristics of semiconductor metal oxides that are stable at high temperatures with a view to providing reproducible detection of oxygen and reducing gases has intensified. First of all, there is a discussion of the specifics relating to these materials, for example the reduction of the effects of grain boundary barriers on the conduction mechanism, the reduction of the humidity cross sensitivities and also on the various reaction mechanisms. Then, the technology for constructing gas sensors of this kind will be described. Examples that have already been implemented, say, @gamma@ detection, O@sub 2@ measurements in the exhaust gases from incinerators, methane alarms, and air quality control as well as certain trends in development are discussed. Keywords: Metal Oxides, Thin Films, High Temperatures, Conduction Mechanisms, Gas Sensors

11:00am **TF-TuM9 A Study of Thermally-Defined Gas Sensing Films on Micromachined Arrays***, **R.W. Walton**, R.E. Cavicchi, J.D. Allen, S. Semancik,* National Institute of Standards and Technology

Film microstructure and interfacial composition of sensing materials can have a profound effect on the performance of solid state gas sensors. We report on an efficient, array-based study of property/performance relationships for conductometric gas sensing films done on micromachined devices called microhotplates. Four-element arrays were used primarily in this study. Two types of lithographic processes were employed to deposit the catalytic metal/semiconducting oxide sensing films; each method utilizes the localized heating and temperature control available for the individual elements of the microhotplate array. A CVD process uses the heater to activate surface reactions for selected-area film deposition. We also introduce a new lithographic process that involves coating the entire array with nitrocellulose and exposing chosen elements by eliminating their coatings with a high temperature pulse. Following deposition (by evaporation, sputtering), lift-off of the nitrocellulose removes unwanted material. In situ monitoring of both deposition processes makes use of built-in electrical contacts for measuring conductance. We demonstrate the power of this array approach for studying film deposition, thermal treatments (sintering), and sensor testing. CVD films of SnO@sub 2@ films were prepared by heating each 50µmx50µm hotplate to 500° C in a flow of tetramethyltin and O@sub @ in Ar. We correlate the effects of catalyst thickness (0-200 Å), annealing (to 700° C), and composition (evaporated Pd and Pt) with gas sensing response from 100° C to 500° C. SEM images show anneal treatments as low as 500° C change the morphology of the catalysts on the oxide grains to produce islands or porous structures that enhance sensitivity to reducing gases.

11:20am **TF-TuM10 Germanium Films and Their Application in Cryogenic Temperature Sensors***, N.S. Boltovets,* State Research Institute "Orion", Ukraine*; J.P. McFarland, G.G. Ihas,* University of Florida*; R.V. Konakova, **V.F. Mitin**,* Microsensor Co. Ltd., Ukraine

The principal objectives of our work were: (i) to prepare Ge films on GaAs suitable to develop temperature sensors; (ii) to study the structure and electrical properties of Ge films; (iii) to develop and design miniature wide-range thermometers capable of operating in the 30 mK to 300 K temperature range; and (iv) to investigate sensors at low temperatures and in high magnetic fields. The films have been prepared by Ge thermal evaporation in a vacuum on semi-insulating GaAs substrates. The electrical properties of the films obtained depended on the details of their fabrication. To fabricate a resistance temperature sensor capable of operating over a wide temperature range, several different conduction mechanisms are to be realized in the Ge film, each of which providing thermo-sensitivity in its own temperature range. This may be achieved through multi-component doping and compensation of the Ge film. At least three main sources of extra charge carriers exist in the Ge films on the GaAs substrates; namely, Ga and As atoms and structural defects. A relationship between them is determined by the film growth conditions. By varying the conditions during the film fabrication, one can prepare Ge films having different doping levels and degrees of compensation, i.e., different thermo-sensitivities. In this way, temperature sensors having different thermometric characteristics and capable of operating over different temperature ranges can be produced. Films with a monotonic temperature dependent resistance in the 30 mK to 300 K range have been fabricated. We present the miniature temperature sensor design based on Ge films, and results of sensor investigation in this temperature range and in magnetic field up to 6 Tesla. We also discuss the mechanism of conductivity in the films responsible for magneto- and thermo-sensitivity.

11:40am **TF-TuM11 Characterization of Sol-Gel Prepared WO@sub 3@ Thin Films as a Gas Sensor***, **M.Z. Atashbar**, Y. Li, M.K. Ghantasala, W. Wlodarski,* RMIT University, Australia

Increasing awareness of well human being to environmental issues has attracted many scientific researches in the field of gas sensing. Tungsten trioxide (WO@sub 3@) thin films have promising electrical and optical properties for different applications, such as electrochromic displays, photolysises and gas sensing. The change of its conductivity due to the gas exposure has made itself a excellent candidate for nitrogen oxide (NO@sub x@) and ozone (O@sub 3@) sensing applications. In this study, the effect of the structure, micro-morphologies and composition of the WO@sub 3@ film on NO@sub x@ and O@sub 3@ sensing properties has been investigated. WO@sub 3@ thin films were prepared from starting precursors via sol-gel route in dry nitrogen atmosphere (@<=@10%RH). The used precursors was tungsten ethoxide (W(OC@sub 2@H@sub 5@)@sub 3@) with an analytic purity, which was dissolved in different analytical solvents. After ultrasonic mixing at room temperature for 1 hour the precursor solution was dropped on substrates and spin-coated at different speeds. The film thickness (20 to 200 nm) was controlled by changing the solution concentrations and spinning speed. After annealing at temperature of 400°C to 700°C crack-free WO@sub 3@ thin films were obtained. The morphology, microstructure, crystalline structure and composition of the deposited films were analyzed by SEM, XRD and RBS. The SEM analysis showed that that film is porous and the grain size is the rang of 20nm to 100nm. The RBS results indicated that the film is sub-stoichiometric. XRD analysis showed that the films are polycrystalline in nature. A detailed analysis of these results on the O@sub 3@ and NO@sub x@ sensitivity of the film has been discussed. The electrical resistance of the film has been examined for the detection of ozone in ppb level and NO@sub x@ ppm level.

Vacuum Metallurgy Division
Room 328 - Session VM+TF-TuM
Advances in Hard and Superhard Coatings

Moderator: A. Inspektor, Kennemetal, Inc.

8:20am **VM+TF-TuM1 Deposition, Structure, and Properties of Superlattice Thin Films***, **S.A. Barnett**, A. Madan, P. Yashar, I. Kim,* Northwestern University **INVITED**

In this talk, superlattice thin films with nitride/nitride, metal/nitride, and oxide/oxide layers are described. Processing issues for high-rate superlattice deposition using reactive magnetron sputtering are described, including reactive-gas partial pressure control for obtaining stoichiometric layers and use of substrate bias to achieve ion bombardment densification. The stability of the layered structures at elevated temperatures is described; it is found that nanometer thick layers can exhibit excellent stability in cases where the relevant phase diagram shows little miscibility. The key materials criteria for obtaining hardness enhancements are delineated by making comparisons between different superlattice systems. Hardness predictions based on dislocation glide mechanisms are discussed. For cases where both superlattice layers have the same structure, a substantial difference between the layer shear moduli is required to limit dislocation motion and thereby strengthen the material. Superlattices where the layers have different structures, such that there is no common dislocation glide system, can also exhibit large hardness enhancements.

9:00am **VM+TF-TuM3 In-situ and Ex-situ Ellipsometric Analysis of Cr, CrN, Cr@sub 2@N Thin Films***, D.M. Mihut, S.R. Kirkpatrick, **S.L. Rohde**,* University of Nebraska, Lincoln

Chromium nitride thin films have technological applications in the tool and decorative coating industries, as well as providing an "environmentally-friendly" alternative to hard chrome coatings due to their unique combination of properties such as: low cost, high hardness (1600 - 3000 HK), excellent wear, corrosion, and oxidation resistance (up to 800 °C). An array of chromium and chromium nitride film monolithic and multilayered films were deposited in a ultra-high vacuum chamber equipped with an unbalanced magnetron sputtering system that combines the advantages of high-rate magnetron sputtering with high-flux, low energy ion bombardment. Ellipsometric analysis of the films was carried out by modeling layers of both stoichiometric and off-stoichiometry Cr, CrN and Cr@sub2@N thin films deposited on silicon. The ex-situ ellipsometry measurements were compared with X-ray diffraction measurements, and in-situ obtained ellipsometric information. The optical constants for CrN and Cr@sub2@N obtained using optical ellipsometry are given and compared with the optical constants for CrN and Cr@sub2@N found in the literature, and the potential of using ellipsometry in the monitoring and/or control of ionized PVD processes explored.

9:20am **VM+TF-TuM4 AlN/cBN Magnetron Sputtering: Effects on Adhesion and Phase Stabilization***, **W. Otaño**, L.J. Pilione, R. Messier,* Pennsylvania State University*; J.J. Santiago-Avilés,* University of Pennsylvania*; G. Lamaze,* National Institute of Science and Technology

The deposition of cubic boron nitride (cBN) thin films is of interest from a technological and fundamental point of view. It has been well established that the cubic phase stabilization depends on the energetic bombardment of the growing film. As a result of this bombardment the films show high stress levels that eventually produce delamination from the substrate. It is therefore interesting to consider atomic additions and compliant interfaces as alternative pathways to reduce the cBN stress level and/or improve film adhesion. With this purpose cBN thin films were co-deposited with Al reactively sputtered. The effects of the addition of aluminum and/or the use of AlN interlayers in the stabilization and adhesion of cBN films will be presented. The BN films were deposited by rf unbalanced magnetron sputtering and the substrate was biased using a low frequency dc pulsed excitation signal. Films with over 70% of the cubic phase, as measured by FTIR, were deposited at low negative bias voltages. A second dc pulsed power supply was used to reactively sputter the aluminum. AlN was added as an interlayer between the substrate and the BN film as well as co-deposited at different sputtering powers. The films were analyzed by FTIR, RBS and neutron depth profiling. It was found that the addition of Al to the BN films leads to a destabilization of the cubic phase for AlxB1-xN compositions above x=0.04. AlN interlayers deposited at specific pressures were found to prevent the delamination of the cBN films. A 0.7 micron multilayer coating of AlN/cBN was prepared that did not delaminate from the substrate.

9:40am **VM+TF-TuM5 Energetics of Cubic Boron Nitride Deposition***, **R. Clarke**, D. Litvinov,* University of Michigan **INVITED**

As a structural analog of diamond, cubic boron nitride (c-BN)is attracting increasing interest as an ultrahard coating material. An ongoing challenge towards exploiting the favorable properties of c-BN, including its chemical intertness and high thermal conductivity, is its tendency to build up substantial levels of stress at practically useful thicknesses of a few microns. If this stress is not remediated, it can lead to loss of adhesion. In this talk we present recent results demonstrating our approach to characterizing and controlling the intrinsic stress in c-BN coatings. Through an improved understanding of the kinetics of c-BN growth, using dc-biased ECR-assisted sputtering, we have achieved highly adhesive coatings on Silicon with film thicknesses up to 2µm. A novel multibeam optical wafer curvature method allows us to track, in-situ, the stress build-up during growth, and to implement 'reduced-bias' conditions after the initial nucleation and coalescence of c-BN islands. Reducing the kinetic energy of arriving nitrogen ions in this way (to ~ 50eV), leads to fewer defects in the film, reduced levels of stress, and higher growth rates, compared to values obtained at bias conditions necessary to initiate c-BN growth. Work partly supported by ONR grant N00014-94-J-0763, and by k-Space Associates Inc.

10:20am **VM+TF-TuM7 Deposition and Characterization of Ultra Thin CNx Films as a Thin-Film Disk Overcoat***, **X. Chu**, Z.D. Yang, J.F. Ying, S. Wang, B. Zhang,* MMC Technology Inc.

The deposition of CNx films has received great attention recently because of the potential of this material to have mechanical properties similar to diamond. One practical application of magnetron sputtered CNx films is for use as a protective coating for thin film magnetic recording disks. Ever increasing magnetic recording density requires not only a robust head-media interface, but also minimum spacing loss due to fly height, carbon thickness and magnetic layer thickness. A functional overcoat with a thickness of 50 to 100 Å is needed for the next generation recording medium. In this paper, we investigate sputtering process parameter effects on CNx film structure and mechanical properties. Target power, N% in the sputter gas, substrate temperature, and substrate bias were varied and correlated to film properties. XPS and Raman spectrum were used to study the bonding structure of the film. Sputtered CHx and CHNx films with 80 Å thicknesses and ion beam deposited CHx films were also studied for comparison. Nano-scratch wear tests showed that the 80Å film had the best wear property with 10-15% N in the gas. CNx films appear to be more wear resistant than CHx and CHNx films based on the nano-scratch test. Tribology properties of lubricated disks were tested using Contact Start Stop (CSS) testers and CNx carbon wear results can be correlated to the AFM nano-wear test. CHx films also showed good CSS results, suggesting that lubricant - carbon interaction is another important factor in head - media tribology.

10:40am **VM+TF-TuM8 Carbon and Carbon Nitride Films Prepared by Low-Energy, Isotopically-Mass-Separated, Negative C@sub 2@@super -@ and CN@super -@ Ions**, ***N.T. Tsubouchi,*** *A.C. Chayahara, A.K. Kinomura, C.H. Heck, Y.H. Horino,* Osaka National Research Institute, AIST, Japan

Amorphous carbon (a-C) and carbon nitride (a-CN@sub x@) films were prepared by ion beam deposition using isotopically mass-separated, hyperthermal (50-400 eV) negative ion species such as @super 12@C@sub 2@@super -@ and @super 12@C@super 14@N@super -@ under ultra high vacuum (UHV) condition. Variation of optical constants as a function of ion's kinetic energy was investigated in the infrared-visible light region (0.8-1.5 eV). Optical band gaps of the films were estimated from optical constants. For the amorphous carbon films, the gaps were about 1.0-2.3 eV depending on kinetic energy of negative carbon ions. For the CN films, the values which did not almost depend on kinetic energy were about 0.8 eV.

11:00am **VM+TF-TuM9 Investigation on Multilayered Chemical Vapor Deposited Ti/TiN Films**, ***J.C. Hu,*** National Tsing Hua Univ., Rep. of China, Republic of China; *T.C. Chang,* National Nano Device Lab, Rep. of China, Republic of China; *L.-J. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China; *Y.L. Yang,* National Nano Device Lab, Rep. of China, Republic of China; *P.T. Liu,* National Chiao Tung Univ., Rep. of China, Republic of China; *S.Y. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China; *C.Y. Chang,* National Chiao Tung Univ., Rep. of China, Taiwan, Republic of China

As the device dimensions scale down to deep submicron level, chemical vapor deposition (CVD) for TiN films provided excellent step coverage and uniformity. Cu is likely to replace Al for interconnect metallization in future integrated circuits. On the other hand, the CVD-TiN films are usually of columnar structure. As a result, the fast diffusion of Al (or Cu) and Si atoms along TiN grain boundaries would degrade the device performance severely. In the present study, a novel multilayered CVD-Ti/TiN structure is formed to alleviate the grain boundary effects. To investigation the barrier property of the multilayered Ti/TiN films, junction leakage current was also measured. All the films were deposited by CVD processed in a MRC multichamber cluster tool, using TiCl@sub 4@, NH@sub 3@ and H@sub 2@ as reactants. The Ti and TiN films were deposited by plasma enhanced CVD and low pressure CVD, respectively. In order to reduce chlorine concentration of the films, NH@sub 3@ plasma post-treatment was applied to multilayered CVD-Ti/TiN films. In addition, electroless deposition of Cu was deposited on the multilayered CVD-Ti/TiN films. Transmission electron microscopy and X-ray diffractometry were utilized to investigate the microstructure and crystal orientation. Auger electron spectrocopy was applied to determine the stoichiometry and uniformity along the depth direction. The morphology was studied by a field emission scanning electron microscopy. Electrical measurement was used by HP-4145. The enhanced multilayered Ti/TiN stack found to be a robust barrier against Al/Si interdiffusion. It also improved the electrical property of the films. The resistivity of the film was found to reduce from 240 to 120 µm@OMEGA@-cm by multilayered Ti/TiN structure with the NH@sub 3@ plasma post-treatment. The leakage current can also be kept low enough for device application. In addition, the thermal stability of electroless Cu/mutilayered (CVD-Ti/TiN)/TiSi@sub 2@/Si structure was improved.

11:20am **VM+TF-TuM10 Chemical Vapor Deposition of Metal (Ti) and Ceramic (TiO@sub 2@, TiN) Thin Films via Gas-Phase Reaction of Titanium Tetrachloride and Sodium Metal Vapor**, ***J.H. Hendricks,*** *M.I. Aquino, J.E. Maslar, M.R. Zachariah,* National Institute of Standards and Technology

A new route for Chemical Vapor Deposition (CVD) of metal and ceramic thin films has been demonstrated. This novel method involves the use of a low pressure coflow diffusion reactor to react sodium vapor with titanium tetrachloride in the presence of a non-reactive gas (Ar) or a reactive gas (N@sub 2@, O@sub 2@). This reaction chemistry is described by the following general equation: (mn)Na + nMX@sub n@ --@super Ar@--> (M)@sub n@ + (nm)NaX. Here, Na is an alkali metal (e.g. Na, K, Cs, or Rb), M is a metal (e.g. Ti, Ta, Pt, W, ...) or non-metal (e.g. B, C, Si, ...), X is a halogen (e.g. F, Cl, Br, or I), Ar is a non-reactive gas (e.g. Ar or He) and m and n are integers. In this reaction, the alkali metal strips halogen from the metal or non-metal halide. The metal or non-metal is then free to form a thin film on a substrate placed in the reaction zone. This chemistry should be generic for the deposition of a wide class of metallic and ceramic thin films, and it is suggested that this technique could be used to grow superhard BN and CN thin films at temperatures which are significantly lower than conventional CVD techniques. Guided by theoretical modeling, reactant concentrations and substrate temperatures were adjusted to prevent salt (NaCl) incorporation into the deposited thin films. Using the described techniques, we have now produced Ti and TiN thin films on Cu substrates at 610 °C, and TiO@sub 2@ thin films on Si substrates at 600 °C. These temperatures are considerably lower than the (1000 to 1200) °C required for conventional CVD of Ti (by decomposition of titanium tetraiodide). The quality and composition of the thin films were analyzed by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS), x-ray diffraction (XRD), Raman spectroscopy, transmission electron spectrometry (TEM), and selected area electron diffraction (SAED). Future work will focus on the use of this novel technique to grow CN and BN thin films.

11:40am **VM+TF-TuM11 Low Energy Ion Beam Deposition of Oriented Diamond Microcrystallites**, ***P.K. Tse,*** *R.W.M. Kwok, K.M. Lui, W.M. Lau,* The Chinese University of Hong Kong, China

Ion beam deposition provides an additional control of film properties over the chemical vapor deposition (CVD) via the change of ion beam energy. In this study, low energy ion beam deposition of carbon films on silicon in the ion energy range of 200 - 1050 eV was studied. The ion beam was characterized by a Faraday cup equipped with a retarding lens. The films were characterized using X-ray photoelectron spectroscopy, characteristic electron energy loss analysis, and atomic force microscopy. It was found that graphitic films, amorphous carbon films and oriented diamond microcrystallites could be obtained separately at different ion beam energies. Highly oriented diamond microcrystallites were deposited on Si (100) wafer at energy of 200eV and substrate temperature of 420°C. The ion beam deposition will be used as a diamond seeding process which will be followed by a typical hot filament CVD process, for the growth of oriented diamond films on Si (100).

Vacuum Technology Division
Room 329 - Session VT-TuM
Molecular Drag Pumping

Moderator: J.C. Helmer, AVS Fellow

8:20am **VT-TuM1 Performance of Molecular Drag Pumping Stages in Hybrid Turbopumps**, ***M.H. Hablanian,*** Varian Associates

Quantitative evaluation of molecular drag pumping action in turbopump channels allows an optimized placement of such channels among the stages of a high-compression hybrid turbine-type high-vacuum pumps. Although the drag action can be utilized in the entire range of pressures, the practical engineering considerations dictate the actual design (certain cross-section, length, parallel and series arrangement, and angular position) and placement of drag stages within the entire architecture of the pump which is to have a desired overall performance. The usual broad range of interest is between 0.1 and 100 torr but often can be more practical between 0.5 to 10 torr. Above 10 torr exit pressure, it is usually more effective to use other type of impellers. Theoretically, it may be desirable to have each stage of a hybrid turbopump of a different configuration but practical design (regarding size, ease of manufacture and assembly, and cost) necessitate some compromises. This is especially true of rotor design requirements. In addition, the choice of drag stage involves considerations of the wide range of pressure conditions in which a turbopump must function, the associated power requirements, and the crossing of various gas flow regimes. It is relatively simple to establish general guidelines for proper stage arrangements but actual design demands a complete knowledge of the performance of each individual impeller type.

8:40am **VT-TuM2 Turbodrag Pump Technologies**, ***O. Ganschow,*** Schorch GmbH, Germany

Turbodrag pumps, i.e. molecular pumps with a bladed section followed by a drag section on a common shaft, have become the most popular high vacuum pump in the last 12 years, as they tolerate backing pressures approximately a hundred times larger than pure turbopumps. The paper reviews various technologies for turbodrag pumps in terms of the merits and limitations of their design principles. This covers rotor dynamics aspects, response to thermal loads, maximum rated backing pressure and throughputs, compression ration versus size as well as mechanical design considerations and potential future developments.

Tuesday Morning, November 3, 1998

9:00am **VT-TuM3 Pumping Mechanism of Helical Grooved Molecular Drag Pumps***, **T. Sawada**, W. Sugiyama,* Akita University, Japan

The flow on a rotor of molecular drag pumps varies from viscous to slip to free molecule flow according to the decrease in pressure. As the first step, the flow through a groove facing a wall moving along the groove is analyzed. On the assumption that the flow in the groove is steady, isothermal, incompressible and laminar, the Navier-Stokes equations are simplified in the viscous and slip flow regimes and can be solved numerically with relative ease. In the free molecule flow regime, the drag (or friction) is caused by the momentum carried to a wall-piece by gas molecules colliding with the wall-piece, and the drag must be equated to the force exerted by the pressure on the two cross-sections sandwiching the wall-piece. The weighted linear combination of the two equations for slip and free molecule flows can describe the flow through the three flow regimes. The flow in ridges which leads a leak is treated in the similar way to the flow in grooves. Then, the flows in grooves and ridges hitherto treated separately are connected by the continuity condition of mass flow rate normal to the groove-ridge interface. The pressure gradient which is discontinuous at the groove-ridge interface is smoothed by Boon and Tal's "Narrow groove theory ". The pressure difference or the pressure ratio across the pump is obtained from the relationship between the smoothed pressure gradient and the axial mass flow rate derived above. The calculated results suggest that the radial clearance can be enlarged by factors of 20-100, compared with that of a conventional Holweck-type pump.

9:20am **VT-TuM4 Measurements Illustrating the Importance of Desorption and Molecular Residence Times on the Molecular Drag Process***, **A.D. Chew**, R.A. Abreu, I. Creaye,* BOC Edwards, United Kingdom

Knowledge of the molecular residence time is a fundamental factor in the understanding of molecule-surface interactions and has special relevance in the analysis of the molecular drag process. In this paper we describe experiments based on a technique originally devised by Holst and Clausing.@footnote 1@ In this technique molecules are beamed onto a variable high speed rotating disc and the point of desorption is measured. This in principle provides a means for the direct determination of the residence time. Preliminary results for various gas-surface combinations including nitrogen, helium, oxygen, krypton and perfluorocarbons on aluminium are presented. The method was further exploited to investigate the effect of surface speed on the desorption flux distribution, and to give insight into the mechanism of the molecular drag process for gases of different molecular mass. The possible application of this phenomenon to gas separation is discussed. @FootnoteText@ @footnote 1@G Holst and P Clausing, Physica 6, 48 (1926)

9:40am **VT-TuM5 Improved Design of a Multi-Groove Vacuum Pump Compressing Directly to the Air***, E.S. Valamontes, **S.E. Valamontes**, C.N. Panos,* Technological and Educational Institute of Athens, Greece

For a multi-groove vacuum pump the shortening of its length, during its function, is related to the increase of the velocity of molecules of the pumping gas. We are trying to achieve it without increasing the number of the turns, which leads to the increase of the velocity, but by using some new ideas. We study the exact behavior of the coefficient of internal viscosity by introducing a disc with blades in the pump which indirectly leads to the desirable shortening of its length and finally to have a pump compressing directly to air. The appropriate shape of the disk and its design are the main problems of the present work.

10:00am **VT-TuM6 Matching of Turbine Stages to a Drag Stage under Viscous Flow Conditions***, Ch. Beyer, H. Englaender, **P.J. Klingner**,* Leybold Vacuum GmbH, Germany

The design of the adapter part between the turbo molecular part and the drag stage of a compound pump is decisive for - the high vacuum performance (a) the fore vacuum pressure tolerances (b) the manufacturing costs and (c) the degree of compactness of this pump (d) especially in process applications under viscous or molecular-viscous transition flow conditions. The authors present approaches for the layout of turbo rotor stages at viscous flow (Leybold Advanced Technology). Operation diagrams illustrate the combination of turbo molecular and drag stages as part of pump optimization; measurement data give first informations about the influence of specially designed filling stages on the adapter efficiency.

10:20am **VT-TuM7 Flow Investigation of Siegbahn Pump by CFD Methodology***, **H.-P. Cheng**,* Precision Instrument & Development Center, Tawain. Read by J. Helmer, with historical figures by L. Westerberg.

The maximum flow through turbomolecular pumps or turbodrag pumps is limited by the maximum rotor temperature resulting from gas friction. Further, a variety of applications, especially in the semiconductor industry, require a high pumping speed in the 1 - 100 mtorr pressure range. Main subject of the presentation is the special design of the drag section of a turbodrag pump and the resulting improvements related to the features: maximum gas flow and high pumping speed in the 1 - 100 mtorr pressure range.

10:40am **VT-TuM8 Performance of a Peripheral Drag Pump***, **T. Ohbayashi**,* Osaka Vacuum, Ltd., Japan*; T. Sawada,* Akita University, Japan

This is a theoretical and experimental study of a peripheral drag pump. It has a peripheral pumping channel and a gas inlet and outlet which are separated by a "stripper", this is similar to a Gaede's drag pump. In that type of pump, a pumping channel comprises an annular groove and a chamber wall. In the pump in this study, two pumping channels which work in parallel comprise a rotating disk and two annular stators. This modification keeps the leak small with a relatively large clearance between the rotor and the stator. The performance of the peripheral drag pump is determined by the flow through the pumping channel, the "carry back", the leak in the "stripper" region, and the leak in the clearance between the rotor and the stator. In the theoretical calculations, the flow through the pumping channel is evaluated as Poiseuille flow and Couette flow through rectangular channels and the flow in the stripper region and in the clearance are evaluated as Poiseuille flow and Couette flow between parallel plates. Experiments were carried out on the peripheral drag pump of a single stage in a pressure range of 3 - 1300 Pa for air and 9 - 1200 Pa for hydrogen. The theoretical predictions agreed with the experimental results.

11:00am **VT-TuM9 Development of New Generation Turbo Molecular Pump***, **Y. Maejima**, C. Urano,* Seiko Seiki, Japan

300mm wafer process requires extremely high process gas flow. Therefore, pumping requirements for vacuum pumps have increased up to 3,000 l/s. However, large pumps have disadvantages such as heavy weight, effect in case of failure. Our solution and concept for the new generation vacuum pump is to develop a 2,000 l/s dimension pump with higher performance than a 3,000 l/s pump at process pressure range. (from 1 Pa to 3 Pa) To accomplish this development, our target was to maintain pumping performance down to 5 Pa. We have simulated the influence of turbine blade parameter (blade length, dimension, shape) for maximum gas flow performance.

11:20am **VT-TuM10 Power Dissipation in Turbomoleculars Pumps at High Pressure***, **R. Cerruti**, M. Spagnol, J.C. Helmer,* Varian VPT, Italy

The operating range of Turbopumps is being extended to higher pressures as a consequence of many demanding applications. Varian VPT has specialized in the design of Gaede stages for extending the operating pressure of the pump. In this paper, another important design aspect of a Gaede stage is identified and analyzed: the power consumption in viscous flow conditions Starting form the analysis of the pressure distribution into a single Gaede stage, already presented in a previous paper, a transitional power consumption model is derived. The model allows to predict the power consumption of a single Gaede stage as a function of the pumping channel dimensions and clearances, the rotational speed, the nature of the gas pumped and the operating pressure. The model is based on three main assumptions: 1. the pressure distribution along the channel satisfy a diffusion viscous model at zero net gas flow 2. the gas flow boundary layer across channel is derived from a simple viscous model 3. the gas viscosity obeys a transition expression valid for the pumping channel geometry Results are compared with the experimental data provided by different single Gaede stages, with different dimensions, at different speed and operating pressure. The behavior of the model with different pump stage clearances is analysed and results are compared with the experimental evidence. A useful use of the model is in the optimization of the design of multistage Gaede pumps.

Biomaterial Interfaces Group
Room 326 - Session BI+AS+MM+NS+SS-TuA

Nanoscale to Mesocale Biomaterial Structures

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

2:00pm **BI+AS+MM+NS+SS-TuA1 Self-Assembly of a Multidomain Protein: Fibronectin at Lipid Model Interfaces***, **V. Vogel**, G. Baneyx,* University of Washington **INVITED**

Fibronectin, an adhesion protein with multiple recognition sites, mediates cell attachment to synthetic and biological surfaces. In solution, fibronectin 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, it is known that on the surface of cells fibronectin assembles into detergent insoluble fibers, which are considered to be the main functional form of the protein. Fibronectin is hence a prime example of a protein with multiple recognition sites that can be regulated through environmental control. Unfortunately, the molecular pathways of activation and self-assembly are still poorly understood. We have recently found that fibronectin can self-assemble into fibrillar networks at receptor-free phospholipid monolayer interfaces under physiological conditions. This is a crucial observation since the paradigm in biology is that fibril assembly of fibronectin is mediated by membrane-bound receptor molecules. Availability of a simplified model system allows investigation of the molecular pathways by which appropriate surfaces can activate fibronectin and facilitate self-assembly.

2:40pm **BI+AS+MM+NS+SS-TuA3 Nanofabricated Substrates for Probing Single Biomolecules by Surface Enhanced Raman Scattering***, **S. Petronis**, L.K. Hedberg, H. Xu, M. Käll, B. Kasemo,* Chalmers Univ. of Technology and Univ. of Gothenborg, Sweden

The effect of Raman scattering enhancement when coherent laser light interacts with molecules attached to rough surfaces and microscopic metal domains has been known for more than two decades and is called Surface Enhanced Raman Scattering (SERS). The intensity of the Raman signals for such molecules is frequently enhanced by a factor 10@super 5@-10@super 6@ at best.@footnote 1,2@ However recently much larger enhancement factors, in the range 10@super 14@-10@super 15@, have been observed for molecules adsorbed on colloidal silver particles of specific dimensions.@footnote 3,4@ This giant enhancement allows the recording of vibrational spectra from a single molecule for the first time, instead of the ensemble averaged spectra from many molecules, which are normally obtained in optical spectroscopies. Here we report on an attempt to use nanolithography to fabricate structures of silver in the size range 100 - 200 nm and having different shapes in order to explore the size and geometry dependence of the SERS effect. Microfabricated structures which give the highest enhancement could be used for probing different biomolecules and perhaps designing a biosensor. SERS active substrates were prepared as arrays of silver particles on a Si wafer. Within each array the silver particles had a constant shape, size and separation. Three particle shapes (circular, triangular and square), two particle sizes (100 nm and 200 nm), and five different particle separations (10, 50, 100, 150 and 200 nm) were produced by electron beam lithography with a double-layer resist system and "lift-off" procedure. A reference area of uniformly deposited Ag film mimicked an infinite silver surface. The final structures and the chemical composition of the silver particles were characterized by Scanning Electron Microscopy (SEM) and Auger electron spectroscopy (AES), respectively. Preliminary Raman scattering experiments have been performed on the dye-molecule Rhodamin 6G adsorbed on the nanofabricated substrates. A giant enhancement of the Raman signal was observed on all patterns, but not on the Ag film or the Si surface. @FootnoteText@ @footnote 1@M.Moskovits, Rev. of Mod. Phys., vol. 57, No 3, 1985, pp 783-826 @footnote 2@A.G.Mal'shukov, Phys. Rep., vol 194, Nos 5&6, 1990, pp 343-349 @footnote 3@K.Kneip et al., Phys. Rev. Lett., vol. 78, No 9, 1997, pp1667-1670 @footnote 4@S.Nie, S.R. Emory, Science, vol. 275, No 21, 1997, pp 1102-1106

3:00pm **BI+AS+MM+NS+SS-TuA4 Nanostructured Surfaces for Biorecognition - A Novel Templating Approach***, **H. Shi**, B.D. Ratner,* University of Washington

Materials that specifically recognize proteins may find a variety of applications in separations, sensors and medical materials. Molecular imprinting provides an intriguing approach to plastic antibodies against small molecules, but the use of proteins as templates has been less successful in making protein recognition materials. In this study, nanostructured surfaces with tailored protein-binding cavities are prepared by an imprinting technique based on RF-plasma deposition of organic thin films. A polysaccharide-like surface with protein-imprinted nanopits allows only the template protein to fill the pits, and to bind strongly, because the nanopits are complementary to the template protein in shape and in the distribution of functional groups. The bound protein in its pit is prevented from exchange with protein in the solution due to a strong binding and steric hindrance, while the non-template protein that is weakly adsorbed on the surface is displaceable. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed that nanometer-sized pits, in the shape of imprinted proteins, were created on the surfaces of our protein-imprinted polymer films. Imprinting fidelity was confirmed by AFM analysis of imprints of monodisperse colloidal gold nanoparticles. Electron spectroscopy for chemical analysis (ESCA) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) indicated that template proteins were washed off the surfaces of protein imprints while sugar molecules were covalently incorporated. Radiolabeled -protein adsorption showed that a protein imprint recognized its template protein from a binary mixture with a high specificity. This study illustrates a novel templating strategy for biological molecules that can be exploited for fabrication of biorecognition materials.

3:20pm **BI+AS+MM+NS+SS-TuA5 Sensing and Analyzing Single Molecular Interactions with Microfabricated Devices@footnote 1@***, J.-B.D. Green, **G.U. Lee**,* Naval Research Laboratory **INVITED**

There is an intense effort to create new tools for manipulating and characterizing single macromolecules because of the power that these techniques can bring to the analysis of biological macromolecules. Due to the high force and displacement sensitivity of the atomic force microscope (AFM) it has been used to measure inter- and intramolecular forces between model ligand-receptors, i.e., streptavidin-biotin, complimentary strands of DNA, and biologically relevant supra-molecular structures, i.e. titin. With the success of these measurements, there are efforts to obtain even more detailed force measurements and to establish these techniques in the biotechnology laboratory. Our efforts focus on: 1. Designing force transducers with force (10@super -12@N), time (10@super -5@s) and spatial (10@super -9@m) resolutions that push the thermal noise envelope. 2. Developing immobilization strategies that produce more reliable force measurements. We will discuss two new microfabricated devices under development in our laboratory. The first microfabricated apparatus offers an excellent platform for detailed measurements of intermolecular interactions and possibly even analysis of combinatorial arrays. The second is an ultra-sensitive detector based on piezoresistive force transduction and magnetic microparticles. The future of these and similar devices will be considered. @FootnoteText@ @footnote 1@This work has been conducted in collaboration with Alexey Novoradovsky, Jonah Harley, Mohan Natesan, Steven Metzger, David Baselt, and Richard Colton.

4:00pm **BI+AS+MM+NS+SS-TuA7 Nanomechanical Properties of Cellular Components Determined by Interfacial Force Microscopy***, **P.R. Norton**, K de Jong, J.F. Graham, N.O. Petersen,* University of Western Ontario, Canada

The cell membrane is the contact surface between the cell's internal environment and the outside world. Increasingly it is recognized the there is strong active coupling between mechanical properties and cellular functions in properties such as locomotion and adhesion and in cytoskeletal diseases such as muscular dystrophy.@footnote1@ There is therefore an urgent need to understand the mechanical properties of cells and cellular subcomponents at length scales << 1µm. We will describe our initial experiments to achieve this goal. We have used three different imaging techniques in our investigation of the nanomechanical properties of larynx cells. First, immunofluorescent labelling was used to permit visualization of specific cell components in the confocal microscope, for example to determine whether the cell nucleus was removed in a shearing process. The same cell was then imaged in the atomic force microscope (AFM), permitting identification of components involved in motion such as microspikes. The nanomechanical properties of cells were then studied by nanoindentation using the interfacial force microscope (IFM).@footnote2@ While we have not yet succeeded in imaging and measuring the same cell used in the confocal and atomic force microscopies, we have demonstrated the feasibility of our approach and have obtained quantitative force-distance curves on different regions of a single cell fixed in paraformaldehyde, sodium periodate and lysine, which cross-links the proteins. From these data we can derive the elastic modulus, hardness etc of the specific region of the cell. The modulus of such a cell was ~ 3GPa, comparable to a soft polymer. Similar measurements are planned on unfixed cells. @FootnoteText@

@footnote1@Chen, C.S., et al. Science 276, 1425 (1997) @footnote2@Warren, O.L., et al. Physics in Canada 54, 122 (1998)

4:20pm **BI+AS+MM+NS+SS-TuA8 Unbinding Force of NTA-M@super 2+@--Histidine Complexes. The His-Tag Immobilization Force*, J.G. Forbes,*** *P. Yim,* University of Maryland, College Park

A sequence of six or more histidines will bind tightly to a Cu, Ni, or Co complex. The compound typically used to immobilized the metal is N-(5-amino-1-carboxypentyl)iminodiacetic acid (NTA). Most proteins will not bind to the complex unless there is a sequence of histidines, which is readily added using recombinant DNA techniques. The histidine tag may be removed from the metal complex with a high concentration of imidazole or by protonating the histidines at a pH below 6. We have studied the the unbinding strength of this interaction with the atomic force microscope (AFM). To perform this measurement, we have functionalized silicon nitride AFM tips with NTA-M@super 2+@. A glass slide was coated with recombinant DNAse I with a his-tag on the C-terminus. Unbinding force measurements were made in phosphate buffered saline (PBS) to reduce electrostatic interactions. We find that the unbinding force for the NTA-M@super 2+@/His-tag interaction to be ca. 85~pN for each of the metal complexes. Interestingly, 0.5~M imidazole does not remove the interaction, but only changes the distribution of the measured forces. This is a result of the non-equilibrium condition of the tip being forced into the protein coated surface. The interaction is almost completely removed by lowering the pH to 5.0 where the histidines are protonated and can no longer coordinate with the nickel. The remaining interaction forces are due to the histidines which are exposed when the tip presses into the surface. These results provide a quantitative measurement of mechanical strength of binding of proteins to surfaces functionalized with NTA-M@super 2+@.

4:40pm **BI+AS+MM+NS+SS-TuA9 Sieving of DNA Molecules in Nanofluidic Channel*, J. Han,*** *H.G. Craighead,* Cornell University

Entropic trapping and sieving effect of long DNA molecules was studied in variable thickness nanofluidic channels. We used photolithography and etching techniques to define fluid channels on Si wafers, and anodic bonding method to seal the channel with a thin pyrex glass coverslip. The channel consists of alternating regions with two different channel thicknesses(~100nm and 1.6µm). We studied electrophoretic motion of lambda phage DNA in this channel by epi-fluorescence microscopy. Since the radius of gyration of a typical long DNA molecule is larger than the smaller gap of the channel, the shallow part of the channel can be an entropic barrier for DNA motion.Therefore, DNA molecules were retarded when they entered into the thin region from the thick region. We measured the mobility of DNA molecules in these channels and observed that below a certain electric field, mobility of DNA molecule decreased to near zero drastically, showing that DNA molecules be entropically trapped and sieved. The threshold electric field was mainly dependent on the geometry of channel(e.g. gap size) and the length of DNA driven. This suggests a new type of separation device for DNA and other polymers.

5:00pm **BI+AS+MM+NS+SS-TuA10 Detection of Molecular Ion and Quantification of Pentapeptide on Plasma Hydroxylated Fluoropolymer by Time of Flight Secondary Ion Mass Spectrometry***, J.A. Gardella,* ***L.M. Sun,*** State University of New York, Buffalo

Abstract: Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) was modified by a hydrogen/methanol radio frequency glow discharge plasma. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was employed to characterize the modified FEP surface and three pentapetides (YGGFM, YGGFL, YIGSR) which were microsyringe deposited on the modified FEP film. New fragments of OH (CF@sub 2@)n in negative ion SIMS of the modified FEP film indicated that -OH functional group had been incorporated on the FEP surface after plasma treatment. In the positive ion SIMS of three pentapeptides on the hydroxylated FEP film, protonated molecular ions were dominant signals from the peptides whereas not many fragments were observed either from the peptides or the impurity. Sodium and potassium adduct molecular ions were detected as well as oxidized protonated molecular ion of YGGFM in the positive ion SIMS spectrum. Negative ion SIMS of YGGFL yielded a deprotonated molecular ion. The mixture of these three pentapetides was also studied by TOF-SIMS. The relative intensity of protonated molecular ions of YGGFL, YGGFM and YIGSR showed the possibility of quantification on the hydroxylated fluoropolymer by TOF-SIMS. As a study of substrate effects, TOF-SIMS spectra of these peptides on oxidized Ag substrate were recorded. Comparing SIMS results of pentapetides on Ag and on modified FEP film, fewer fragments occurred from the FEP film than that from the Ag substrate. A substrate like the FEP fluoropolymer might be beneficial for the quantification of peptides because of the intensity of parentlike species in SIMS measurement.

Electronic Materials and Processing Division
Room 316 - Session EM+PS+SE-TuA

Plasma Processing of Compound Semiconductors

Moderator: C. Eddy, Boston University

2:00pm **EM+PS+SE-TuA1 Thermally Induced Improvements on SiN@sub x@:H/InP Devices*, E. Redondo,*** *N. Blanco, I. Mártil, G. González Díaz,* Universidad Complutense de Madrid, Spain*; R. Peláez, S. Dueñas, H. Castán,* Universidad de Valladolid, Spain

The electron cyclotron resonance (ECR) plasma technique has been recently proved to be optimum as insulator deposition method in Al/SiN@sub x@:H/InP devices.@footnote 1@ In this communication we present a study of the influence of rapid thermal annealing (RTA) treatments on the interface characteristics of Al/SiN@sub x@:H/InP devices. The insulator was obtained by the ECR plasma method at 200°C-deposition temperature. The films were deposited in two steps: we deposited first a film with x=1.55 and then another with x=1.43. Total film thickness was 500Å in one set of samples and 200Å in other. RTAs were conducted in Ar atmosphere during 30s in a temperature range between 400 and 800°C. The electrical characteristics of the devices have been obtained by capacitance-voltage (C-V) and deep-level transient spectroscopy (DLTS) measurements. Those films annealed between 400 and 500°C/30s in Ar atmosphere give structures with the minimum interfacial trap density. The interface trap density behavior with the annealing temperature has been observed to show the same trend with both CV and DLTS measurements, reaching lower values in the latest ones. The minimum interfacial trap density value achieved with the best annealing is of 3x10@super 11@ cm@super -2@ eV@super -1@, obtained for 400°C/30s annealing on the thinnest structure (200Å). Besides, DLTS measurements show the presence of features in the spectrum that are characteristic of phosphorus vacancies, V@sub p@, and deep centers. The annealing at 400°C/30s reduces the V@sub p@ content. This suggests that the nitrogen from the insulator is filling these vacancies so InP surface is being passivated. @FootnoteText@ @footnote 1@ S.García, I.Mártil, G.González Díaz, E.Castán, S.Dueñas, M.Fernandez. J.Appl.Phys, 83 (1), 1998, pp 600-603.

2:20pm **EM+PS+SE-TuA2 Damage to III-V Devices During Electron Cyclotron Resonance Chemical Vapor Deposition*, F. Ren,*** University of Florida, Gainesville*; J.W. Lee, D. Johnson, K. McKenzie,* Plasma-Therm, Inc.*; T. Maeda, C.R. Abernathy, Y-.B. Hahn, S.J. Pearton,* University of Florida, Gainesville*; R.J. Shul,* Sandia National Laboratories

GaAs-based metal semiconductor field effect transistors (MESFETs), heterojunction bipolar transistors (HBTs) and high electron mobility transistors (HEMTs) have been exposed to ECR SiH@sub 4@/N@sub 2@, SiH@sub 4@/N@sub 2@O and SiH@sub 4@/NH@sub 3@ discharges for deposition of SiN@sub x@ or SiO@sub 2@ passivating layers. The effect of source power, rf chuck power, pressure and plasma composition have been investigated. Effects due to both ion damage and hydrogenation of dopants are observed. For both HEMTs and MESFETs there are no conditions where substantial increases in channel sheet resistivity are not observed, due primarily to (Si-H)@super o@ complex formation. In HBTs the carbon-doped base layer is the most susceptible layer to hydrogenation. Ion damage in all three devices is minimized at low rf chuck power, moderate ECR source power and high deposition rates.

2:40pm **EM+PS+SE-TuA3 Anisotropic Etching of InP using CAIBE (Cl@sub 2@/Ar): Importance of the Sample Temperature Stability and the Reactive Gas Distribution*, B. Lamontagne,*** *M. Gagnon, J. Stapledon, P. Chow-Chong, M. Davies,* National Research Council, Canada

Process development has been performed for the dry etching of InP using our Chemically Assisted Ion Beam Etching (CAIBE) system (Ionfab 300 from Oxford Inst.). We studied the etching mechanisms in order to obtain vertical, deep and smooth InP sidewalls. Such etching profiles are essential for optoelectronic discrete devices such as turning mirrors, reflector gratings, deeply etched waveguides, etc. The CAIBE system has a 15 cm diameter R-F driven ion source, the ion beam is usually composed of argon while chlorine is introduced through the gas ring located in front of the heated platen. The sample temperature - a critical parameter when etching InP with chlorine - has been calibrated and monitored using a non-contact sensor: a diffuse reflectance spectrometer (DRS 1000 Thermionics

Northwest Inc.). It gives an accurate temperature measurement of the sample itself using the shifting effect of the temperature on the absorption edge position of semiconductors. This diagnostic tool allowed us to monitor the sample temperature increase under ion bombardment (CAIBE process) for various conditions; sample heating and mounting technique, ion beam current and energy. In some extreme process conditions the sample temperature has increased from 20° C to 300° C in less than one minute. Our results point out the need to use a stable process temperature in order to obtain vertical sidewalls. The influence of the reactive gas distribution has also been investigated, for example, by modifying the gas ring design. Etching conditions characterized by vertical (>89°) and long (up to 15 µm) sidewalls and SiO@sub 2@ mask selectivity of 30 were obtained.

3:00pm **EM+PS+SE-TuA4 Hydrogen in Compound Semiconductors***, **M.D. McCluskey**, N.M. Johnson,* Xerox Palo Alto Research Center **INVITED**

Hydrogen can be inadvertently introduced at any of several steps in the fabrication of optoelectronic devices. In particular, incorporation of hydrogen can occur during growth, wet chemical processing, or dry etching. The most common consequence of hydrogenation is the passivation of dopant impurities, which leads to a decrease in the electrical conductivity of the material. The most successfully applied experimental technique for directly determining the involvement of hydrogen has been infrared-absorption local vibrational mode (LVM) spectroscopy, which will be illustrated with representative examples. In GaN:Mg grown by metalorganic chemical vapor phase deposition, hydrogen passivates Mg acceptors during the growth. Through experimental and computational studies it has been determined that hydrogen incorporated during growth forms electrically inactive complexes with Mg, and that a furnace anneal dissociates these complexes to activate the acceptor dopant. LVM spectroscopy was essential in the identification of the Mg-H complex. The observed frequency of the hydrogen LVM verified the theoretical prediction that hydrogen attaches to a host nitrogen atom. Recently, large hydrostatic pressures have been applied to compound semiconductors to probe the vibrational properties of hydrogen-related complexes. In GaAs, the pressure dependent shifts of hydrogen stretch modes provide clues about the location of hydrogen in the complexes. In AlSb, pressure was utilized to resolve a mystery as to why the Se-D complex gives rise to one stretch mode peak while the Se-H stretch mode splits into three peaks. This anomalous splitting is explained in terms of a new resonant interaction between the stretch mode and combination modes involving a wag mode harmonic and extended lattice phonons.

3:40pm **EM+PS+SE-TuA6 The Interaction of Electrons with Hydrogenated GaN(0001)***, V.J. Bellitto, **B.D. Thoms**,* Georgia State University*; D.D. Koleske,* Naval Research Laboratory

Although Group III nitrides have recently been used to produce blue LEDs and laser diodes, many surface properties and processes have yet to be fully understood. One issue important to many applications of these materials is the effect of hydrogen during growth and processing. For example, hydrogen has been reported to significantly affect incorporation of dopants, Group III constituents, and contaminants. We have studied GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). The ELS spectrum of GaN is seen to be particularly sensitive to exposure to atomic hydrogen (produced by a tungsten filament heated to 2073 K). A new peak appears at a loss energy of approximately 12 eV after atomic-hydrogen exposure but is not seen after exposure to molecular hydrogen alone. However, this peak is strongly affected by low energy electron irradiation of the surface. Substantial reduction in the 12 eV peak intensity is observed following exposure to 1.8 microamps of 90 eV electrons for two minutes. After 10 minutes of electron impingement on the hydrogen-atom-exposed surface, ELS spectra appear identical to those taken with no hydrogen atom exposure. Heating to 690 K is also seen to remove the hydrogen-related peak from ELS spectra. Recently, Gillis et al. have shown that simultaneous exposure of GaN to hydrogen atoms and low energy electrons results in anisotropic etching. Implications of these data for both surface science and etching of GaN will be discussed.

4:00pm **EM+PS+SE-TuA7 III-V Surface Plasma Nitridation: A Challenge for III-Nitride Epigrowth***, G. Bruno, **M. Losurdo**, P. Capezzuto,* MITER-CNR, Italy*; E.A. Irene,* University of North Carolina, Chapel Hill

A challenge in the growth and processing of III-V nitrides is the control and optimization of the substrate/epilayer interface. It has been reported that high quality epilayers of GaN and related materials can be obtained by nitridation of the sapphire and GaAs substrates before the film growth. Substrate nitridation allows to accomodate the lattice mismatch between substrates and GaN epilayers and crucially affects the cristalline quality and structure of both the buffer and epitaxial GaN layers. In this contribution, the focus is on the nitridation process of GaAs and GaP (100) substrates to form GaN layers and of (0001) sapphire surfaces to form thin AlN. In order to elucidate the chemistry and kinetics of these solid state anion exchange reactions, the nitridation of (100) InP is also investigated. Nitridations are performed in a remote radiofrequency plasma metalorganic chemical vapor deposition (MOCVD) apparatus by exposing surfaces to the downstream flow of N@sub 2@ and N@sub 2@-H@sub 2@ plasmas, taking the advantages of low process temperatures and minimal surface damage. In situ optical diagnostics such as optical emission spectroscopy (OES) and spectroscopic ellipsometry (SE) are used to fingerprint in real time the gas phase and surface modifications, respectively. Thus, the chemistry and kinetics of the plasma-surface interactions are described toghether with the surface/interface composition and morphology. AFM analysis has been used to measure the surface roughness and to validate the effectiveness of plasma nitridation with respect to the conventional thermal nitridation by NH@sub 3@. Transmission electron microscopy (TEM) is used to highlight the different structural aspects of the nitride layers obtained by N@sub 2@ and N@sub 2@-H@sub 2@ mixtures. Optimizing the surface temperature and the N@sub 2@/H@sub 2@ ratio the formation of an interfacial As-rich layer in the GaAs/GaN growth is minimized, the nitridation depth is increased up to 15nm and compact and chemically stable GaN layers are obtained.

4:20pm **EM+PS+SE-TuA8 III-Nitride Dry Etching - Comparison of Inductively Coupled Plasma Chemistries***, **H. Cho**, Y-.B. Hahn, D.C. Hays, C.R. Abernathy, S.M. Donovan, J.D. MacKenzie, S.J. Pearton,* University of Florida, Gainesville*; J. Han, R.J. Shul,* Sandia National Laboratories

A detailed comparison of etch rates, etch yields, surface morphology and sidewall anisotropy has been performed for GaN, InN and AlN etched in Inductively Coupled Plasma discharges of BCl@sub 3@, BI@sub 3@, BBr@sub 3@, ICl and IBr. Etch selectivities of 100:1 for InN over GaN and AlN are obtained in BI@sub 3@ due to the relatively high volatility of the InI@sub x@ products and the lower bond strength of InN. The selectivities are much lower in the other chemistries. The etched surfaces of the nitrides are smooth over a broad range of source and chuck powers, pressures and discharge compositions, and there is typically a slight deficiency of N@sub 2@ in the near-surface (@<=@ 100Å) region. The etch yields for all of the chemistries are relatively low (@<=@ 2), indicating that the high ion flux in the ICP tool is a critical factor in obtaining practical etch rates for the nitrides.

4:40pm **EM+PS+SE-TuA9 Photoenhanced RIE of III-V Nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ Plasmas***, **A. Tempez**, N. Medelci, N. Badi, I. Berichev, D. Starikov, A. Bensaoula,* University of Houston*; A. Chourasia,* Texas A&M University

Boron nitride (BN) and gallium nitride (GaN) are known as superior semiconductor materials for UV optoelectronic and high power, high temperature applications. As a consequence of their high molecular bond strength, these materials are extremely difficult to etch. In order to address the device processing issue, reactive ion etching (RIE) tests were performed on BN and GaN thin films. Our experiments show that optimum etching occurs using BCl@sub 3@/Cl@sub 2@/Ar chemistries for GaN and Cl@sub 2@/Ar for BN. In the case of GaN, the BCl@sub 3@/Cl@sub 2@/Ar mixture results in the highest reported RIE GaN etch rates.@footnote 1@ Auger and x-ray photoelectron spectroscopy analyses of the etched surfaces always show a depletion of the surface nitrogen atomic composition which increases with the dc bias (rf power). The impurity incorporation, C and Cl also shows the same trend. In order to improve the etch rates at lower powers, a photoenhanced RIE process was investigated. A BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ plasma in combination with a xenon arc lamp was utilized. Preliminary results show a 33% increase in GaN etch rates for a -220 V dc bias (100 W rf power). The dependence of etch rates, surface composition and chemistry, and surface morphology on dc bias (rf power) and photo-irradiation flux will be presented. In addition, the energy and angle distribution of the reaction species from nitride materials exposed to well characterized reactive beams were investigated. The results will be compared to those from RIE and Photo-RIE data and a model for the possible surface etch reactions will be discussed. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061. This material is also based upon work supported by the U.S. Civilian Research and Development foundation under Award No. REI-247. @FootnoteText@ @footnote 1@N.

Medelci, A. Tempez, E. Kim, N. Badi, I. Berichev, D. Starikov and A. Bensaoula, 1998 MRS Spring Meeting (in print).

5:00pm **EM+PS+SE-TuA10 Characteristics of Cl@sub 2@ -based Inductively Coupled Plasmas during the GaN Etching**, ***H.S. Kim**, J.W. Jang, Y.H. Lee, G.Y. Yeom,* Sungkyunkwan University, Korea*; J.W. Lee, T.I. Kim,* Samsung Advanced Institute of Technology, Korea

Planar inductively coupled Cl@sub 2@-based plasmas have been used to etch GaN and etch properties having smooth and nearly vertical etch profiles with the etch rates close to 850 nm/min could be obtained with Cl@sub 2@-rich gas combinations. To understand the effects of plasma conditions on the GaN etch properties, The quarupole mass spectrometry(QMS), optical emission spectroscopy(OES), and an electrostatic probe have been used. Especially, the quadrupole mass spectrometer system we used in the analysis of the plasmas was configured with ion optics, energy filter, and integral electron impact ion source for plasma diagnostics. Therefore, not only the radical densities but also positive and negative ion densities and their energy distributions were also measured. As process conditions used to study the effects of plasma characteristics on the GaN etch properties, Cl@sub 2@ was used as the main etch gas and Ar, BCl@sub 3@, and CH@sub 4@ were used as additive gases. Operational pressures were varied from 5mTorr to 30mTorr while other conditions such as inductive power, bias voltage, and substrate temperature were fixed at 600 watts, -120 volts, and 70 centigrade, respectively. The relative amounts of reactive ions (Cl@super +@, Cl@sub 2@@super +@, Cl@super -@, etc.), Ga-containing etch products(GaCl, GaCl@sub 2@, and GaCl@sub 3@ for Cl@sub 2@ plasma), and nitrogen-containing etch products (N, N@sub 2@, NH@sub 3@, etc.) were estimated by the plasma mass spectrometric measurements. The results showed that the enhancement of GaN etch rate was related to the increase of Cl radical and reactive ion such as Cl@super +@, Cl@sub 2@@super +@, etc. measured by the QMS and OES during the Cl@sub 2@-based inductively coupled plasma etching. Therefore, chemical reactions between Ga in GaN and Cl and Cl@sub 2@@super +@ from Cl@sub 2@, under the sufficient ion bombardments to break GaN bonds, appear to be important in the GaN etching. More detailed analysis of plasmas and their relation to GaN etching will be given in the presentation.

Magnetic Interfaces and Nanostructures Technical Group Room 324/325 - Session MI-TuA

Emerging Materials and Hybrid Structures

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

2:00pm **MI-TuA1 Spin Transport Effects in Ferromagnetic/Superconductor Heterostructures Grown using Molecular Beam Epitaxy**, ***A.M. Goldman**, V.A. Vas'ko, K.R. Nikolaev, V.A. Larkin, P.A. Kraus,* University of Minnesota **INVITED**

Heterostructures consisting of half-metallic ferromagnetic oxides in the lanthanum manganite family and high temperature superconductors in the YBCO family have been fabricated using the technique of ozone-assisted molecular beam epitaxy, and characterized using a number of techniques. These compounds have similar perovskite lattices, and therefore can easily be formed as epitaxial heterostructures. The fabrication and characterization of these heterostructures and the physics of the interplay between ferromagnetism and superconductivity at the interface between the ferromagnet and superconductor the will be discussed. High-resolution X-ray diffractometry, Rutherford back scattering and helium ion channeling were used to characterize the composition and crystal quality of samples. Simple patterning techniques were employed to prepare configurations in which the effects of carrier injection on superconductivity and the properties of the interfaces could be investigated. Injection of carriers from the magnetic oxides, which exhibit the phenomenon of "Colossal Magnetoresistance," into high temperature superconductors was shown to lead to the suppression of superconducting properties such as critical current and critical temperature. This suggests that spin-polarized transport can be used to investigate spin-dependent electronic properties of high temperature superconductors, and opens the possibility of a new class of superconducting devices utilizing spin injection. The differential conductances of superconductor-ferromagnet interfaces were also studied. The most striking feature of these investigations was the observation of a differential conductance dip at zero bias which was a decreasing function of temperature and/or magnetic field. This phenomenon has been interpreted using a picture of Andreev reflection as a consequence of the high spin polarization of the carriers in the half-metallic ferromagnet.

2:40pm **MI-TuA3 Enhanced Curie Temperature of GdN in GdN/Fe Multilayers**, ***W.J. Antel Jr.**, F. Perjeru,* Ohio University*; W.L. O'Brien,* University of Wisconsin, Madison*; G.R. Harp,* Ohio University

Both magnetic and semiconductor systems as distinct entities have found a wide variety of applications, however work on magnetic semiconductor systems is still in its infancy. The GdN/Fe multilayer system is investigated here as a function of GdN thickness. GdN alone is a ferromagnet with a Curie temperature of 60 K. In the multilayer structure, exchange coupling between the Fe and GdN is found to drastically raise the Curie temperature. The films are grown using reactive sputtering with a N and Ar atmosphere for the GdN, and a pure Ar atmosphere for the Fe. Magnetic moment measurements, using x-ray magnetic circular dichroism, are performed at the L@sub 2,3@ edge of Fe and M@sub 4,5@ of Gd. At room temperature, the Gd is found to maintain a significant moment up to a layer thickness of 3 Å. Measurements performed at 100 K indicate a constant Gd moment of approximately 6 µ@sub B@ out to at least a thickness of 10 Å.

3:00pm **MI-TuA4 Unusual Magnetic Ordering at Room Temperature in La-Ca-Mn-O Thin Films**, ***S.E. Lofland**, V.V. Srinivasu, S.M. Bhagat, R. Shreekala, M. Rajeswari, T. Venkatesan,* University of Maryland

Epitaxial thin films with a nominal composition of La@sub 0.8@Ca@sub 0.2@MnO@sub 3@ were grown by pulsed-laser deposition with thicknesses ranging between 300 and 2600 Å. The resistivity of the as-grown films had a peak near 210 K, similar to the value found in the bulk material. Electron spin resonance studies showed the films to be magnetically very inhomogeneous with no indication of ordering above 240 K. Subsequent heat treatment of the films at 900° C for an hour in flowing oxygen led to dramatic property changes. The resistvity peak temperature increased significantly, and in most cases was above 300 K while the magnitude of the resistivity was markedly less. Resonance experiments suggested that treated films less than 1000 Å thick were paramagnetic at room temperature; however, films thicker than 1000 Å showed multiline spectra at 300 K, with at least one line resulting from a ferromagnetic spin system. In the thickest film, resonance data suggested that 10% of the film was ferromagnetic at room temperature. This is in contradiction to the accepted phase diagram ordering temperature of around 220 K and the maximum ordering temperature of 270 K for the La@sub 1-x@Ca@sub x@MnO@sub 3@ system. We discuss how these observations may be reconciled. Supported in part by the National Science Foundation under Grant No. DMR-9632521.

3:20pm **MI-TuA5 Flux Pinning in Superconductors by Arrays of Submicron Structures***, ***I.K. Schuller**,* University of California, San Diego **INVITED**

We have used electron beam lithography to prepare triangular and square lattices, lines, etc. of submicrometer magnetic dots (Ni, Co, and Fe) and holes and studied their properties using a variety of techniques including magnetotransport, magnetization, Magnetic Force Microscopy and light scattering. We showed that the interaction between an ordered array of small magnetic particles and superconducting thin films leads to strong pinning effects due to the synchronized interaction with the vortex lattice. The resistivity vs. magnetic field curves present sharp minima close to the transition temperature, whereas the transport critical currents exhibit pronounced maxima. These minima and maxima appear at constant field intervals (@Delta@H), clearly related with the lattice parameter of the vortex lattice array. The angular dependence reveals that this interval @Delta@H increases with the angle between the field and the film normal (@theta@) as @Delta@H proportional to 1/cos@theta@, showing that only the perpendicular component of the magnetic field is relevant for this synchronized pinning effect. Comparisons with arrays of holes and normal submicrometric dots reveal the magnetic origin of these effects. Studies as a function of the various geometric parameters helps elucidating the pinning mechanisms involved. *Work done in collaboration with A. Hoffmann, Y. Jaccard, P. Prieto, M.-C. Cyrille, F. Sharifi, J. Martin, M. Velez, J. Nogues, J.-M. George, M. Grimsditch, M.J. Van Bael, K. Temst, C. Van Haesendonck, V.V. Moshchalkov and Y. Bruynseraede. Supported by the US-DOE and AFOSR.

4:00pm **MI-TuA7 Low-Field Magnetoresistive Properties of Manganite and Chromium Oxide Films**, ***A. Gupta**,* IBM T.J. Watson Research Center **INVITED**

The magnetotransport properties of the manganites has been the subject of intense research during the past few years. These oxides exhibit orders of magnitude change in resistance when subject to a magnetic field in the Tesla range. Reducing the field scale for magnetotransport has been a major goal of many research groups. We have followed two approaches in reducing the field scale in the manganites: (1) exploiting the spin-dependent scattering at grain boundaries by using polycrystalline and bi-epitaxial films for pinning the magnetic domains; and (2) fabrication of magnetic tunnel junctions, in the form of manganite/insulator/manganite structures, where the tunneling current between the ferromagnetic manganite layers depends sensitively on the relative orientation of their magnetization vectors. Both approaches benefit from the nearly half-metallic nature of the manganites and result in significant low field magnetoresistance (up to 100%) at low temperatures. Recent magnetoresistance results obtained using another half-metallic system, chromium oxide, will also be presented and the similarities and differences between the two systems will be discussed.

4:40pm **MI-TuA9 Epitaxial Growth of Co Layers on Sb-passivated GaAs(110) Substrates**, ***M. Martin,*** *C. Teodorescu,* LURE, Centre Universitaire Paris Sud and ICMM, France; *H. Ascolani,* Centro Atomico Bariloche, Argentina, Argentine; *J. Chrost, J. Avila, M.C. Asensio,* LURE, Centre Universitaire Paris Sud and ICMM, France

The growth of magnetic epitaxial layers on semiconductors has attracted considerably attention since it allows the integration of low dimensional magnetic materials with the silicon technology. The largest body of work has been focused to the magnetic 3d transition metals and the zinc blende semiconductors, which have similar lattice constants . In practice, however, the growth of transition metals on semiconductor substrates is difficult due to intrinsic surface states present at the gap of the semiconductors which dominate the electronic and reactivity of the interfaces. Pervious studies on Co/GaAs(110) have indicated that BCC Co can be grown epitaxially for thicknesses up to 300 Å. However, the metallic films are not flat and the As interdiffusion modifies the magnetic properties of the Co overlayer. In this work, we present new results of the growth of Co on a pervious Sb-GaAs(110) passivated surface, where the interdiffusion process is dramatically reduced and the quality of the metallic Co overlayer enhanced. The reactivity of the interface has been tested at different temperature and coverage conditions by high energy resolution synchrotron radiation photoemission and the morphology of the metallic overlayer determined by photoelectron diffraction.

Manufacturing Science and Technology Group
Room 317 - Session MS-TuA
Process, Integration, and Modeling

Moderator: K. Aitchison, Novellus Systems

2:00pm **MS-TuA1 Pattern/Etch/Clean Process Interactions for 0.18um CMOS Gate Formation**, ***R.J. Gale***, *R. Kraft, R.T. Laaksonen, A.L.P. Rotondaro,* Texas Instruments **INVITED**

As device dimensions continue to shrink to 0.18um and below, the interaction between steps in a process flow becomes more critical. These interactions can be synergistic. In many cases, however, the processes must be co-optimized to minimize the negative effects. One of the most critical process modules in a CMOS device flow is the formation of the gate geometry. We will focus on pattern, etch, and post-etch clean interactions in forming the gate. Dry etch is used to reduce the photoresist patterned line width. This approach permits the wafer patterning to be performed in a more robust process regime thus producing less variation. Once the desired line width reduction has been accomplished, the polysilicon is dry etched, stopping on the thin (<30A) gate oxide. Finally, the remaining photoresist and etch polymer residues must be removed without stripping the thin gate oxide protecting the active regions of the device. Changes in the dry etch process to maximize anisotropy to provide vertical profiles for the gate geometry and high selectivity to gate oxide drive a more aggressive post etch clean process that also must be optimized for oxide selectivity and critical dimension control. This paper discusses the challenges and tradeoffs to successfully accomplish the 0.18um gate formation.

2:40pm **MS-TuA3 Dual Damascene : Etching Process Characterisation of "Self Aligned" and "Counter Bore" Architectures**, ***P. Berruyer,*** *F. Vinet,* LETI-GRESSI, France; *H. Feldis,* SGS-Thomson, France; *E. Tabouret, Y. Trouillet,* LETI-GRESSI, France; *Y. Morand,* SGS-Thomson, France

One of the main challenges of the next few years is the improvement of interconnect performances, namely integration density and dynamic performances. This can not be done without combining improvement in both design and technology. In term of technology, different ways are explored : introduction of low k dielectric and low resistivity metal. Concerning low resistivity metal, copper seems to be the best candidate to replace AlCu. But the main disadvantage of this material is its high resistance to plasma etching. Taking into account that copper is highly resistant to plasma etching, that Chemical Mechanical Polishing processes are available and that dual damascene architecture can significantly increase interconnect density, copper is usually introduced in a damascene architecture. Among the different ways of achieving dual damascene structures, two of them, called " self aligned " and " counter bore " have to be taken into account. In this paper we will first describe the process steps of these two architectures. We will point out that both architectures require the development of a specific high aspect ratio dielectric etching process with high selectivity to nitride. A medium density reactor (TEL Unity DRM) will be used for the experiments. Different process conditions will be applied to dual damascene structures for a morphological characterisation. Major attention will be paid on selectivity to nitride, microloading, etch stop and CD control. Etch rate and selectivity to photoresist will also be studied. The architectures and the etching processes will be compared on an electrical lot with copper metallisation. Contact resistance and yield on 10 million contact chains will be measured. The advantage and drawbacks of each architecture will be discussed with regard to etching processes. An optimised dual damascene process will be proposed.

3:00pm **MS-TuA4 Low k Polymer Etching for Dual Damascene Technology Application to SILK Material**, ***F. Vinet***, *E. Tabouret,* LETI-GRESSI, France; *Ch. Vivensang,* Tokyo Electron Europe LTD, France

Scaling down of interconnect requires a change in architecture and materials to be integrated. Dual Damascene scheme in combination with copper as metal conductor, appears to be the most acurate choice for sub 0.18 µm design rule technology. The dielectric material necessary for this application is still under improvement to achieve the required properties such as, dielectric constant<2, thermal stability and good adhesion on mineral or organic layers. The most advanced materials are based on polymers. In order to etch these materials, a hard mask is necessary due to their poor resist selectivity (1:1).Silicon dioxide (SiO2)is the most commonly used hard. Depending on the polymer composition, the compromise between high aspect ratio and mask erosion has to be found. Among the different available materials, SILK from Dow Chemicals, presents a chemical stability compatible with the thermal budget of our current technology. Moreover, this material is purely organic and contents no silicon; in this case an etching chemistry without fluorine can be used, ensuring a good selectivity to the hard mask. The etching properties, as well as the requirements related to the use of a Dual Damascene architecture have been investigated in this paper. A 1500Å thick SiO2 hard mask was deposited on top of 1µm spin coated SILK. By using DUV lithography 0.225 µm holes and 0.3/0.3 µm L/S patterns were defined. A medium density etcher from TEL, DRM85 UnityII was used for the experiments. By using a pure O2 chemistry, an overhang between hard mask and SILK is observed ; moreover due to isotropic etching, the sidewalls after etching are bowed. In order to overcome these effects, different chemistries have been tested in combination with etching process parameters to form a passivating layer. With optimised conditions, 0.225 µm holes were obtained with straight profiles. In our experiments, the limitation for higher aspect ratios is due to lithography and not to etching conditions. Whatever the Dual Damascene structure is used, successive steps of fluorinated and non fluorinated chemistry has to be used to etch alternatively SiO2/SILK/SiO2.The effect of such a sequence has been studied on the etched profiles as well as the influence of reactor fluorine memory effect. Optimised conditions for both, process and reactor, are proposed to ensure a reliable process for sub 0.18µm technology.

3:20pm **MS-TuA5 Manufacturing Issues for MEMS Production**, ***K.W. Markus,*** MCNC **INVITED**

As the commercial and military implementation of MEMS technology solutions moves further up the line from research to consumer and commodity applications, the need for a robust manufacturing technology base for MEMS continues to increase. MEMS, the merging of computation with sensing and actuation into an integrated system-based solution for problems pertaining to the physical world, has benefited greatly and grown rapidly out of the widespread infrastructure developed in the U.S. for the manufacture of integrated circuits (IC). The U.S. approach to MEMS applies the repetitive layering, batch-processed wafer methods of the integrated silicon circuit manufacturing industry to achieve revolutionary strides in mechanical miniaturization and system integration. This outgrowth from the IC industry has both benefits and pitfalls, and it is going to be capitalizing on the benefits and navigating the pitfalls that will determine the success of the transition of MEMS from its current low or sporadic volumes to the high-volume successes that will demand large-scale production capabilities. One of the many benefits that MEMS derives from its common base with the IC industry is the methodology behind its fabrication sequences. Most MEMS processes can be decomposed to a repeating series of material deposition, patterning and subsequent removal of specific areas of the material. This layering is repeated until the basic structure is created either on or within the silicon wafer. While many of these steps, or unit processes, are similar to those used in IC processing, the mechanical nature of MEMS puts additional stringent requirements on the processes that do not exist in the IC processes. Beyond the fabrication of the basic wafer structure, the releasing of the structures, the handling of these released wafers or die, the packaging, and the testing of the MEMS devices all can challenge even the most sophisticated and technically advanced manufacturing line. While there is a strong and vibrant manufacturing infrastructure for the IC industry, the uniqueness of some of the key steps of MEMS technology challenge the existing manufacturing technology infrastructure and place challenges and potential limitations on the development of a comparable support-structure for MEMS. Much of the IC industries infrastructure has grown as a result of, and not in advance of, the explosive growth the IC industry in the last 15 years. While the outlook for MEMS is quite strong ($9B - $30B by 2000)@footnote 1@ , it is a mere trifle when compared against the $148B@footnote 2@ (1995) IC market (year 2000 projection $371B) . MEMS will need to find creative and unique ways to ensure that the level of attention necessary to help drive the growth of manufacturing infrastructure are found and nurtured, despite the overwhelming shadow of the IC market. This presentation will discuss the manufacturing issues affecting the growth of MEMS from commercial curiosity to manufacturing reality, including design and simulation tools, fabrication equipment, through-put and resources, packaging, testing and reliability. @FootnoteText@ @footnote 1@ Micromachine Devices newsletter, August 1997 @footnote 2@ World-wide Merchant Semiconductor Forecast, Source: ICE, Status 1996

4:00pm **MS-TuA7 Design of a 300 mm CVD Tungsten Reactor using Computational Fluid Dynamics***, **E.J. McInerney**, T.M. Pratt, A. Tahari,* Novellus Systems

Over the next several years, the semiconductor industry will transition to 300 mm wafers for IC fabrication. To support this shift, the semiconductor equipment companies must develop 300 mm processing tools that are both manufacturing worthy and cost effective. In the past, designing equipment for larger sizes was primarily a matter of scaling the components: chamber, showerheads, heaters, etc. For batch systems, often the batch size would also be reduced to minimize the gain in footprint. However, as capital equipment costs become an increasing fraction of wafer fabrication costs, it becomes necessary for semiconductor equipment to not only handle larger sizes, but also to be substantially more cost effective. We report here on how computational fluid dynamics modeling was used to guide the design and development of a high throughput, 300 mm multi-station CVD tungsten reactor. Through modeling we were able to investigate novel gas-based isolation schemes that allowed the individual deposition stations to run separate processes, without cross contamination. The resulting reactor can simultaneously deposit silane reduced and hydrogen reduced tungsten films at adjacent deposition stations without the danger of gas phase nucleation or WF@sub 6@ device attack. This leads is a significant drop in the idle time of deposition stations and a large boost in throughput.

4:20pm **MS-TuA8 Computational Flow Modeling for Electrostatic Chuck Applications***, **L.A. Gochberg**,* Novellus Systems, Inc.

An electrostatic chuck used in a deposition or etching process is comprised of a ceramic material with an embedded electrode, on which a wafer is placed in the reactor chamber. The gas flow paths on the backside of the wafer can be adjusted to help control the wafer temperature. The dimensions of these flow pathways can be as small several microns, and at typical backside gas operating pressures (1-10 Torr), the flow can be anywhere between continuum and free molecular flow. Though tools are available to model these flows (Direct Simulation Monte Carlo and Navier-Stokes with slip boundary conditions), these flow conditions, typical in wafer processes, bring up some significant computational challenges. Also, the 3D nature of the real chuck flow with all its complex geometry compounds the numerical difficulties. In this paper, the focus will on a 2D approximation to the flow on the backside of the wafer, which is essentially flow between two flat, parallel circular disks. This geometry is quite similar to the 3D geometry in the electrostatic chuck, but without the complex set of gas grooves. Computations will be performed using Navier-Stokes computational fluid dynamics (CFD) with and without slip boundary conditions, Direct Simulation Monte Carlo (DSMC), and an analytical solution to the problem. These results will be compared to experimental data for helium gas flow through that same geometry. Comparisons show an excellent agreement between all the computations and the experiments in the continuum and near-continuum transition flow regime. The DSMC results and analytical solution match well with the data throughout all the flow regimes. However, the CFD with slip shows a capability in this 2D geometry to capture the trends seen in the data and DSMC out to much higher Knudsen numbers than would be typically expected. These CFD with slip results can be used as a design tool to conservatively estimate backside gas pressure distributions and reliably design gas distribution channels.

4:40pm **MS-TuA9 TEOS CVD Topography Simulation Using Surface CHEMKIN and EVOLVE***, **A.H. Labun**,* Digital Equipment Corporation*; T.S. Cale,* Rensselaer Polytechnic Institute*; P. Ho, H.K. Moffat, M.E. Coltrin,* Sandia National Laboratories

Although the pyrolysis of Si(OC@sub 2@H@sub 5@)@sub 4@ (TEOS) leads to formation of a highly reactive deposition precursor, increasing the residence time in a chemical vapour deposition (CVD) process leads to more, not less, conformal SiO@sub 2@ deposition in high aspect ratio features, contrary to the assumption of a first order deposition reaction commonly used in topography simulation. A newly developed Surface CHEMKIN interface in the EVOLVE 5.0 topography simulator allows EVOLVE to be used in conjunction with CHEMKIN-based reactor codes to explore this and other CVD reaction mechanisms and make process recommendations. Ab initio calculations and experiments lead to consideration of a network of 8 reversible, heterogeneous reactions and 3 reversible, homogeneous reactions, involving 5 surface species and 6 gasses. Under short reactor residence time conditions relatively little TEOS decomposes and it remains the dominant constituent of the bulk gas, but transport limitations cause byproduct gasses to dominate in submicron features. They promote the reverse heterogeneous reactions, slowing the deposition rate inside the features and causing nonconformal films. The sticking coefficients of TEOS and the precursor may vary substantially over the topography and during the deposition. Decomposition of the TEOS under longer reactor residence time conditions leads to similar gas compositions inside and out of the features and hence film deposition in the features becomes conformal.

5:00pm **MS-TuA10 Plasma-Induced Nitridation of the Gate Oxide Dielectrics: Linked Equipment-Feature-Atomic Scale Simulations***, **V. Sukharev**, S. Aronowitz, H. Puchner, V. Zubkov, J. Haywood, J. Kimball,* LSI Logic Corporation

Quantum chemical calculations were employed to get insight into the mechanisms involved in plasma-induced nitridation of gate oxide that will suppress boron penetration. The roles played by the nitrogen cations and atoms were explored. Based on these results, we assumed the following model for the nitrogen incorporation: nitrogen cations cleave bonds in substrate subsurface region; the depth of the damaged layer is determined mainly by the energy of the incident ion, binding energy of nitridated material and its density. Nitrogen atoms, whose concentration is usually several orders of magnitude greater than the cation concentrations, readily react with dangling bonds to produce @>=@Si-N- and @>=@Si-O-N- radicals. A subsequent anneal produces an appropriate condition for reaction between the above radicals and results in the nitrogen insertion into the SiO@sub 2@ ring structure. Thus the nitrogen cations play the role of the promoter for the entire SiO@sub 2@ nitridation. It was shown that B interaction with siloxane rings that contain incorporated nitrogen yielded a larger energy gain than rings without nitrogen. This explains the chemical nature of the nitrogen-induced barrier effect. Monte Carlo (PROMIS) simulations were used to simulate the necessary energy of incident N@sub 2@@super +@ cations to produce the bond cleavage down to a particular depth in the amorphous SiO@sub 2@ layer. A combination of the Hybrid Plasma Equipment Model and Plasma Chemistry Monte Carlo Simulation codes were used to simulate nitrogen atomic and cation fluxes and their angular and energy distributions at the wafer surface. Combining simulated cation energies with PROMIS Monte Carlo simulation results make it possible to derive the plasma process parameters that will permit a desired level of nitridation to be reached.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS-TuA

Quantum Wires and Quantum Dots

Moderator: Ph. Avouris, IBM T.J. Watson Research Center

2:00pm **NS-TuA1 Self-organized Ge Quantum Wires on Si (111) Substrate*,* *G. Jin**, Y.S. Tang, J.L. Liu, K.L. Wang,* University of California, Los Angeles

Self-organized nanostructures have been of considerable interest recently due to the fact that self-organization provides a possible way to realize nanostructures without process-induced damage as frequently seen in those defined by electron beam lithography and reactive ion etching. However, very few work has been reported on self-organized quantum wires. In this work, self-organized Ge quantum wires on Si (111) substrate grown by MBE have been realized and studied. Regular surface steps were formed on cleaned Si (111) substrate after annealing at 870°C in a UHV MBE system, then selforganized Ge quantum wires were formed on the substrate after growing 300 nm Si buffer layer. Atomic force microscopy (AFM) studies showed that regular surface steps were formed along [11 -2] direction and the terrace width was about 120 nm and the step height was about 0.6 nm. The self-organized Ge quantum wires with the width of about 65 nm and the height of about 5.5 nm were parallel to the direction of [11 -2] with the pitch close to the terrace width, or about 120 nm. The uniformity of the quantum wires was found to be reasonably good. Raman studies indicated that the peak of Ge-Ge mode shifted to a higher energy. This suggests that the Ge quantum wires are tensilely strained on the edge sites of the steps. The result of polarized Raman studies confirmed the existence of the wires and the wire orientation which is consistent with the AFM result. The size distribution and the optical properties of the Ge quantum wires are also under study. @FootnoteText@ The work was supported in past by National Science Foundation (DMR-9520893)

2:20pm **NS-TuA2 Formation and Characterization of Metal Atom Nanostructures on Si(112) Facet Surfaces*,* *S.M. Prokes**, O.J. Glembocki,* Naval Research Laboratory

Facet semiconductor surfaces have been suggested for use as templates in the formation of ordered dots and lines. A bulk-terminated Si(112) surface is of particular interest since it consists of distinguishable (111) terraces and (001) steps which can serve as a template for the formation of well-ordered nanostructures, such as metallic wires or dots, with the aim of producing electron gratings and magnetic nanostructures. We have studied the formation of Ga, Al and Sc nanostructures on facet Si(112) surfaces, which were investigated using LEED, Auger spectroscopy and Reflectance Difference Anisotropy (RDA). Although the clean Si(112) surface exhibits (1x2) reconstruction, we found that the deposition of Ga or Al above 300°C removes this reconstruction and leads to a periodic stepped structure of alternating (111) terraces and (001) steps. Ga or Al chains then form by a self-limiting process, which we can track from the rapid change of the (2x1) Si(112) reconstruction under sub-critical coverage, to chain formation leading to a 5x1 reconstruction followed by a 6x1 reconstruction, using RDA. Furthermore, AES and RDA results show the replacement of Ga atoms by Al atoms at the step edges during sequential deposition of Ga and Al, indicating a stronger Al-Si bond. Using RDA, we have also observed that depositions at lower temperatures can lead to the formation of Ga metallic wires on the Si(111) terraces. For Sc, we find that its higher surface energy precludes the formation of wires but leads to the formation of nanometer-size Sc islands, which may exhibit enhanced magnetic moments. Using Monte Carlo techniques to model the time evolution of the deposition at various temperatures, we are also able to extract highly accurate values for the surface kinetic parameters involved in the formation of these nanostructures.

2:40pm **NS-TuA3 Nanotubes and Nanowires: Physics, Chemistry and Applications*,* *C.M. Lieber,*** Harvard University **INVITED**

One-dimensional nanostructures, nanowires and nanotubes, represent an exciting and intellectually challenging area of research that crosses the borders between many areas of the physical sciences and engineering. Interest in these structures has been driven by fascinating issues in chemistry and physics, and the potential to impact science and technology. For example, it remains a great challenge to understand the intrinsic and potentially unique properties of nanowires and nanotubes, and thereby define new applications. This presentation will focus on addressing these critical issues. First, STM studies of the atomic structure and tunneling density of states of single-wall carbon nanotubes (SWNTs) will be described. Measurements show that SWNTs exhibit semiconducting and metallic behavior that depends predictably on helicity and diameter, and also exhibit well-defined 1D van Hove singularities. These results are compared and contrasted with theoretical calculations, and their implications discussed. Second, atomic force microscopy studies of the bending and stretching of individual nanowires and nanotubes will be discussed. The implications of these results on potential structural applications will be discussed. Lastly, the application of nanowires and nanotubes as molecular resolution, functionally-sensitive probes for chemistry and biology will be described.

3:20pm **NS-TuA5 Self-Assembled Nanostripes on Silicon*, D.Y. Petrovykh,*** University of Wisconsin, Madison*; J. Viernow,* Universität Hannover, Germany*; J.-L. Lin,* University of Wisconsin, Madison*; F.M. Leibsle,* University of Missouri, Kansas City*; F.-K. Men,* National Chung Cheng University,Taiwan, R.O.C., Republic of China*; A. Kirakosian, F.J. Himpsel,* University of Wisconsin, Madison

We report on the successful fabrication of one-dimensional structures on silicon with sizes of a few nanometers. As templates we use stepped Si(111)7x7 surfaces, which can be prepared with high precision (only one kink in 20,000 edge sites).@footnote 1@ On top of such a template, CaF@sub 2@ stripes are produced by step flow growth. They play the role of a photoresist in nanolithography. Various growth modes of CaF@sub 2@ are found by chemically-sensitive scanning tunneling microscopy, including a regime at 600-650@super o@C where regular, 10 nm wide stripes are formed and a second regime at 700-750@super o@C where the stripes break apart spontaneously into strings of 10 nm diameter dots. Chemical sensitivity to CaF@sub 2@ is achieved in STM via current images at a bias voltage where electrons from the tip tunnel into the band gap of CaF@sub 2@. After producing passivating CaF@sub 2@ stripes, metallic wires are to be deposited on the remaining reactive silicon, e.g., by selective CVD, electroplating or evaporation and diffusion off the CaF@sub 2@. Test experiments on these processes will be reported. @FootnoteText@ @footnote 1@J. Viernow, J.-L. Lin, D. Y. Petrovykh, F. M. Leibsle, F. K. Men, and F.J. Himpsel, Appl. Phys. Lett. 72, 948 (1998) @footnote 2@J.-L. Lin, D. Y. Petrovykh, J. Viernow, F. K. Men, D. J. Seo, and F.J. Himpsel, J. Appl. Phys. 84, July 1 (1998)

3:40pm **NS-TuA6 Fabrication of Metallic Nanowires via UHV-STM Lithography and Thermal CVD*, M.C. Hersam*,** *G.C. Abeln, D.S. Thompson, J.S. Moore, H. Choi, S.-T. Hwang, J.W. Lyding,* University of Illinois, Urbana-Champaign

The selective removal of hydrogen from a passivated Si(100) surface with an ultrahigh vacuum (UHV) scanning tunneling microscope (STM) allows nanometer-sized "templates" of clean Si(100) to be defined on an otherwise unreactive surface. By delivering chemically reactive species to the surface in the gas phase, different materials can be selectively deposited on the unpassivated Si(100) areas. In particular, nanopatterned metallization is achieved through selective thermal chemical vapor deposition (CVD) of organometallic precursor molecules. This paper systematically analyzes such precursor molecules to determine their suitability for selective CVD of metal on Si(100) in UHV. Initially, a novel aminoalane precursor was employed for CVD of aluminum at ~200°C. STM images of the surface after exposure to this precursor suggest monolayer coverage and evidence of a 2X2 reconstruction. However, variation of the dose and deposition conditions did not lead to the growth of a thicker film. Hence, in an effort to produce a more receptive surface for the growth of metallic thin films, CVD of nucleating agents (e.g., TiCl@sub 4@) was also studied. XPS and STM data show the selective deposition of Ti on clean versus H-passivated Si(100) after TiCl@sub 4@ exposure at room temperature. In an effort to grow TiN, the TiCl@sub 4@ experiments were repeated on an ammonia coated Si(100) surface. Again, XPS and STM data show the selective deposition of Ti. Finally, multiple precursor molecules were integrated for the growth of multi-layer structures. As a footnote, our efforts for interfacing these STM patterned nanowires with macroscopic external electronics will be updated.

4:00pm **NS-TuA7 STM/AFM Nanofabrication Process on Atomically Flat Substrate for Single Electron Device*, K. Matsumoto,*** Electrotechnical Laboratory, Japan **INVITED**

Planar type single electron transistor(SET) and SET memory are proposed and realized on the atomically flat @alpha@-Al@sub 2@O@sub 3@ substrate using a STM/AFM nanofabrication process. Using STM tip/AFM cantilever as a cathode, the surface of the titanium(Ti) metal which was on an atomically flat @alpha@-Al@sub 2@O@sub 3@ substrate is selectively oxidized to form a few tens of nanometer wide oxidized titanium(TiO@sub x@) line just under the tip. The surface roughness of the 2.5nm thick Ti metal is less than 0.15nm and retains the atomically flat condition. The surface roughness of TiO@sub x@ is also less than 0.15nm. The TiO@sub x@ works as an energy barrier for an electron, and the barrier height between Ti and TiO@sub x@ is 468meV. Therefore, the narrow TiO@sub x@ line could be used for the tunneling junction for SET. The size of the SET island is 8nm x 26nm square. The width, the thickness, and the length of the two tunnel junctions are 19nm, 2nm, and 26nm, respectively. The tunnel junction capacitance calculated from these structure parameters is C@sub t@=0.12aF. The gate electrode is set 964nm away from the island. The SET operates even at room temperature and shows the Coulomb oscillation with the periods of ~1.8V at the drain bias of -0.3V. At the different drain bias from -0.2V to -0.7V, the drain current shows the same oscillation periods of ~1.8V against the gate bias change. From this periods of Coulomb oscillation, the gate capacitance is estimated to be C@sub G@=0.1aF. Owing to the atomically flat @alpha@-Al@sub 2@O@sub 3@ substrate, the uniformity and reproducibility of the TiO@sub x@ line improves drastically, and it makes possible to fabricate the SET memory with complicated multi-tunnel junction structure.

4:40pm **NS-TuA9 Raman Scattering Studies of Multiple Ge Dots on Si (100) By Solid Source Molecular Beam Epitaxy***, **J.L. Liu**, Y.S. Tang, G. Jin, K.L. Wang,* University of California, Los Angeles

Recently, the growth of Ge dots on Si substrate has attracted much attention due to its potential applications in Si-based optoelectronics and its possible contribution to the scaling-down devices. The optical properties of these dots are particular interest in the investigation. In this work, we report the Raman scattering studies of multiple Ge dots on Si (100) substrate grown by solid source molecular beam epitaxy. The sample contains 20 periods of boron-doped Ge dots with 6 nm Si as barriers. The cross-sectional transmission electron microscopic observations illustrate that the size and height uniformities of the Ge dots are not worse that 7 percent. Raman spectrum shows the upper shift of Si-Ge mode and downward shift of Ge-Ge mode which are attributed to the alloying of the wetting layers and the phonon confinement in the Ge dots, respectively. From the polarization dependence Raman spectrum, we find the possibility of the strong intersubband absorption in the dots.

5:00pm **NS-TuA10 Surface Oxidation of Germanium Quantum Dots Produced by a Laser Vaporization-Controlled Condensation Technique***, **S. Li**, S. Wen, M. Wiess, J.A. Carlisle, M.S. El-Shall,* Virginia Commonwealth University

Weblike aggregates of coalesced Ge quantum dots are produced by a laser vaporization-controlled condensation technique. The surface oxidation of Ge quantum dots is studied with Fourier-Transform Infrared Spectroscopy (FTIR), core-level X-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD). The freshly prepared Ge particles possess the bulk Ge crystal lattice. After the particles are removed from the reaction chamber for 10 min, the surface of the particles becomes oxidized as seen by XPS and FTIR. However, the FTIR peaks are very weak. Further oxidation of the Ge core, by exposure of the Ge quantum dots to air, results in the epitaxial growth of surface oxidation layers, as confirmed from XRD and XPS. After the particles are stored in air for two months, sharp features corresponding to crystalline GeO@sub 2@ are observed in the XRD spectrum. The surface-oxidized Ge quantum dots do not show photoluminescence from the core Ge particles, but rather show the emission characteristics of GeO@sub 2@, with photoluminescence lifetimes less than 20 ns. The photoluminescence is thus attributed to defect states in GeO@sub 2@.

Organic Electronic Materials Topical Conference
Room 327 - Session OE+BI+EM-TuA

Organic Thin Film Growth

Moderator: N. Karl, Universität Stuttgart, Germany

2:00pm **OE+BI+EM-TuA1 Structural Characterization of Organic Overlayers Physisorbed on the Surface of Self-Assembled Monolayers (SAMs) of Alkanethiols on Au(111)***, P. Schwartz, D.J. Lavrich, M.C. Gerstenberg, **G. Scoles**,* Princeton University **INVITED**

We have been able to grow well-ordered crystalline monolayers of alkylthiols, and multilayers of dodecane on the surface of alkanethiol SAMs by exposing the surface of the c(4x2) phase of the SAM to the appropriate amount of flux at carefully controlled temperatures. Low energy atomic diffraction shows that all but one of the overlayers proved to be considerably more ordered than the underlying c(4x2) surface as judged by the specular and diffraction peak intensities. While the surfaces of the dodecane overlayers have the same structure whether grown on a C@sub 11@SH or C@sub 10@SH c(4x2), monolayers of C@sub 10@SH on a C@sub 10@SH c(4x2) surface were distinctly different from and of higher quality than monolayers of C@sub 11@SH on a C@sub 11@SH c(4x2) surface. Debye Waller measurements reveal that, besides improving the overall order of the surface, an overlayer has a stiffer surface than the underlying c(4x2) that supports it. Temperature Programmed Desorption experiments have shown that, although the adsorption energy of organic molecules on a gold surface is much greater than that of the bulk heat of vaporization, the adsorption energy of an overlayer on an organic substrate is similar to the bulk value of the overlayer substance as soon as the metal-overlayer distance is greater than 5 Å. To the best of our knowledge, this is the first time that, making use of the great surface specificity of low energy atomic scattering, organic monolayers are structurally characterized after adsorption on an organic substrate of different structure.

2:40pm **OE+BI+EM-TuA3 Influence of Lattice Misfit on Morphology of Vanadyl-Phthalocyanine Epitaxial Thin Films and Their Growth Mechanisms***, **S. Nakao**, H. Hoshi, K. Ishikawa, H. Takezoe,* Tokyo Institute of Technology, Japan

In organic molecular beam epitaxy (MBE) process, the lattice matching condition has been considered not so critical for the epitaxial growth because of the weak interaction between organic molecules and substrates. In fact, however, the morphology of the MBE films depends on the species of substrates. Hence the systematic study for the parameters affecting the MBE growth is required. In this paper, we first demonstrate the influence of lattice misfit on the morphology of vanadyl-phthalocyanine (VOPc) MBE films on alkali-halide (AH) substrates. Substrates with continuously varied lattice constants were prepared by using KCl/KBr mixed crystals, supplying the positive and negative lattice misfit. The domain size of the VOPc MBE film becomes larger as the lattice misfit becomes smaller. This fact indicates that the lattice misfit plays an important roll in organic MBE processes and the smooth large domain could be grown under the zero-misfit condition. We also discuss the growth mechanism in the same system. The reflection high energy electron diffraction (RHEED) study showed that the lattice of the VOPc films is commensurate with that of the substrate in spite of large lattice misfit up to 5%, and then rapidly relaxes to the stable lattice constant independent of lattice misfit. More detailed study of the growth process clarified that the process takes two steps; The 2-dimensional (2-D) tetragonal lattice grows at first and the 3-D monoclinic domains nucleate and grow from the edge of the first layer when the first layer reaches a certain height defined by the lattice misfit. This two-step growth process is thought to be typical in MBE growth of VOPc on AH substrates.

3:00pm **OE+BI+EM-TuA4 Preferential Orientation of Copper Phthalocyanine Molecular Columns on Vicinal Si(001)-(2x1)-H***, M. Nakamura,* JRCAT-ATP, Japan*; T. Matsunobe,* Toray Research Center, Inc., Japan*; **H. Tokumoto**,* JRCAT-NAIR, Japan

Fabrication of Pc films on silicon substrates has an advantage in terms of having electrical interfaces with silicon devices. Furthermore, it is a great scientific interest to study organic film growth on various atomically controlled surfaces utilizing well established methods to prepare clean silicon surfaces with a chemical passivation by hydrogen. In our previous work,@footnote 1@ we investigated the molecular arrangement of CuPc films on atomically flat Si(001)-(2x1)-H. Atomic force microscopy (AFM) showed that the molecular column laid parallel to the surface, and the orientational angle between the column and the substrate directions was around 17°. The angle was also supported by molecular mechanics (MM) simulations using simple atom-atom van der Waals potentials. The results suggested that the CuPc crystals were placed so as to make the linear corrugation of the surface parallel to the substrate H rows, although their periods were still incommensurate with each other. In this work, we therefore used vicinal Si(001)-(2x1)-H as substrates which contain atomic steps of approximately 4 nm period to further control the in-plane orientation. A continuous film of which thickness was distributed within 16.5±2.5 molecular layers was grown at 60°C. 90% of the molecular columns in the film were estimated to be aligned to across the step rows by observing a frictional force image. The preferential orientation is considered to be due to a kind of artificial surface lattices which are formed with the striped 'effective contact area' between the rigid Pc crystals and the vicinal surfaces. Detailed discussions and optical property of the films will be presented. @FootnoteText@ @footnote 1@M. Nakamura and H. Tokumoto, Surf. Sci. 398 (1998) 143.

3:20pm **OE+BI+EM-TuA5 Long Range Crystalline Order for Thin Films of an Organic Salt Grown by Low Pressure Organic Vapor Phase Deposition**, ***M. Deutsch***, *S.R. Forrest, M.C. Gerstenberg,* Princeton University*; H.F. Gossenberger, V.S. Ban,* PD-LD Inc.

There is a growing interest in new organic materials with large second-order hyperpolarizabilities, ß, for use in nonlinear optical (NLO) devices. In particular, small organic-molecule salts can exhibit very large ß, due to their non-centrosymmetric crystal structure. The organometallic charge-transfer salt DAST is an ideally suited material for NLO device applications, having a large electro-optic (EO) coefficient and low dielectric constants, which eventuate in a high figure of merit. Thin films of DAST with very long-range structural ordering were grown by organic vapor phase deposition (OVPD). In this technique vapor transported precursors of the stilbazole and methyl-tosylate combine on a substrate in the heated zone of a low pressure, hot wall reactor. This method enables the stoichiometric growth of polar, multiple-component compounds with highly incongruent vapor pressures, which cannot be otherwise deposited by vacuum evaporation. The DAST films were grown on amorphous TiO2 substrates, which was pre-sputtered on thermally oxidized [111] Si wafers. The films exhibit very long-range structural ordering, limited only by substrate size. The strong azimuthal dependence of the relative second harmonic generation (SHG) efficiencies, together with polarized microscopy studies indicate that the structural ordering extends typically ~2 cm across the substrate surface. Using x-ray diffraction we have identified the films as consisting of the SHG-active crystalline phase of DAST belonging to the monoclinic space group Cc, with a well-defined [001] orientation with respect to the substrate normal. Such very long-range crystalline order is a prerequisite for realizing high-performance, low-loss NLO devices.

3:40pm **OE+BI+EM-TuA6 Control of Self-Assembled Monolayer Film Structure and Properties**, *P.S. Weiss,* ***L.F. Charles***, *L.A. Bumm, T.D. Dunbar, D.L. Allara,* The Pennsylvania State University

Scanning tunneling microscopy (STM) has been used to investigate self-assembled film formation of molecules in single and varied compositions of alkanethiols on Au(111). While the average surface composition of these films typically reflects that of the deposition solution, STM is used to determine the position and motion of these molecules on the surface. We also use STM to measure electron transport through these molecules to ascertain the roles of chain length and chemical contact with the substrate. We discuss how spacer molecules such as adamantanethiol (C10H15SH) can be used to isolate other molecules for such studies. Our investigation of this system shows that ordered films can be produced from such molecules for this purpose. Unlike alkanethiolate films, this produces structural domain boundaries and other defects that do not involve significant conformation relaxation. In our studies we focus on the modification of self-assembled surfaces to tailor the films to our needs. Our growing abilities to control the placement of molecules within these films are presented.

4:00pm **OE+BI+EM-TuA7 Growth, Modification, and Control of the Structures of Mixed Composition Organic Monolayers**, *T.D. Dunbar,* The Pennsylvania State University*; T.P. Burgin, J.M. Tour,* The University of South Carolina*; D.L. Allara,* ***L.A. Bumm***, The Pennsylvania State University

Control of the molecular-scale structure of multi-component self-assembled of organic thiols on Au(111) can be achieved by selecting a combination of deposition and processing techniques. These include competitive adsorption (growth) and subsequent exchange (modification). The effects of this processing on the molecular-scale structure have been studied by conventional and AC scanning tunneling microscopy. Lateral epitaxy has been observed where a growing domain of one molecular species is grafted onto an existing crystalline lattice of a different molecular species with no lattice mismatch. In other examples, the limited substrate access afforded by structural defects in the films has been utilized to insert single molecules for further use or study. We also use these mixed composition monolayers to gain insight into the mechanism by which these films can be imaged and the extent to which organic molecules conduct. By analyzing images and local spectra of isolated and aggregated molecules, we can determine the extent to which neighboring molecules contribute to these processes. We believe that none of the structures we obtain are equilibrium structures. We discuss relevant considerations for stabilizing the nanometer-scale structures created.

4:20pm **OE+BI+EM-TuA8 A Grazing Incidence X-ray Diffraction Study of the Organic-Organic Interface for PTCDA Films Grown on Self-assembled Monolayers of Thiols on Gold**, ***M.C. Gerstenberg***, Princeton University*; F. Schreiber,* Max-Planck-Institut für Metallforschung, Germany*; P. Fenter,* Argonne National Laboratory*; T.Y.B. Leung, S.R. Forrest, G. Scoles,* Princeton University

We present results from a grazing incidence X-ray diffraction study of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) films deposited on self-assembled monolayers (SAMs) of either decanethiols or 1,6 hexanedithiols on Au(111). The aim is to study the effect of changes at the organic-organic interface on the in-plane ordering of PTCDA and the SAM. Changing the number of chemisorbed Sulphur (S)atoms in the layer between the PTCDA and the metallic substrate is of interest in view of the importance of the charge injecting properties of the organic-inorganic interface in organic semiconductor devices. PTCDA is one of the most thoroughly studied van der Waals epitaxial systems. It has previously been shown that under non-equilibrium growth conditions (high incident flux of PTCDA and low substrate temperature) PTCDA layers order parallel to the Au(111) substrate with a well-defined in-plane structure in registry with the underlying substrate. Under the same conditions our first measurements have indicated an unaltered PTCDA in-plane ordering on both thiol SAMs. However, the orientation of the PTCDA in-plane structure changes with respect to the Au surface in both cases. No change in the ordering of the thiols was observed as the PTCDA was deposited. The confined full coverage c(4x2) layer of decanethiols melts at higher temperatures than the unconfined SAM. With melting, the order of the SAM was lost and was not fully recovered upon cooling. However, no significant change was seen in either the out-of-plane or in-plane scattering of PTCDA.

4:40pm **OE+BI+EM-TuA9 The Adsorption of azo Compounds on Si(001)**, ***M.D. Ellison***, *R.J. Hamers,* University of Wisconsin, Madison

Recent investigations have demonstrated that unsaturated organic compounds can bond to the Si(001) surface by interaction of the C=C bond with the Si=Si dimers, forming a 4-member Si@sub 2@C@sub 2@ ring at the interface. We have investigated whether analogous reactions can be used to link azo bonds (N=N) to the Si(001) surface using XPS, FTIR, STM, and ab initio calculations. The experimental evidence indicates that the unsaturated N=N bond reacts with a Si=Si dimer in an analogous fashion to a [2+2] cycloaddition reaction, forming a 4-member Si@sub 2@N@sub 2@ ring. Although the thermal [2+2] reaction is forbidden by symmetry considerations, this and other studies have shown the reaction of unsaturated bonds with the Si(001) surface to be quite facile. The facility and selectivity of this reaction reveals the potential of azo compounds to be used in creating ordered organic layers on a Si(001) surface.

Plasma Science and Technology Division

Room 318/319/320 - Session PS+MS-TuA

ULSI Technology

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

2:40pm **PS+MS-TuA3 Front End Integration for ULSI Technologies**, ***W.A. Mueller***, SIEMENS Microelectronics, DRAM Development Alliance, Germany **INVITED**

Key frontend integration challenges for sub 0.25 µm technologies will be discussed. For device isolation shallow trench isolation (STI) has emerged as the main road; the different approaches for STI fill and planarization will be evaluated. For the transistor integration shallow retrograde wells, sub 5 nm gate dielectrics, dual work function gates and shallow source/drain junctions are the key technologies. Logic and DRAM applications are posing different boundary conditions for integration, thus leading to different solutions for the device architecture. For high packing density memory arrays and cell based designs selfaligned contact- and local interconnect schemes has to be integrated in the frontend process flow. As a DRAM specific topic the integration challenges for trench- and stack capacitors will be addressed.

3:20pm **PS+MS-TuA5 Transient Diffusion Effects in Silicon Technology**, ***C.S. Rafferty***, Bell Laboratories, Lucent Technologies **INVITED**

In modern silicon technology, there is a steady trend to reduce the "thermal budget" of fabrication processes. The intent has been to reduce the thermal diffusion of dopants. However low temperatures have exposed significant non-equilibrium diffusion effects. The most striking of these, transient enhanced diffusion, causes many unexpected influences on devices. Transient diffusion (TED) is the enhanced diffusion rate of dopants due to point defects introduced during ion implantation. The enhancement can be as much as four decades above thermal diffusion rates. TED by its nature is cooperative in nature, where implanting one species can lead to enhanced diffusion of all the other species in the wafer, even those located some distance from the implantation window. The effects of such local and remote diffusion transients on transistors is manifold. In some cases, the transistors may fail completely to function as intended, in others, their properties may be degraded or shifted from their intended targets. This talk describes some of the experimentally observed impacts of transient diffusion in technology. It is shown how a better understanding of the materials science involved can lead to better devices.

4:00pm **PS+MS-TuA7 Technology Requirements for Logic ICs*, M. Brillouët,*** France Telecom, France **INVITED**

The logic ICs are targeting an higher packing density for increased performances and cost effective manufacturing. In the 'front-end' part of the process (i.e. the transistor and the lateral isolation), this higher integration is obtained - along with higher operating frequencies and reduced power consumption - in shrinking the feature sizes. As the materials stay basically the same (i.e. Si and SiO@sub 2@), this trend stresses strongly the photolithographic techniques : the etch process has to define structures at the atomic level ; selectivity, CD and profile are key parameters to control in these features with such an high aspect ratio. The density of the interconnections ('back-end' part of the process) can be improved by shrinking the feature sizes and by increasing the number of metal layers. Unfortunately, if one stays with the classical Al/SiO@sub 2@ system, while shrinking the metal pitch, the performance of the integrated circuit is degraded : there is thus a growing need to move to new materials (e.g. dual Damascene copper lines and insulators with a lower dielectric constant). Advanced developments will be required in the etching of these materials and, due to the introduction of the Damascene approach, the equipment set will be radically changed in a manufacturing line. The metallisation process impacts strongly the behaviour of the transistor : plasma induced damage during processing degrades the active devices and specific care need to be taken in order to minimize this detrimental effect. Finally, as the number of metal levels is increased, manufacturability is a major issue in the cost of the final product: improving the defectivity level of the interconnects is a key point, as more than half the process steps are now involved in the fabrication of the interconnection system.

4:40pm **PS+MS-TuA9 Advanced Deep-UV and 193 nm Optical Lithography: The Role of Resists, Reflectivity Control and Resolution Enhancement Technologies*, O. Nalamasu*,** *R.A. Cirelli, G.P. Watson,* Bell Laboratories, Lucent Technologies **INVITED**

The fabrication of integrated circuits with optical lithography faces several challenges as the industry is moving from I-line to deep-UV and 193 nm lithographies. For the immediate future, the technical challenges in developing manufacturing processes with k values below 0.5 have been identified and are the subject of intense R&D activity across the world. The low k lithography solution requires fundamental understanding of, as well as innovations in optical and resist materials, reflectivity control and resolution enhancement (mask and optical) techniques. In this presentation, we will detail our research efforts in Resist materials, Reflectivity control and Resolution enhancement techology areas with special emphasis on 193 nm lithography and identify the issues and opportunities in extending the optical lithography for patterning sub-0.1 µm devices. We will also demonstrate 60 nm resolution with 193 nm lithography by combining research advances in single layer resist, dielectric anti-reflective layer/hard mask with a levenson phase-shifting mask.

Surface Science Division
Room 308 - Session SS1-TuA
Semiconductor Surface Chemistry

Moderator: J.A. Yarmoff, University of California, Riverside

2:00pm **SS1-TuA1 The Effect of Phosphorus and Germanium on Silicon Surface Chemistry*, J.E. Crowell*,** *M.L. Jacobson, G.J. Batinica, M.C. Chiu,* University of California, San Diego

Our studies focus on the deposition surface chemistry of Group IV semiconductors. We have examined the effect that adatoms such as P, Ge, and both P/Ge have on (i) the Si precursor chemisorption behavior and (ii) the hydrogen desorption behavior. Surface phosphorus contains a lone pair of electrons rather than a dangling bond and is thus passive to adsorbing gas molecules, and acts as a site blocker to species diffusing on the surface. In contrast, Ge adatoms contain a dangling bond and behave in a way similar to Si. However, both adatoms modify the surface chemistry of silicon. This presentation will describe TPD, AES, and MIRIRS studies aimed at determining the effect of pre-adsorbed P and Ge on the reactivity of Si(100) and Si(111) surfaces. For example, disilane (Si@sub 2@H@sub 6@) reacts with the Si(100) surface at 300K to form a mixture of SiH@sub x@ species. At higher temperatures, recombination reactions occur which produce silane (SiH@sub 4@) and H@sub 2@ that subsequently desorb. The reactivity of the Si(100) surface decreases with increasing P coverage, as determined by the increase in the selectivity of the Si@sub 2@H@sub 6@ reaction toward SiH@sub 4@ production over H@sub 2@ production. The H@sub 2@ desorption temperature increases with increasing P coverage while the SiH@sub 4@ desorption temperature decreases. A similar increase in H@sub 2@ desorption energy was seen upon H atom exposure of the P/Si surface, whereas Ge pre-adsorption decreases it. These results, a comparison of the (100) and (111) Si surfaces, and the combined effect of P and Ge will be discussed within the framework of electronic and morphological modifications of the surface and ensemble size effects caused by the presence of these pre-adsorbed adatoms.

2:20pm **SS1-TuA2 In situ Boron Doping of Si(100): Effects of Low Boron Concentration on Hydride Surface Reactions*, B. Gong*,** *D.E. Brown,* University of Texas, Austin*; S.K. Jo,* Kyung Won University, South Korea*; J.G. Ekerdt,* University of Texas, Austin

Hydrogen desorption and hydride adsorption will potentially control film growth rates during in situ doping of Si(100) in chemical vapor deposition processes involving hydride gases. The reactions of hydrogen and disilane with boron-doped Si(100) have been studied with temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED). Recent studies by our group have been conducted in the boron concentration range from 0.001 to 0.05 monolayer (ML) to illustrate the kinetic effects of in situ doping, which has a typical doping level of 10@super 16@-10@super 20@ cm@super -3@. With ~0.001 ML boron, TPD and HREELS show essentially no dihydride formation on the boron doped surface. After H-passivation, the boron doped surface (@theta@@sub B@~0.001 ML) shows a 2x1 reconstruction by LEED, while the H induced reconstruction on a clean surface at the same conditions shows a 3x1 reconstruction. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boron-induced silicon dimer vacancy defects. At slightly higher @theta@@sub B@, monohydride starts to be suppressed and decreases with increasing @theta@@sub B@. At @theta@@sub B@= 0.01 ML, monohydride formation decreased 15% and then more slowly with increasing boron coverage due to islanding. A boron electronic effect that deactivates silicon dangling bonds reduces active sites on the surface, which in turn shows less monohydride adsorption with increasing @theta@@sub B@. The saturation coverage of disilane decreases with increasing @theta@@sub B@ due to less dangling bonds as a result of the boron deactivating effect. However, the disilane adsorption rate increases with @theta@@sub B@ while the hydrogen desorption rate is not affected by the addition of boron. We propose that the boron effects on silicon deposition rate is a result of enhanced disilane adsorption rather than enhanced hydrogen desorption.

2:40pm **SS1-TuA3 Chemical Modification of Semiconductor Surfaces: Functionalization Using Cycloaddition Reactions*, S.F. Bent*,** New York University **INVITED**

Due to the increasing importance of organic-based electronic and optical devices, there is much interest in developing attachment chemistries to join organic structures with inorganic semiconductor substrates. In this presentation, the use of unsaturated hydrocarbons to form the initial organic layer by direct bonding to silicon and germanium surfaces in vacuum will be discussed. A series of unsaturated molecules, both cyclic and non-cyclic, have been investigated using various methods including multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, near-edge X-ray absorption fine structure (NEXAFS), and temperature-programmed reaction/desorption (TPR/D). Conjugated dienes such as butadiene can undergo Diels-Alder-like [4+2] cycloaddition reactions on both Si(100)-2x1 and Ge(100)-2x1 surfaces, whereas non-conjugated dienes and alkenes react by direct [2+2] addition. The relative reactivity of Si(100)-2x1 and Ge(100)-2x1 toward unsaturated molecules will be compared. An overview of the bonding and thermal reactivity of the different compounds will be presented, and the potential for these types of cycloaddition reactions in future applications will be discussed.

3:20pm **SS1-TuA5 Cycloaddition Reactions at Germanium Surfaces***, S.W. Lee, L.M. Nelen,* University of Missouri, Columbia*; H. Ihm,* University of Texas*; **C.M. Greenlief**,* University of Missouri, Columbia

The adsorption and reaction of a number of cyclic unsaturated hydrocarbons with the Ge(100) surface is investigated. It is shown that well-defined ordered organic layers can be formed on semiconductor surfaces. On semiconductor surfaces the majority of the reactions with hydrocarbons occur at or near the dangling bonds of the reconstructed surface. The dangling bonds on a Ge(100)-(2x1) surface are arranged in surface dimers. This arrangement of dangling bonds means that it is possible to form a molecularly ordered thin film that is covalently bound to the surface, provided that one can have the reaction occur at the dangling bond sites. In this paper we present an investigation of the structure and chemical bonding of the organic film/semiconductor interface. Data are obtained for a number of different starting precursor molecules using photoelectron spectroscopy, high resolution electron energy loss spectroscopy and temperature programmed desorption. The molecules investigated include 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene. The possibility of a surface Diels-Alder [4+2] cycloaddition, as well as, a [2+2] cycloaddition reaction are explored. Either cycloaddition reaction leads to an organic layer that is ordered with respect to the germanium surface.

3:40pm **SS1-TuA6 Binding Energies of Hydrogen on Flat and Vicinal Silicon Surfaces***, **M.B. Raschke**, U. Höfer,* Max-Planck-Institut für Quantenoptik, Germany

Despite the importance of hydrogen interaction with silicon in many technological applications and its role as a model system for chemisorption on semiconductor surfaces, the binding energy of hydrogen on silicon surfaces is not well known. In a novel experimental approach, a bakeable UHV-quartz apparatus was used to establish thermal equilibrium between molecular hydrogen and well-defined Si(111) and Si(001) surfaces at gas pressures of 10@super -5@ 1 mbar and temperatures of 770 - 980 K. Under these conditions, continuous dissociative adsorption and recombinative desorption of H@sub 2@ lead to an equilibrium hydrogen coverage on the surfaces which is measured sensitively using optical second-harmonic generation (SHG). The resulting adsorption isotherms allow for the accurate determination of the hydrogen binding energies and their dependence on surface coverage. In the case of H/Si(111)7x7, the binding energy increases from 2.9 eV to 3.1 eV in the investigated coverage range between 0.05 ML and 0.3 ML. The Si-H bond is thus found to be considerably weaker than hydrogen bonding in silanes (3.7-3.9 eV). The values are compatible with a large barrier (0.9 eV) for phonon-assisted sticking of H_2/Si.@footnote 1@ They are in good agreement with theoretically predicted Si-H bond strengths at the adatoms and restatoms of this surface.@footnote 2@ Exploiting substantial differences in reactivity between the step and terrace sites towards molecular hydrogen, equilibrium and non-equilibrium hydrogen coverages on vicinal Si(001) could also be investigated. From measurements for various surface temperatures on samples with different angles of miscut it is inferred that the steps are thermodynamically favored by approximately 0.2 eV. @FootnoteText@ @footnote 1@P. Bratu and U. Höfer, Phys. Rev. Lett. 74 (1995) 1625. @footnote 2@H. Lim, K. Cho, I. Park, J. D. Joannopoulos, and E. Kaxiras, Phys. Rev. B 52 (1995) 17231

4:00pm **SS1-TuA7 The Reactions of Trimethylgallium and Ammonia on GaN(0001)***, **H.-T. Lam**, J.M. Vohs,* University of Pennsylvania

The reactions of trimethylgallium and ammonia on MOVPE-grown GaN(0001) were studied using temperature programmed desorption, high-resolution electron energy loss spectroscopy, Auger electron spectroscopy, and Rutherford backscattering spectrometry. The results of this study show that TMGa dissociates on GaN(0001) to form monomethylgallium (MMGa) and/or dimethylgallium (DMGa) and surface methyl groups at temperatures above 250 K. The MMGa/DMGa species either desorb between 250 and 450 K or undergo further dissociation forming adsorbed methyl groups and Ga atoms. For low TMGa coverages, surface methyl groups desorb near 600 K producing gaseous methyl radicals. At higher coverages a fraction of the methyl groups undergo dehydrogenation produces methane at 590 K and surface carbon atoms. The reaction of ammonia on GaN(0001) was found to proceed via dissociation to form surface NH@sub x@ species and atomic hydrogen above 300 K.

4:20pm **SS1-TuA8 An Investigation of the Surface Reaction Mechanisms of Alternating-Grown Ordered Layers: CdS on ZnSe(100)***, **M. Han**, Y. Luo, J.E. Moryl, R.M. Osgood, Jr.,* Columbia University

In previous experiments we have found that ordered layers of CdS on ZnSe(100) substrate were formed by a binary surface reaction sequence using gas-phase dosing of the substrate with (CH@sub 3@)@sub 2@Cd and with H@sub 2@S. This system provides a prototypical example of the interplay between reaction and desorption in such a binary sequence. In this talk we report a careful investigation of the surface chemistry using TPD. The experiments were performed in a UHV chamber, which is also equipped with AES, LEIS and LEED. Analysis of the TPD spectra show clearly that adsorbed DMCd irreversibly dissociates on ZnSe(100)-c(2x2) surface, and that the previously reported self-limiting reaction results from a methyl-termination of the surface. At ~ 370K, DMZn desorbs from this surface due to a methyl exchange reaction. This desorption temperature is independent of coverage, indicating a first-order reaction. In addition, at high DMCd exposures, the adsorption and desorption process leads to replacement of surface Zn by Cd. The experiments have also examined the reaction of the methyl-terminated surface with H@sub 2@S. This reaction is also self-limiting, yielding desorbed CH@sub 4@ and forming a sulfur-hydride-terminated surface. Studies of surfaces formed by more than one binary reaction sequence showed that the alternating growth surfaces are also terminated with either methyl group or sulfur-hydride. The methyl-passivated surface above the first layer preferentially desorbs methyl radicals at ~390K instead of metal-alkyl species. For the sulfur-hydride-terminated surface the recombinative reaction of HS species causes desorption of H@sub2@S at 480K. In this case, the symmetric peak shape and its shift to lower temperature with increasing the coverage suggest a second-order reaction mechanism. In more general terms the above results indicate that the relative strengths of bonding energy for methyl-metal(II) and metal-VI element play an important role in the surface reactions.

4:40pm **SS1-TuA9 Competition Between Passivating and Etching in Halogen Reactions with III-V Semiconductor Surfaces***, **W.K. Wang**,* University of California, Riverside*; W.C. Simpson,* Pacific Northwest National Laboratory*; J.A. Yarmoff,* University of California, Riverside

Halogen adsorption on III-V semiconductor surfaces with certain reconstructions leads to the formation of an ordered overlayer, while other III-V surfaces become disordered and etch. It has been suggested that the initial atomic structure and stoichiometry play important roles in determining whether a surface passivates or etches. A single crystal face of a given III-V material can have many surface reconstructions, each of which has a slightly different stoichiometry in the outermost few atomic layers. In this study, a direct comparison is made of the adsorption of halogens on different reconstructions of the same material. From the results, the microscopic mechanism underlying the predilection for ordering or disordering can be ascertained. Synchrotron-based soft x-ray photoelectron spectroscopy and low energy electron diffraction were employed to investigate surfaces following reaction. These techniques provide information about the chemical bonding and ordering on the surface. For example, for I@sub 2@ reaction with the In-terminated InAs(100)-c(8x2) surface, a well-ordered (1x1) structure forms and all of the iodine attaches to In. The As-terminated InAs(100)-c(2x8) surface, on the other hand, becomes disordered and iodine attaches to both In and As atoms. This can be explained by a preference for iodine to initially bond with the electron-deficient group III In atoms. In contrast, I@sub 2@ reaction produces ordered structures on both the Ga-terminated and As-terminated GaAs(100) surfaces. Cl@sub 2@ reactions almost always lead to etching after sufficient exposures, no matter what the initial surface structure, although following small exposures some ordered structures may form. In this presentation, the microscopic mechanisms underlying this behavior will be discussed.

5:00pm **SS1-TuA10 A Scanning Tunneling Microscopy Study of [(t-butyl)GaS]@sub 4@ Adsorption on GaAs***, **R.I. Pelzel**,* University of California, Santa Barbara, U. S. A.*; B.Z. Nosho,* University of California, Santa Barbara*; B. Fimland,* Norwegian University of Science and Technology, Norway*; W.H. Weinberg,* University of California, Santa Barbara

Gallium sulfide layers grown using the single-source molecular precursor [(t-butyl)GaS]@sub 4@ have shown promise in providing long-term chemical and electrical surface passivation for GaAs.@footnote 1@ With this in mind, we have conducted an ultrahigh vacuum investigation of the initial stages of [(t-butyl)GaS]@sub 4@ adsorption on GaAs(100)-(2x4) and (4x2). Adsorbing [(t-butyl)GaS]@sub 4@ at elevated surface temperatures (> 650 K) results in carbon-free adsorption as judged by Auger electron spectroscopy. For low coverages on both reconstructions, low energy electron diffraction (LEED) data indicate that both the (2x4) and the (4x2) surface reconstructions remain intact. Scanning tunneling microscopy (STM) images show that the adsorption of submonolayer coverages of [(t-butyl)GaS]@sub 4@ disorders the surface reconstructions. Subsequent deposition results in further disordering until a coverage of approximately 1 ML where a weak (2x1) LEED pattern is observed. The (2x1) surface order is not observable in STM prior to annealing to a temperature of approximately 780 K. The (2x1) surface observed using STM following annealing is well-ordered, and images will be presented. Possible models of GaS growth achieved using [(t-butyl)GaS]@sub 4@ will be discussed. @FootnoteText@ @footnote 1@ P. P. Jenkins, A. N. MacInnes, M. Tabib-Azar, and A. R. Barron, Science 263, 1751 (1994); A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 62, 771 (1993); M. Tabib-Azar, S. Kang, A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 63, 625 (1993).

Surface Science Division
Room 309 - Session SS2-TuA
Morton M. Traum Student Award Session

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

2:00pm **SS2-TuA1 Hot Ethene Desorption by Dissociative Electron Attachment of Adsorbed Halocarbons***, **A.S.Y. Chan**[1], R.G. Jones,* University of Nottingham, United Kingdom

The electron stimulated reactions of adsorbed 1,2-dihalocarbons have been studied by measuring the time-of-flight (TOF) velocity distributions of the ethene product ejected from the surface. Both 1,2-dichloroethane (DCE) and 1-bromo-2-chloroethane (BCE) have been found to undergo dissociative electron attachment from secondary electrons generated by a pulsed 2 keV electron beam impinging on the Cu(111) surface, leaving chemisorbed halogens and ethene desorbing in the gas phase. The TOF distributions of the ethene product from both adsorbate molecules are quite similar; both exhibit a bimodal distribution with a hyperthermal channel of ~ 1200 K and a slow channel of ~ 200 K. When the distributions obtained from identical coverages of DCE and BCE are compared, a consistently smaller intensity of the slow channel is observed from the latter molecule. This slow component appears to grow with increasing number of adsorbed layers, indicating that it is most likely due to ethene molecules that have thermalised by interactions with the adsorbate. By comparing the possible dissociation dynamics of the two molecules, we discuss the possibility that a direct dissociation of the adsorbed molecule after electron capture, rather that a surface-mediated energy transfer mechanism, may be responsible for the high translational energy of the hyperthermal ethene.

2:20pm **SS2-TuA2 Combined Experimental and Quantum Chemistry Study of the Disproportionation of Dimethylalane on Aluminum Surfaces***, **B.G. Willis**[2], K.F. Jensen,* Massachusetts Institute of Technology

A combined experimental/theoretical approach has been employed to study the decomposition reactions of trimethylaluminum and dimethylalane on aluminum surfaces. Together with UHV surface science experiments, plane wave pseudopotential density functional theory calculations have been implemented to augment the experimentally derived reaction mechanism. The plane wave surface calculations provide additional details of the surface reactions not easily probed with experiments, and where the two approaches overlap, comparisons are made. Dimethylalane is found experimentally to decompose on aluminum via a disproportionation reaction to produce trimethylaluminum. Trimethylaluminum follows the same reaction pathways on aluminum, but due to the difference in stoichiometry there is no net growth, and a dynamic equilibrium exists between the gas phase and surface at low temperatures. Based on the experimentally observed mechanism, the calculations are employed to generate thermodynamic heats of reaction for each elementary reaction step, and a complete mechanism is presented for the surface reactions. Results suggest exothermic steps for breaking down the dimethylalane and trimethylaluminum monomers to surface monomethylaluminum fragments. Further decomposition of these fragments, the desorption of hydrogen, and additional recombination reactions are found to be endothermic. The overall heat of reaction is calculated to be approximately -16 kcal if written in terms of monomeric gas phase units. If it is considered that trimethylaluminum and dimethylalane may exist as dimer gas phase units, the reaction is endothermic by approximately 16 kcal. At high temperatures both dimethylalane and trimethylaluminum share a strongly activated pathway for methyl dehydrogenation which produces a carbon contaminated surface. The experimental barrier is found to lie near 40 kcal for the methyl decomposition reaction. Theoretical calculations of this impurity incorporation pathway predict a methyl decomposition activation barrier near 40 kcal, in good agreement with experiments. The full ab initio model includes elementary reactions leading to growth, surface diffusion of the active methyl groups, methyl decomposition reactions to produce surface carbon, and the alternative (not experimentally observed) surface reaction pathway to form methane. Comparisons are made where both theory and experiment overlap and agreement is found to be good (within approximately ±5 kcal).

2:40pm **SS2-TuA3 Low-Symmetry DFT Diffusion Barriers and Dimer Dynamics in Homoepitaxial Growth of Al(111)***, **A. Bogicevic**[3], J. Strömquist, P. Hyldgaard, G. Wahnström, B.I. Lundqvist,* Chalmers Univ. of Tech. and Göteborg Univ., Sweden

From fractals to compact islands, epitaxial growth offers an exotic variety of surface morphologies that emanate from a handful of elementary atomic diffusion processes. Adsorption calculations have hitherto been limited to high-symmetry configurations, or to semi-quantitative methods. Using extensive density-functional calculations on parallel computers, we map out barriers for self-diffusion at steps, kinks, and corners on Al(111). The results include an unexpected exchange mechanism at kinks and a large barrier anisotropy at corners. Using transition state theory we are able to transform the barriers into a set of activation temperatures and hereby predict various growth modes as a function of temperature. New STM experiments confirm four of our main results in great detail, including the fractal-compact island transition and the transition to equilibrium shaped islands. The central role dimer stability and mobility plays during nucleation and in later stages of growth has motivated us to study Al dimer diffusion at 0 and 5% compressive strain. The smooth potential energy surface enables a long-ranged attraction between the dimer atoms, leading to a substantial temperature window in which dissociation is frozen and fascinating dimer dynamics takes place. Surface relaxations play a prominent role in the uncovering of unexpected ground states, which should be easy to verify with, e.g., STM measurements of dimer height or dimer direction. A new diffusion mechanism is found, where dimers migrate by concerted sliding. The effect of elastic strain on dimer diffusivity is addressed, and its impact on the epitaxial growth mode is discussed.

3:00pm **SS2-TuA4 STM and LEIS Study of Oxygen-Induced Restructuring of Rutile TiO@sub 2@(110)(1x1) Surface***, **M. Li**[4], W. Hebenstreit,* Tulane University*; D.R. Jennison,* Sandia National Laboratories*; U. Diebold,* Tulane University

The rutile TiO@sub 2@(110) surface is one of the most-popular substrate in the surface science of metal oxides. We show that the exact surface preparation conditions critically influence the surface structure and morphology of this material in a rather unexpected way. TiO@sub 2@(110) surfaces, prepared by sputtering and annealing at 850 K in UHV, exhibit a (1x1) surface termination and flat, several hundred Å wide terraces. After exposure to oxygen at elevated temperatures (onset ~470 K), the surfaces are covered with small (typically tens of Å wide) terraces with monoatomic step height and the same (1x1) structure. On top and in between these terraces appear patches of an irregular network consisting of interconnected rosettes (width ~ 7 Å) with pseudohexagonal symmetry. The positions of atoms within the network are consistent with an incomplete TiO@sub 2@(110) layer. Ab-initio LDA calculations support the stability of the proposed structural model. It contains undercoordinated atoms with an electronic structure that is distinctly different from (1x1) terminated surfaces. LEIS measurements of surfaces annealed in @super 18@O@sub 2@ clearly show that new TiO@sub 2@ layers are formed through outdiffusion of interstitial Ti cations from the reduced bulk to the surface where they react with ambient oxygen. The kinetics of this 'restructuring' mechanism as well as possible implications for the surface chemistry of TiO@sub 2@ are discussed.

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3:20pm **SS2-TuA5 A Study of the Relationship Between Si/SiO@sub 2@ Interface Charges and Roughness***, **L. Lai**[1], K.J. Hebert, E.A. Irene,* University of North Carolina, Chapel Hill

This study examines the correlation between interface micro-roughness and charges. Atomic force microscopy (AFM) and a newly developed area roughness function, A(RMS,D@sub F@)@footnote 1@ which couples two roughness parameters, root mean square (RMS) and fractal dimension (D@sub F@), are used to reliably and accurately characterize surface micro-roughness. For the common surface area computation methods, this leads to large round-off errors. This new area roughness function obviates this problem, and it is not only a sensitive roughness parameter, but also a reliable area extracting tool for surfaces with micro-roughness. Micro-roughness has a small vertical magnitude relative to the large horizontal data sampling interval. Interface charges (D@sub it@ and Q@sub f@) are measured using high frequency and quasistatic capacitance-voltage methods. These charges are reported in per unit area, so in order to obtain reliable charges levels, one must know the area. This study is divided into three parts where smooth, purposely roughened, and purposely smoothened Si substrates are used to make MOS capacitors. For smooth samples, we found that interface charges decrease as the oxidation time increases. Purposely roughened substrates show that there is a correlation between interface roughness and charges. When the correct area, A(RMS,D@sub F@), is used, the excess interface charges due to roughness are accounted for. Roughened then smoothened substrates show that the rate of decrease of the corrected charges with respect to oxidation time become about the same as those from smooth substrates. We conclude that the increases of D@sub it@ and Q@sub f@ with Si roughness are due entirely to the area increase and orientation changes that result from roughness. @FootnoteText@ @footnote 1@ L. Lai and E. A. Irene, J. Vac. Sci. Technol. A. submitted (1998).

3:40pm **SS2-TuA6 The Chemistry and Formation of Ordered Organic Molecular Films on Silicon (001)-2x1 Surfaces***, **J.S. Hovis**[2], R.J. Hamers,* University of Wisconsin, Madison

We have recently developed a novel method for growing ordered organic films on the technologically important Si(001)-2x1 surface. The reaction involves the interaction of a surface Si=Si dimer with a C=C double bond from an unsaturated alkene, resulting in the formation of two new Si-C @sigma@ bonds. Due to the directional nature of @pi@ bonds the Si=Si dimer bond is able to act like a template, controlling the locations and rotational orientation of the individual adsorbed molecules. One unique aspect of this growth method is the fact that the molecules adsorb without dissociation, leading to a well defined interface between the silicon substrate and the organic film. We find that a number of molecules, including cyclopentene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene form films that exhibit in-plane optical anisotropies on the length scales of centimeters when adsorbed on 4°-miscut (single-domain) wafers. The molecules 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene form monolayers that terminate with ordered arrays of C=C double bonds at the vacuum-surface interface and the ability to grow further layers will be discussed. We have also examined the adsorption of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene on the Si(001) surface. These molecules can form two different products on the surface; one of which is more thermodynamically favorable. Our studies show that both possible products are formed, indicating that kinetics play a larger role in the adsorption probability than do thermodynamics. Experimental evidence using scanning tunneling microscopy (STM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) will be shown as will the results of ab inito calculations.

4:00pm **SS2-TuA7 ToF-SIMS Characterization of the Interaction Between Vapor-Deposited Al Atoms and an Ordered Array of Organic Functional Groups***, **G.L. Fisher**[3], A.E. Hooper,* The Pennsylvania State University*; R.L. Opila,* Bell Laboratories, Lucent Technologies*; D.L. Allara, N. Winograd,* The Pennsylvania State University

The room temperature vapor deposition of up to 4Å of Al metal onto monolayers of @omega@-functionalized alkanethiolate molecules, of structure HS-(CH@sub 2@)@sub n@-X, self-assembled on polycrystalline Au was studied using static ToF-SIMS, XPS and IRS. Deposited Al was found to be highly reactive with methylester organic functional groups (OFGs). The data indicate a titration of one Al atom per methylester OFG, and the ether bonds appear to be unperturbed. Thus, deposited Al reacts solely with carbonyl oxygen of the OFG forming a uniform dielectric with an Al-O-C bonding arrangement. Upon saturation of methylester OFGs with deposited Al, further deposition results in formation of metallic overlayers. Deposited Al was found to be unreactive with methyl OFGs. Instead, the deposited Al diffuses through the monolayer to the monolayer/Au interface via thermally activated transient defects. Here, the Al atoms are observed to disrupt the Au-S bonding to form stable Au-Al-S bonds that quench further transient defect formation. As the deposition progresses deposited Al is observed to form islands on top of the monolayer. Island formation in this case is a result of physisorbed Al; no chemical reaction is observed. Penetration of deposited Al through the methylester-terminated monolayer to the monolayer/Au interface was not observed. Reaction between deposited Al and the methylene backbone of methyl-terminated and methylester-terminated monolayers was not observed.

4:20pm **SS2-TuA8 The Reactivity of Surface Defects on the MoS@sub 2@(0001) Basal Plane: Methanethiol and Thiophene Reactivity Studies***, **C.G. Wiegenstein**[4], K.H. Schulz,* Michigan Technological University

Molybdenum disulfide based materials are important industrial catalysts for the removal of aromatic organosulfur compounds from petroleum feedstocks. The removal of sulfur compounds is important since sulfur is a known catalysts poison. Although there have been significant amounts of study on the structure of the industrial hydrodesulfurization catalysts, there is still a significant amount of uncertainity as to the surface chemistry and reactivity of the organosulfur compounds on the catalyst surface. Information on surface intermediates and adsorbate structures is hindered by the high pressures used in commercial HDS reactors. MoS@sub 2@ grows large sheets of sulfur terminated planes which are not catalytically active towards thiophene. Wiegenstein and Schulz@footnote 1@ attempted to prepare basal surfaces with large defect densities using deuterium adsorption, but were not successful. Although defects were produced by adsorption of deuterium atoms on sulfur anions which subsequently desorbed as deuterium sulfide, no significant changes were observed in the population of ethyl-thiolate surface species following repeated sample exposures to atomic deuterium. However, reactive MoS@sub 2@(0001) surfaces have been prepared using short ion bombardment times. Three different surface preparation treatments were used: a freshly cleaved surface; a 30 second ion-bombarded surface; and a 60 second ion-bombarded surface. An increase in the population of the higher temperature state was observed as ion-bombardment time was increased. AES results demonstrated that surface sulfur was preferentially removed via ion-bombardment, and thus, the higher temperature state has been identified as arising from methyl-thiolate adsorption at defect sites thought to be sulfur vacancies. This paper will give the details of these studies, and will report on present efforts examining thiophene decomposition on ion-bombarded MoS@sub 2@(0001) surfaces. Finally, the usefulness of the defective basal plane as a model HDS catalyst will be discussed. @FootnoteText@ @footnote 1@Wiegenstein and Schulz, Surface Science, 396 (1998) 284.

4:40pm **SS2-TuA9 The Influence of Chlorine on the Dispersion of Cu Particles on Cu/ZnO(0001) Model Catalysts***, **A.W. Grant**[5],* University of Washington*; A. Jamieson,* Massachusetts Institute of Technology*; T. Evans,* University of Manchester, United Kingdom, UK*; G. Thornton,* University of Manchester, United Kingdom*; C.T. Campbell,* University of Washington

Adsorbed chlorine is thought to affect the dispersion of metal catalysts on oxide supports. We have studied this by vapor depositing thin films of Cu onto Zn-terminated ZnO(0001), both with and without a pre-exposure of Cl@sub 2@. First, the adsorption of Cl@sub 2@ was studied on ZnO using XPS, LEIS, work function, and band-bending. A close-packed monolayer of Cl adatoms forms at saturation with 0.31 Cl adatoms per Zn site. The work function increase of 2.2 eV indicates anionic Cl@sub ad@. Without Cl@sub ad@, vapor-deposited Cu grows in two-dimensional islands that cover ~33% of the ZnO, after which these islands thicken (i.e., as 3D Cu particles) while the clean ZnO between these Cu islands gets covered with Cu only very slowly. The presence of Cl@sub ad@ decreases the fraction of the surface that is covered by Cu islands by ~3-fold, so Cl@sub ad@ either decreases the number of 2D Cu islands or their critical area before thickening. This is consistent with weaker binding of Cu to the Cl covered surface than to the clean ZnO. In addition, Cl@sub ad@ not only covers the surface of the ZnO, but also covers the surface of the Cu islands, as suggested by the constant Cl-LEIS signal during Cu deposition. This was verified further by following the formate-derived TPD features from

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HCOOH adsorption, which are distinctly different for Cu and Zn sites on Cl-free Cu/ZnO(0001). Pre-dosed Cl virtually eliminated the 575K Zn-formate peak. When Cu was vapor-deposited onto a Cl-precovered surface, neither the Zn- nor Cu- formate peaks were observed. Apparently, Cu displaces some of the Cl adatoms from Zn sites, and they subsequently cover the Cu islands.

5:00pm **SS2-TuA10 Modeling Molybdenum Carbide-Based Hydrodesulfurization (HDS) Catalysts Using Carbon and Sulfur-Modified Mo(110) Surfaces***, **C.L. Roe**[1], K.H. Schulz,* Michigan Technological University

Mo@sub 2@C catalysts have shown potential for commercial use in hydrodesulfurization (HDS) processes. Although these molybdenum carbide catalysts look encouraging as replacements for MoS@sub 2@-based catalysts, questions remain regarding the fundamental surface chemistry associated with the HDS of organosulfur molecules on carbided and sulfided molybdenum catalyst surfaces. Previous surface science studies examining HDS reactions have focused on using Mo(110) and Mo(100) surfaces as model catalysts, but have not been extended to include models of the newer Mo@sub 2@C-based materials. To further investigate the suitability of Mo@sub 2@C for HDS applications, the interaction of sulfur-containing molecules with molybdenum surfaces was examined by utilizing carbon and sulfur-modified Mo(110) single crystals as model catalysts. Specifically, the reactivity of ethanethiol, 1,2-ethanedithiol, and thiirane were studied on the clean Mo(110) and p(4x4)-C/Mo(110) surfaces as a function of sulfur coverage. Ethanedithiol TPD experiments performed on the clean and carbon modified Mo(110) surfaces produced similar reaction products, although changes were observed in selectivity. On the clean Mo(110) surface, the major products observed during TPD experiments were acetylene, ethylene, vinyl thiol, and ethanethiol. However, the reaction of ethanedithiol on the p(4x4)-C/Mo(110) surface produced acetylene, ethylene, and ethanedithiol. Product molecules are thought to arise from two distinct types of surface intermediates: 1) a monodentate thiolate species and 2) a bidentate organosulfur metallocycle. We propose that vinyl thiol and ethanethiol are produced via C-S bond scission and subsequent hydride elimination of the thiolate intermediates, and that the surface metallocycles undergo C-S bond scission to yield acetylene and ethylene. On the carbon-modified surface, complete desulfurization of ethanedithiol occurs upon decomposition, yielding only hydrocarbon products. With increasing sulfur coverage, a decrease in reactivity and a shift in desorption features to lower temperatures is observed for ethanedithiol on the clean and carbon-modified surfaces. Additionally, experimental results on the reaction of ethanethiol and thiirane on the Mo(110) and p(4x4)-C/Mo(110) surfaces will be discussed.

Surface Science Division
Room 314/315 - Session SS3-TuA
Photon- and Electron-Induced Chemistry

Moderator: R.G. Tobin, Tufts University

2:00pm **SS3-TuA1 Photon Driven Chemistry of Adsorbates***, **J.M. White**,* University of Texas, Austin **INVITED**

The photon driven chemistry of adsorbates on Ag(111) will be illustrated using results from sulfur dioxide, trifluoromethyl iodide and, in greater detail, methyl nitrite. The focus of the presentation will be a discussion of the angular and velocity distributions of nitric oxide moieties ejected from irradiated methyl nitrite. The dependence of these properties on photon energy (3 to 6 eV) and coverage (submonolayer to thick multilayer) is interpreted in terms of direct excitation of methyl nitrite with negligible contributions from substrate mediated processes. Comparisons with gas phase photochemistry of methyl nitrite will be made.

2:40pm **SS3-TuA3 Negative Ion Enhancement in Transport of Low Energy F@super -@ Ions Through Rare-Gas (Xe) Films***, **Q.B. Lu**, T.E. Madey,* Rutgers, The State University of New Jersey

As part of a program to understand the energy-transfer and charge-transfer processes that affect ion transport through surface layers, we have studied the transmission of low energy (<10 eV) F@super -@ through ultrathin Xe films (up to several monolayers (ML)). The ions are created by electron-stimulated desorption from CF@sub 2@Cl@sub 2@-covered Ru(0001) at ~25 K, and their yields and angular distributions are measured by a digital detector with time-of-flight (TOF) capability. Our new findings include the following. (i) A strong enhancement is observed as 0.5~1.0 ML Xe is deposited onto a fractional monolayer CF@sub 2@Cl@sub 2@ covered surface, and most strikingly, the magnitude of enhancement depends on the intensity of incident electron current. (ii) The negative ion enhancement decreases with increasing precoverage of CF@sub 2@Cl@sub 2@. (iii) The angular distribution of F@super -@ is centered along the surface normal under all conditions. These results will be discussed in terms of several different mechanisms: dielectric screening of the Xe overlayer, coupling between an anionic exciton (Xe@super *-@) and a [CF@sub 2@Cl@sub 2@]@super *-@ state, and charge transfer between a Xe@super *-@ and a F atom.

3:00pm **SS3-TuA4 Atomic Scale Femtochemistry: Electron Induced Manipulation of Single CO Molecules on Cu(111) @footnote 1@***, **L. Bartels**, G. Meyer, K.-H. Rieder,* Freie Universität Berlin, Germany*; D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Low Temperature STM experiments on the excitation dynamics of isolated CO molecules on Cu(111) were performed. CO molecules adsorb on-top on Cu(111). By injection of electrons at a minimum sample bias of 2.4V hops of an adsorbed CO molecule can be induced. These hops either lead to the transfer of the CO onto the STM tip or to its diffusion on the sample with a probability of approx. 1:3. It was found that at constant bias the hopping rate linearly depends on the rate of electron tunneling from tip to sample (i.e. the tunneling current), thus bearing witness of a one-electron excitation at the heart of this process. However, the corresponding quantum yield of approx. 10@super -11@ is ultra-low only. Increasing the bias from 2.4V to 3.0V this rate increases. Spectroscopy with the STM reveals in the given energy range an increased density of states of CO-Cu(111) with reference to bare Cu(111). This was confirmed by two photon photoemission spectroscopy (2PPE) to correspond to the 2@pi@* level of CO. Estimating the energy barrier for CO transfer to the tip from the known CO-Cu vibrational energy, the known gap-distance and the know desorption barrier it comes out to be only insignificantly lower than the desorption barrier itself. This allows to treat this STM-induced excitation process in terms of a stimulated desorption experiment. Then the MGR-model can be applied to deduce the electron attachment rate from the net quantum yield, if an isotope effect can be found. Carefully comparing the hopping rates on mixed coverages of @super 12@C@super 16@O and @super 13@C@super 18@O an isotope effect of 2.7 can be estimated. This allows to estimate that 0.5% of the tunneling current passes through 2@pi@*. Parametrization of the isotope effect in a semiclassical model with the lifetime of the excited state and its potential slope only yields correct results, if a lifetime of the excited state of less than 3.5fs is assumed. This is in good agreement with the rang of 0.8-5fs obtained by time-resolved 2PPE. @FootnoteText@ @footnote 1@ L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Phys. Rev. Lett. 80, 2004 (1998)

3:20pm **SS3-TuA5 Surface Femtochemistry: Electrochemistry with Ultrafast Lasers and/or Slow Nanostructures?***, **J.W. Gadzuk**,* National Institute of Standards and Technology

Inelastic resonance scattering of hot electrons is the fundamental mechanism underlying many electron-stimulated f-sec processes such as desorption or dissociation of molecules adsorbed on metal surfaces. The hot electrons may be produced by an ultrafast laser pulse or by a solid state tunnel device ("slow nanostructure"). Theoretical reaction rates or yields are given as an integral product of the energy distribution of the flux of incident hot electrons with the the inelastic electron scattering cross section (which contains the influence of the fs intra molecular dynamics). For fixed laser fluence, the temporally narrowest pulses produce the hottest electrons. The flux of laser-generated hot electrons incident upon the surface is given by an electron-temperature-dependent expression that is akin to the oldtime Richardson equation for thermionic emission. The all important consequences of this fundamental quantum statistical mechanical constraint on our current understanding of the so-called two-temperature model of DIMET (M=Multiple) will be discussed in detail. In contrast, the incident electron flux produced by the tunnel device may be given by the (again oldtime) Fowler Nordheim equation for field emission. In either case, what is important is the energy of the incident electron relative to the energy level position of the acceptor/LUMO/negative-ion resonance of the reactant. But this is exactly one of the fundamental problems in both hardcore electrochemistry and its contemporary embodiments. Implications of the full circle linkage between venerable electron emission/electrochemistry and ultra-modern Surface Femtochemistry will also be visited.

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

3:40pm **SS3-TuA6 Photodesorption of Atomic Hydrogen from Si(100) at 157 nm*, X.-Y. Zhu,*** *T. Vondrak,* University of Minnesota

Irradiation of the Si(100)-(2x1):H monohydride surface by 157 nm light results in the breaking of the H-Si surface bond and the desorption of atomic hydrogen. This process can be attributed to the resonant photo-excitation of the sigma-sigma* transition of H-Si at the photon energy of 8 eV. The photodesorption cross section is 3 x 10@super -21@ cm@super 2@, independent of surface hydrogen coverage. Time-of-flight (TOF) measurement of the photodesorbed atomic hydrogen yields a mean translational energy of = 74 meV. Such a low translational energy is indicative of the short lived electronic excitation on the semiconductor surface. This short-time dynamic process is further explored by wavepacket simulation on ab initio potential energy surfaces.

4:00pm **SS3-TuA7 Study on Photon Energy Dependence of Laser-Induced Chlorine Reaction on Si(111)*, S. Haraichi,*** *F. Sasaki,* Electrotechnical Laboratory, Japan

A photo-induced etching is considered as a powerful candidate of the next-generation device fabrication process from the view point of extremely low damage. However the atomic mechanism of the photo-induced surface reaction has not been well understood. We have investigated photon energy dependence of laser-induced chlorine reaction on Si(111) to elucidate the resonant reaction of this system using surface reflectance spectroscopy (SRS) and second-harmonic generation (SHG). In the SRS study, reflectance spectra from an initial oxidized, a cleaned 7x7, and a chlorinated Si(111) surface have been measured by the p-polarized light at the incident angle of around 74°, which is Brewster angle of silicon, with the photon energy ranging from 3.0 to 5.0 eV. Reflected lights themselves have a peak at around 3.4 eV involving the direct band gap transition E@sub 1@ in bulk silicon, however, the peak intensity shows no significant change due to the variation of the surface condition. On the other hand, the reflectance spectra have a peak at around 4.4 eV whose value changes remarkably due to the surface condition and is probably concerned with some surface states. The threshold laser fluency of etching reaction dependence on the photon energy ranging from 1.5 to 2.5 eV has been studied by the SHG method. The threshold fluency shows the minimum value at around 2.15 eV whose SH energy of 4.3 eV is almost equal to the above surface originated peak of the reflectance spectra. The time constant of the on- and the off-resonant reaction will also be discussed.

4:20pm **SS3-TuA8 Photoinitiated Electron Transfer to Selected Alkyl Bromides Physisorbed on GaAs: The Effects of Alkyl Chain Length on Dissociation Cross-Sections and Fragment Dynamics*, R.M. Osgood Jr.,*** *K.A. Khan, N. Camillone III, J.E. Moryl,* Columbia University

Brominated hydrocarbons adsorbed on semiconductor surfaces serve as ideal model systems for investigating the photoinduced chemistry of oriented molecules in the condensed phase. These adsorbates dissociate via attachment of photoexcited substrate electrons giving rise to energetic alkyl and surface-bound bromine fragments. We will describe the effect on the dissociation cross-section and fragmentation dynamics due to systematic variation of the complexity (alkyl chain length) of the adsorbate. The enhancement in the dissociation cross-section with increased chain-length will be discussed in the context of substrate-mediated dissociative-electron attachment (DEA). Comparison of these observations with those made in the gas-phase DEA of similar haloalkanes allows us to consider the role of the surface in this dissociation process. Increasing the length of the alkyl chain also leads to distinct changes in the alkyl fragment angular distributions. For methyl bromide, the angular distribution is dominated by a focused beam of hyperthermal methyl radicals at 45° (in the [-1,0] direction) from the surface normal. For ethyl and propyl bromide, inelastic scattering of the fragments results in increased importance of a slower diffuse cos@super n@ @theta@ desorption. In addition, significant retention of alkyl fragments is detected by post-irradiation thermal desorption measurements. Increasing the number of degrees of freedom of the adsorbate dramatically alters the energetics of the ejection of the photofragments from the surface. Velocity distributions of the fragments clearly demonstrate that the energy partitioned into translational motion is strongly reduced when the number of rovibrational degrees of freedom is increased. Quantitative variations in the energy and angular distributions are discussed in terms of changes in energy partitioning with alkyl chain length.

5:00pm **SS3-TuA10 Surface Modification on GaAs(110) Induced by 100-3000 eV Electrons*, B.Y. Han,*** *K. Nakayama, J.H. Weaver,* University of Minnesota

Atomic level modification of semiconductor surfaces induced by 100-3000 eV electrons is demonstrated for the first time. Scanning tunneling microscopy results reveal that single-layer deep vacancies are created randomly on GaAs(110) terraces under conditions typical for low-energy electron diffraction and Auger electron spectroscopy. Small regrowth structures resulting from Ga and As atoms ejected onto the terrace are observed. Surface modification is related to electronic excitations, and we discuss the mechanisms in view of the rate of production of defects at various electron energies. We also discuss the consequences of this electron-induced surface modification.

Thin Films Division
Room 310 - Session TF-TuA
In-situ Characterization of Thin Films

Moderator: J.J. Nainaparampil, Air Force Research Laboratory

2:00pm **TF-TuA1 Real Time Ellipsometry Study the Deposition of Barium Strontium Titanate Thin Films*, Y. Gao,*** *A. Mueller, E.A. Irene,* University of North Carolina, Chapel Hill*; O. Auciello,* Argonne National Laboratory, U. S. A.*; A.R. Krauss,* Argonne National Laboratory

(Br, Sr)TiO@sub 3@ (BST) has been considered to be a candidate high K dielectric material in dynamic random access memory(DRAM) capacitors.@footnote 1@ However, the interface layer formed between the BST thin film and substrate is an obstacle to obtain the desired dielectric constant and/or leakage current level for high density DRAM applications. Therefore, a clear understanding and then control of the interface reaction between a high K dielectric film and the substrate is tantamount for further progress in high K film technology. In previous work@footnote 2@ in our laboratory, the oxygen extraction and interface reactions of YBCO superconductor thin films on different substrates have been studied using real time ellipsometry. The results of this study comprise information on film growth kinetics and the oxygen in- and out-diffusion mechanism. Presently a similar study is ongoing on the interface reaction in ion sputtered BST thin films on Si substrates. The results of this study to be presented include: 1. real time film growth kinetics 2. sensitivity of bulk film composition to oxygen background pressure 3. interface reactions with Si and with various buffer layers 4. static and high frequency dielectric constants as well as leakage currents for BST films from various growth conditions 5. optical properties, composition, structure and morphology of BST films from various growth and post-deposition annealing conditions. @FootnoteText@ @footnote 1@D.E. Kotecki, Semiconductor International, Nov. 1996, pp109-116; @footnote 2@A. Michaelis and E.A. Irene et. al, Journal of Applied Physics, June 15, (1998).

2:20pm **TF-TuA2 Optical Constants of Crystalline WO@sub 3@ Deposited by Magnetron Sputtering*, M.J. DeVries,*** *C. Trimble, T.E. Tiwald, D.W. Thompson, J.A. Woollam,* University of Nebraska, Lincoln*; J.S. Hale,* J. A. Woollam Co., Inc.

Crystalline WO@sub 3-x@ is an infrared (IR) electrochromic material with possible applications in satellite thermal control and IR switches. Optical constants of electrochromic materials change upon intercalation, usually with H@super +@ or Li@super +@. Of primary concern for device design are the optical constants in both the intercalated and unintercalated states. In-situ and ex-situ ellipsometric data are used to characterize both the deposition process and the optical constants of the film. Ex-situ data from a UV-Vis-NIR ellipsometer are combined with that from a mid-infrared FTIR-based ellipsometer to provide optical constants over a spectral range of 190 nm to 30 µm.

3:00pm **TF-TuA4 Ordered Binary Oxide Films: V@sub 2@O@sub 3@ (0001)/Al@sub 2@O@sub 3@/Mo(110)*, Q. Guo*,** *D.Y. Kim, S.C. Street, D.W. Goodman,* Texas A&M University

Ordered binary oxide films, vanadium oxide on aluminum oxide, on the (110) molybdenum surface have been prepared in ultra-high vacuum conditions and characterized by various surface analytical techniques. Results from Auger electron spectroscopy, low energy electron diffraction, high-resolution electron loss spectroscopy, X-ray photoelectron spectroscopy and ion scattering spectroscopy indicated that the vanadia films grew on the Al@sub 2@O@sub 3@/Mo(110) surface epitaxially as V@sub 2@O@sub 3@(0001). Results from electronic structure measurements show an increase in energy of the a@sub 1g@ level in the 3d band at 100 K, which is one possible contributor to the metal-insulator transition in V@sub 2@O@sub 3@.

3:20pm **TF-TuA5 In-Situ Thin Film Characterization*, J.M. Gibson,*** University of Illinois, Urbana **INVITED**

Control and understanding provide the two primary motivations for in-situ film characterization. For vacuum deposition, one powerful in-situ probe is the high-energy electron beam. Reflection High-Energy Electron Diffraction(RHEED) is a well-known method, used in Molecular Beam Epitaxy(MBE), for both purposes. Direct imaging using high energy electron beams forms the basis of transmission electron microscopy (TEM), which provides far more microstructural information than RHEED. Due to the instrumental complexity and invasiveness of the technique, however, in-situ TEM is directed at understanding, rather than controlling growth. I illustrate with examples from my group's work which includes: understanding the growth of very thin oxides, both on metals@footnote 1@ and semiconductors;@footnote 2@ the nature of small particle sintering in the formation of nanophase metallic thin films;@footnote 3@ island growth and stress@footnote 4@ in epitaxial Ge on Si; and AlN epitaxy on sapphire.@footnote 5@ The emphasis is that understanding through in-situ microscopy can lead to control, without in-situ probes, through better understanding of growth processes. @FootnoteText@ @footnote 1@J. C. Yang and J. M. Gibson, Appl. Phys. Lett. 70, 3522 (1997). @footnote 2@X. Chen and J. M. Gibson, Appl. Phys. Lett. 70, 1462 (1997). @footnote 3@M. Yeadon, J. C. Yang, M. Ghaly, D. Olynick, R. Averback, and J. M. Gibson, Appl. Phys. Lett. 71, 1631 (1997). @footnote 4@R. D. Twesten and J. M. Gibson, Phys. Rev. B 50, 17628 (1994). @footnote 5@M. Yeadon, M. T. Marshall, F. Hamdani, S. Pekin, H. Morkoc, and J. M. Gibson, Journal of Applied Physics 83, 2847 (1998).

4:20pm **TF-TuA8 Direct Three-Dimensional Characterization of Buried Interface Morphology with Quantized Electron Waves***, I.B. Altfeder,* ***D.M. Chen,*** The Rowland Institute for Science

We present a novel in situ and nondestructive technique for characterizing buried interfaces in metal/semiconductor heteroepitaxy. The principle of the technique is based on the quantum confinement of the internal electron source in the metal film. Due to the high sensitivity of the quantized electron waves to the boundary conditions, discrete interference fringes are formed spontaneously on the surface of the film and can be directly imaged by a scanning tunneling microscope.@footnote 1@ These fringes coincide precisely with the substrate atomic terraces so that the metal appears to be "transparent". The absolute depth of the film, on the other hand, can be accurately determined form the tunnel I-V measurements of the quantized energy spectra near the Fermi level, hence making it possible to characterize the buried interface morphology in all three dimensions nondestructively. @FootnoteText@ @footnote 1@I. B. Altfeder, K. A. Matveev, and D. M. Chen, Phys. Rev. Lett. 78, 2815 (1997).

4:40pm **TF-TuA9 A Novel Design of a Reflecton Analyzer for Elemental and Isotopic Analysis by MSRI (Mass Spectroscopy of Recoil Ions)@footnote 1@*, K.L. Waters,*** *K. Baudin, J.A. Schultz,* Ionwerks

Mass Spectroscopy of Recoil Ions (MSRI) is a recently developed technique which has been reviewed@footnote 2@ and has been used in real time monitoring of nitride@footnote 3@ and oxides growths. The technique is similar to Time of Flight SIMS (TOF/SIMS) in that a pulsed keV primary ion beam is impinging at grazing incidence onto the analyzed surface. Sputtered ions are collected and analyzed by TOF. By careful design of the extraction optics using differential pumping and by placement of the analyzer in the forward scattering angle at around 60-70 degrees, it is possible to achieve mass spectra of directly recoiled binary ions which are devoid of molecular interference at pressures in excess of 1mTorr. For the optic positioned at 1inch from the focal point of the primary ion beam onto the sample, Mo isotopes have been resolved with a resolution at half maximum of 450. Operation at 2 inches from the focal point reduces the resolution to 250 and reduces the collection and transmission of recoiled ions by a factor of two. Examples will be given of the use of the MSRI technique for both exsitu and real time control of deposition process. @FootnoteText@ @footnote 1@Financial support of this work by US Air Force SBIR Contract F33615-970C-1035 @footnote 2@M. S Hammond, J.A Schultz, A. R. Krauss J.Vac.Sci. Technol. A 13(3) 1995 @footnote 3@E. Kim, I. Berishev, A. Bensaoula, S. Lee, S.S. Perry, K. Waters, J.A. Schultz Appl. Phys. Lett. 71 (21) 1997

5:00pm **TF-TuA10 The Interaction of Al Atoms with Surface-Bound Organic Functional Groups Studied by In-situ XPS, Infrared Spectroscopy and ToF-SIMS*, A.E. Hooper,*** *G.L. Fisher,* Pennsylvania State University*; R.L. Opila,* Bell Laboratories, Lucent Technologies*; N. Winograd, D.L. Allara,* Pennsylvania State University

The interaction of vapor-deposited Al atoms with self-assembled monolayers of structure HS(CH2)15CH3 and HS(CH2)15COOCH3 was studied with multiple in-situ techniques over a range of Al coverages from submonolayer to multilayers. XPS and IR show the Al to be unreactive with the CH2 units but highly reactive with the oxygen atoms in the ester group to form a 1:1 Al:ester bridged type of complex with an intact CH3 group and a loss of double bond character for the C=O group. In the case of the CH3-termimnated surface, ToF-SIMS shows the Al atoms penetrate into the organic monolayer and diffuse to the Au-S interface. Both XPS and ToF-SIMS indicates that subsequent reaction with the S atoms appears to occur, but in such a way as not to disturb the packing of the monolayer hydrocarbon chains. A dynamic fluctuation mechanism is proposed to explain the Al atom penetration in the CH3 case. In the ester-terminated film, penetration appears to be thwarted by the rapid reaction of the Al atoms with the ester terminal groups to form a dense monolayer of organometallic species.

Vacuum Technology Division
Room 329 - Session VT-TuA
Drag Pumping and Transition Flow Phenomena

Moderator: T. Sawada, Akita University, Japan

2:00pm **VT-TuA1 How Gaede Was Forgotten*, J.C. Helmer,*** AVS Fellow

In 1913 W. Gaede published a theory of the molecular drag pump, including data from an experimental pump which bears his name. To the author’s knowledge, all reviews of this subject have reproduced Gaede’s theory without qualification. However Gaede himself noted that for molecular flow his theory is off by orders of magnitude. This discrepancy was forgotten by subsequent authors. At Varian SpA, it was found in both molecular and viscous flow, that Gaede's model may be corrected with the addition of an active "pumping" leak at the end of the channel, for which there is an exact and simple theory. Design of the channel to the leak-limited compression ratio is specified by a "golden rule". We also proved that a differential velocity between adjacent channel surfaces is not necessary for the pumping action. Gaede’s later designs suggest that he knew this. The modern Gaede model can now be applied to the pumping action of the Holweck pump in the direction of surface drag. What Gaede did not discuss is the possible influence of Bernoulli and inertial effects at high pressure. We will conclude with a discussion of the importance of inertial effects in the Gaede pump model.

3:20pm **VT-TuA5 Direct Simulation Monte-Carlo Method for Molecular and Transitional Flow Regimes in Vacuum Components*, O. Boulon,*** *R. Mathes,* Alcatel High Vacuum, France*; J.-P. Thibault,* LEGI-IMG, France

With the active development of semiconductor fabrication technology, dilute gas flow phenomena are recently attracting attention. The gas flow through a vacuum component can be continuous, transitional or molecular depending on the pressure range and geometries involved. The present work proposes a method for simulating molecular and transitional flows using the direct simulation Monte-Carlo method (DSMC), first developed by Bird.@footnote 1@ DSMC codes directly simulate nature by moving computational particles through space. The computational model takes as data combinations of pressures, temperature of gas, type of gas and geometry of the vacuum components. The results of the computations are gasflow, local velocities, and molecular density distribution. The model was first tested and validated for several simples geometries such as circular and rectangular finite length tubes with static and moving walls, for different flow conditions. The molecular flow "aspect" is checked by comparing results with existing analytical values in the literature. The model was found to agree well with other published results in this field. From molecular to transitional flow, velocity profiles show the importance of viscosity effect for the different Knudsen numbers varying from 40 to 0.04 (pressure range from 5.e-03 to 5 Pa). The flow rate obtained for the smallest Knudsen number is close to the viscous value corresponding to Poiseuille's law. The aim of the study is to develop a model that we can adapt to more complicated geometries of vacuum components such as stage of turbomolecular or molecular pump and to predict the flow rate from molecular to transition flow regimes. @FootnoteText@ @footnote

1@G.A. Bird "Molecular gas dynamics and the direct simulation of gas flows". Oxford Science Publications, Clarendon Press, 1994.

3:40pm **VT-TuA6 Viscosity and Slip Measurements with a Modified Spinning Rotor Gauge*, J.A. Bentz*,** *S.K. Loyalka, R.V. Tompson,* University of Missouri, Columbia

The spinning rotor gauge (SRG) has become a practical method in determining the coefficients of viscosity, velocity slip, and tangential momentum accommodation for rarefied gases with a high degree of accuracy. In previous papers, we discussed the use of the SRG for measurement of these quantities for noble gases (He, Ar, and Kr), polyatomic gases (N@sub2@ and CH@sub4@), and binary gas mixtures (He-Ar, He-N@sub2@, and He-Ne). In all of our previous experiments, we considered the axis of sphere rotation parallel to the axis of the cylindrical tube inside which the sphere rotates (in the MKS gauge, the sphere rotation axis is normal to the tube axis). Based on these calculations, we suggested how the results could be used for measurements of viscosity, the velocity slip and the tangential momentum accommodation coefficients. However, the theory used for our calculations required a sphere spinning co-axially to the cylinder. We have modified our experimental apparatus to achieve this geometry. A selection of experimental measurements for He and Ar gases which have been made with a modified spinning rotor gauge are reported. All of the experiments were conducted in the slip regime. Theoretical results from a previous paper on the SRG are used to extract values of the viscosity, the velocity slip coefficient and tangential accommodation coefficient from the experimentally obtained data for both gases. These are compared with previous experimental results. The measured viscosities are in excellent agreement with existing literature values.

4:00pm **VT-TuA7 Two Point Calibration Scheme for the Linearization of the Spinning Rotor Gauge at High Pressures*, J. Setina,*** Fotona d.d., Slovenia

Commercial spinning rotor gages (SRGs) use a special linearization procedures to compensate for a vanishing pressure dependence of the rotor deceleration rate in the transition regime from 0.1 to 100 Pa. These procedures have been found to have large errors above 10 Pa,@footnote 1@ but can be significantly improved. An extensive set of experimental data of rotor deceleration rate versus gas pressure up to 130Pa was acquired. A group of six SRGs and four gases (N@sub 2@, Ar, He and H@sub 2@) were used in the study. Temperature measurements where also included to account for heating effects. The data shows that the differences between rotor/thimble combinations are large enough to cause differences of several % if one uses the linearization functions currently in use without adjustable parameters. To get the best accuracy, one parameter is left in our linearization procedure to be determined by calibration. We call it the Knudsen length of the rotor/thimble assembly. This is the second calibration constant of SRG that needs to be determined for accurate pressure measurements above 1Pa. The method to determine the second calibration constant at 100Pa will be proposed. The first calibration constant is the already well-known rotor accommodation coefficient and is determined in molecular regime below 0.01Pa. Achievable accuracy of the new linearization procedure with the two calibration parameters is better than 1% over the entire range from molecular regime up to 130Pa. The effect of thimble temperature on this linearization procedure will also be discussed. @FootnoteText@ @footnote 1@J.Setina and J.P.Looney, Vacuum, 44,1993, p.577

4:20pm **VT-TuA8 Design and Characterization of High Capacity NEG Pumps Embedded Inside the Interaction Regions of DA@PHI@NE*, R. Giannantonio,*** *P. Manini, F. Mazza, R.M. Caloi, D. Dominoni,* SAES Getters S.p.A., Italy*; A. Clozza,* Infn Lnf, Italy*; L. Zanin,* DG Technology Service, Italy

The DA@PHI@NE @PHI@-factory is a twin ring 510 MeV e@super +@e@super -@ collider facility under commissioning at INFN-LNF in Frascati. With a stored beam current of 5.3 A, a mean pressure of 1*10@super -9@ Torr is required in each ring. To cope with a total gas load, mainly consisting of CO, of 1.2*10@super -4@ Torr*l*s@super -1@ for each of the electron/positron ring, sputter ion pumps and titanium sublimation pumps with a total pumping speed of about 1.2*10@super 5@ l*s@super -1@ were installed on each ring. For the KLOE interaction region, where a mean pressure of the order of 1*10@super -10@ Torr is required, an embedded Non Evaporable Getter (NEG) pump with a CapaciTorr@super TM@-type structure was chosen mainly because of the unavailability of room for the installation of lumped pumps and to take advantage of the utmost sorption capability of the NEG pump for CO in the UHV operating conditions of the machine. A NEG pumping system of the kind discussed in this paper seemed to be particularly suitable for the KLOE experiment, where limited servicing and high reliability is required. In this paper we report on pumping speed measurements performed on a first pump prototype, fitted with St-172 NEG alloy, featuring sorption rates as high as 5*10@super 3@ l*s@super -1@. We also discuss on the design and characteristics of the final pump version, where St-185 NEG alloy is used. Computer simulations of the pressure distribution inside the interaction beam pipe are also shown, demonstrating the effectiveness of the selected technical solutions.

4:40pm **VT-TuA9 Hydrogen Pumping Simulation for Cryopumps***, S. Nesterov, J. Vasiliev,* Moscow Power Engineering Institute, Russia*;* ***L.C. Wagner****, M. Boiarski,* IGC-APD Cryogenics Inc.

Cryopumps are an effective way to create clean, high vacuum. When designing a new cryopump, it is desirable to have some tool to predict cryopump performance for the different cryopanel geometries that are being considered. Monte Carlo simulation is a method that has been used for evaluating the pumping speed of a cryopump when it has not yet accumulated any gas. The simulation of hydrogen pumping has its own challenges due to the typical location of the hydrogen pumping sites and interactions with other gases. As gases accumulate on the pumping surfaces, the passageways for hydrogen gas are restricted. This paper describes the work that was done, using Monte Carlo simulation, to study the hydrogen pumping speed and capacity of a typical cryopump as it accumulates hydrogen, water and argon. The hydrogen pumping speed is predicted as a function of the amount of other gases that have been accumulated.

Applied Surface Science Division
Room 307 - Session AS+BI+SS-WeM

Organized Molecular Monolayers

Moderator: H.G. Tompkins, Motorola, Inc.

8:20am **AS+BI+SS-WeM1 Structural Characterization of the Outermost Surface Monolayers of CH@sub 3@ and CF@sub 3@ Terminated n-Alkanethiol Monolayers Self-Assembled on Au(111)**, *L. Houssiau, **J.W. Rabalais**,* University of Houston

Time-of-flight scattering and recoiling spectrometry (TOF-SARS) was used for surface elemental and structural characterization of hexa- and hepta-decanethiols (C@sub 16@ and C@sub 17@ for short) and of 16,16,16-trifluorohexadecanethiol (FC@sub 16@) self-assembled monolayers (SAMs) on a Au(111) surface. The substrate was also characterized after in-situ sputtering and annealing by TOF-SARS and LEED in order to identify its crystalline orientation. The azimuthal angle scans performed on the C@sub 16@ samples displayed unique features, indicating well-ordered structures. The recoiling intensities of the H and C atoms exhibited a clear 60° periodicity, with H recoil maxima and C recoil minima displayed at 30° from the substrate nearest-neighbor directions. Several models were tested by means of classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC). The molecular length, tilt angle, and twist angle were varied in the simulations. Good agreement between the experiments and simulations for both C and H signals was obtained for a (@sr@3x@sr@3)R30 structure of SAM lattice, with the molecules tilted along the substrate nearest-neighbor directions by 35° from the surface normal. Moreover, a twisting of the molecular plane by 55° from the plane normal to the surface had to be considered in order to reproduce the H angular variations. Similar measurements on the C@sub 17@ samples showed much weaker variations for the H and C recoil intensities. This is believed to be due to the high tilt angle of the end methyl group. The FC@sub 16@ samples showed the presence of C and F atoms in the surface layer. No evidence for H and C recoil azimuthal variation was observed on the FC@sub 16@ samples, although a weak azimuthal periodicity was noticed for the F recoils.

8:40am **AS+BI+SS-WeM2 Fundamental Studies of Phase Transitions in Functionalized Amphiphile Monolayers**, ***G.E. Poirier**,* National Institute of Standards and Technology

Alkanethiol molecules chemisorb strongly to noble metal surfaces. Intermolecular dispersion forces compress the molecules into a dense, commensurate, crystalline film that spontaneously terminates growth at one molecular monolayer. The thickness of the film, its dielectric constant, and the physical properties of the exposed surface can be controlled by changing the length of the alkyl chain, its degree of saturation, and its terminal functional group, respectively. These systems are therefore desirable in any application requiring control of the adhesive, tribological, or electron transfer properties of metal surfaces. This talk will outline experiments in which methyl-terminated alkanethiol monolayers were prepared by vapor deposition onto clean Au(111) in ultra-high vacuum and characterized in-situ using molecular-resolution scanning tunneling microscopy.

9:00am **AS+BI+SS-WeM3 Characterization of Fluorinated Monolayers**, ***D.G. Castner**,* University of Washington **INVITED**

Self assembly processes have made it possible to prepare organic monolayers with well-defined surface structures and chemistries. The ability to systematically vary the surface structure and chemistry of these self-assembled monolayers (SAMs) provide an excellent method for examining the relationship between the surface properties of a film and its performance in a given application (e.g., cell culture). To develop these relationships requires detailed characterization of the surface composition, molecular structure, orientation, and topography of the films with techniques such as XPS, ToF SIMS, NEXAFS, and STM. How the methods and molecules used to form fluorinated films affect the resulting film structure will be discussed. The degree of ordering and relative orientation in SAMs prepared with perfluoroalkyl thiols depend on the length of the fluorinated tail. Although SAMs prepared from thiols with long perfluoroalkyl tails are highly ordered, their stability is limited by the single point attachment of the Au-S bond. This stability can be increased by using grafted copolymers containing both perfluorinated and alkanethiol side chains to generate multipoint attachment of each polymer chain. However, this method of increasing film stability also results in a decreased degree of film orientation. Typically films prepared using polymers with perfluorinated side chains are highly disordered. Only at high concentrations of perfluoroalkyl side chains (>50%) is any ordering detected in polymeric monolayers. Other methods, such as trifluoroacetic anhydride derivatization of hydroxyl-terminated alkanethiols can also be used to produce fluorinated surfaces. Depending on the derivatization system, the high degree of ordering in the starting SAM can be retained after derivatization.

9:40am **AS+BI+SS-WeM5 Controlling Defects in Self-Assembled Monolayers**, ***J.J. Jackiw**, J.J. Arnold, J.A. Johnson, T.D. Dunbar, T.L. Spiva, D.L. Allara, P.S. Weiss,* The Pennsylvania State University

Much is known about the formation, structure, stability, and properties of alkanethiolate monolayers on Au (111). We have begun to explore the effects of changing the molecule-surface linkage. In the cases of alkanethiolates and alkaneselenolates, monolayers can be made respectively from: thiols and selenols, disulfides and diselenides, and by deprotecting alkanethioacetates and alkaneselenoacetates, which are less prone to oxidation. Our experiments probe monolayer structures and defects resulting from the deposition of dodecanethiol, didodecane disulfide, didodecane diselenide, dodecaneselenol, and in situ deprotected dodecanethioacetate and dodecaneselenoacetate. We compare the structures and defects in the resulting monolayers. The defect identities and densities are important in determining the properties of the films, especially our ability to manipulate their structures and compositions.

10:00am **AS+BI+SS-WeM6 New Preparation Methods for Self Assembly of Alkanethiolates on III-V Semiconductor Surfaces**, ***C.K. Mars**, D.L. Allara,* Pennsylvania State University

The ability to control the chemical composition of III-V surfaces is vital in semiconductor technology. Alkanethiolate monolayers prepared from thiol melts at temperatures near 100°C have been shown to mimic the improved electronic passivation properties seen on III-V semiconductors with Na@sub 2@S and NH@sub 4@S@sub x@ treatments. We have developed a new process by which these films can be grown reliably in a highly organized state from millimolar ethanol solutions near 50°C. In addition, by adding controlled amounts of base to these solutions, the degree of organization as determined by IR spectroscopy and contact angle measurements, can further be improved. This new process has allowed us to deposit a wide variety of films including aromatic and functionalized molecules as well as layers anchored by other chalcogenide elements.

10:20am **AS+BI+SS-WeM7 The Effect of Solvents and Electrical Fields on the Molecular Conformation in Organic Monolayers**, ***M. Grunze**, M. Buck, F. Eisert, M. Zolk, P. Harder,* University of Heidelberg, Germany*; A. Pertsin,* Russian Academy of Sciences, Russia*; H.J. Kreuzer,* Dalhousie University, Canada **INVITED**

The molecular conformation in self-assembled monolayers (SAMs) of functionalized alkanethiols is affected by the presence of solvents. The polarity and ability of the solvent molecules to form hydrogen bridge bonds, and the lateral density in the SAMs determines the orientation of the terminal functional moiety at the organic film/solvent interface. We will discuss our in situ Sum Frequency Generation (SFG) and protein adsorption experiments on methyl- and oligo(ethylene glycol)-terminated self-assembled alkanethiolate monolayers, and present atomistic force field calculations to explain our data. These results show that spectroscopic measurements taken in vacuum or ambient atmosphere are not necessarily representative for the molecular structure and chemical nature of organic surfaces immersed in a liquid.

11:00am **AS+BI+SS-WeM9 Nanometer-Scale Design and Fabrication of Polymer Interfaces using Polydiacetylene Monolayers**, ***M.D. Mowery*[1]**, *M. Cai,* University of Michigan*; H. Menzel,* University of Hannover, Germany*; C.E. Evans,* University of Michigan

The selective control of polymer interfacial characteristics such as viscoelasticity and electronic properties is crucial for numerous important applications from sensor design to device fabrication. In this work, robust interfacial polymer films are successfully fabricated within a single molecular layer with nanometer-scale control of the polymer physical structure. The formation of these unique polymer films is accomplished by the spontaneous assembly of alkyl disulfide precursors containing conjugated diacetylene groups at the gold-solution interface. The resultant well-defined monomer assembly is covalently linked through UV photopolymerization, forming a highly conjugated polymer backbone parallel to the surface. Nanometer-scale control of the interfacial structure is accomplished by manipulating the vertical position of the polymer

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backbone within the single layer assembly. Additionally, photo-templating affords lateral control over the formation of polymer domains. These subtle variations in physical structure have a profound impact on the global electronic and viscoelastic properties of the polymer interface. The impact of these structural variations is demonstrated by surface infrared and Raman spectroscopy as well as electrochemical capacitance, heterogeneous electron transfer, and reductive desorption measurements. Furthermore, AFM is utilized to physically image the interfacial structure and evaluate the polymer viscoelastic properties. Finally, the application of these monolayer polymers for lithographic applications and the implications for interfacial design are discussed.

11:20am **AS+BI+SS-WeM10 Bias-dependent Contrast in STM Images of Phenyloctadecylethers***, **I.H. Musselman**, H.S. Lee, S. Iyengar,* University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images were acquired from monolayers of the ethers physisorbed onto highly oriented pyrolytic graphite. The contrast exhibited by the X-POE molecules in these images varied as a function of tip-sample bias. For example, STM images acquired at biases of approximately -0.5 to -0.6 V (sample negative) exhibited a dim alkyl tail and a series of bright spots corresponding to functionalities in the head group (e.g. halogen, phenyl group, oxygen). However, at biases more negative than -1.2 V, the largest contribution to contrast was observed for the alkyl tail (e.g. octadecyl group). A comparison of STM images of the adsorbed X-POE molecules with electron density contours calculated using HyperChem suggested a bias-dependent participation of individual bonding molecular orbitals to tunneling. A resonance tunneling mechanism between the tip and molecular orbitals adjacent to and including the highest occupied molecular orbital (HOMO) is proposed.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

11:40am **AS+BI+SS-WeM11 Self-Assembling Trichloro- and Trimethoxy-silanes on TiO@sub 2@(100) Crystal***, **R. Magnée**, J.-J. Pireaux,* LISE - Facultés Universitaires Notre-Dame de la Paix, Belgium

Trichlorosilanes (CH@sub 3@(CH@sub 2@)@sub n@SiCl@sub 3@, n = 1, 7, 17) and trimethoxysilanes (CH@sub 3@(CH@sub 2@)@sub n@Si(OCH@sub 3@)@sub 3@ , n = 2, 7, 17) SAM's were deposited by dipping a TiO@sub 2@ (100) crystal in a 10@super -3@M toluene solution for 4 hours. The titanium dioxide surface was prepared by Ar@super +@ sputtering, annealing in UHV to get a clear LEED (1x3) pattern, then exposed to atmosphere before dipping. Silane molecules need H@sub 2@O or a hydroxylated surface to react but it was not necessary to hydroxylate the TiO@sub 2@ because of the air exposure. Hydroxylation was confirmed by FT-IR and XPS. X-Ray and Ultra-violet Photoelectrons Spectroscopy (XPS, UPS) were then used for the SAM's charaterization. We expect a siloxane network to appear at the interface in addition to the Ti-O-Si bonds. XPS results show that the silane groups do indeed bind to the TiO@sub 2@ surface but that some defects are also present at the interface: for n=17 the amount of OH groups is 4 % of the total oxygen signal while this value is doubled for n=7. Probably due to the higher reactivity of chlorine atoms, trichlorosilanes present less defects than trimethoxysilanes. By comparison with theoretical calculations,@footnote 1@ UPS provides information on the alkane chain conformation: we show that longer silane molecules (n=17) are grafted in a zigzag planar conformation, while n=7 molecules seem to present chain defects. This is consistent with the self-assembling process that depends on long-range interchain interactions. For the smallest chains (n=1,2), the XPS C/Si ratios are always too high, suggesting some contamination: this is probably due to solvent incorporation in the layer. HREELS analysis (not yet performed at the date of abstract submission) may help to get more information on the order of the layers. @FootnoteText@ @footnote 1@ A.-S. Duwez, S. Di Paolo, J. Ghijsen, J. Riga, M. Deleuze, J. Delhalle, J. Phys. Chem. B, 101 (1997) 884.

Electronic Materials and Processing Division
Room 316 - Session EM-WeM

Fundamentals of Si Cleaning and CMP

Moderator: Y. Ma, Bell Laboratories, Lucent Technologies

8:20am **EM-WeM1 Surface Preparation and Contamination Control for Advanced CMOS Processing***, **S.C. O'Brien,*** Texas Instruments, US **INVITED**

Advanced CMOS device manufacturing requires levels of contamination which 20 years ago would have been considered science fiction. Particulates, metals, organics, haze, and residue from sacrificial films represent critical yield issues for DRAM and logic devices. Accurate and precise measurement of these species also represents an incredible challenge. The use of TRXRF, SIMS, EDX, and XPS as surface contaminant metrology techniques will be discussed. In many cases the contrast between metrology and analysis has not yet been fully explored. The use of non-destructive inline contaminant metrology is becoming much more important as the wafer size increases from 200 to 300mm. Quick turnaround time is needed for fast problem solving, while the ability to send a wafer for subsequent processing after measurement is valuable for superior problem solving. In addition, correlation of inline measurements with end of line yield is the only relevant method of discovering problems. Any inline defects which do not correlate with end of line yield are usually irrelevant. Specific areas of cleaning technology to be discussed are pre-cleans for thin gate oxides, pre-furnace cleans for metal gates and other metal gate technology, sidewall polymer removal for polysilicon gates, self-aligned cobalt and titanium silicides, sidewall polymer removal for aluminum lines, corrosion of copper and aluminum lines, contamination from new materials (such as ruthenium or BST), and copper processing.

9:00am **EM-WeM3 Dissolution of Cu and Au into Aqueous Semiconductor Processing Solutions***, **I. Suni**, D. Chopra, A.A. Busnaina,* Clarkson University

Dissolution of Cu into 50:10:1 H@sub 2@O:H@sub 2@O@sub 2@:NH@sub 4@OH from p-type Si wafers was studied by total reflection x-ray fluorescence spectroscopy (TXRF). Starting from an initial surface coverage of approximately 1.2x10@sup 13@ atoms/cm@sup 2@, Cu dissolution was seen to be first order in Cu surface coverage, although slight deviations from this behavior are seen at longer times. The rate constant for this dissolution process was about 2.7x10@sup -2@ sec@sup -1@. Prior literature results indicate that Au dissolution into acidic solutions is also 1st order when dissolution is slow, but deviates from 1st order when dissolution is rapid. One possible explanation for these phenomena is that metal dissolution is a reversible reaction which slows down as the concentration of metal ions in solution increases and diffusion is slow. This explanation is consistent with recent results published by Sony Corp. The dissolution process in a wafer cleaning tank was modeled using experimentally determined constants through finite difference solution of the convective diffusion equation by the ADI method, including a 1st-order surface reaction as a boundary condition. The results demonstrate the transition between rate-limitation by surface reaction and rate-limitation by product diffusion as the dissolution rate is increased. This can be done by raising the temperature, increasing the solution strength, or using a more active oxidizing agent. The possibility is demonstrated of large removal gradients on the wafer surface arising from the coupling of convection, diffusion, dissolution and redeposition.

9:20am **EM-WeM4 A Reduced Carbon Contaminant, Very Low-Temperature Silicon Substrate Preparation for Defect-Free Homoepitaxy***, **P.J. Taylor**, W.A. Jesser,* University of Virginia*; M. Martinka, K. Singley, J. Dinan,* US Army CECOM-Night Vision and Electronic Sensors Directorate*; R. Lareau, M. Wood, W.W. Clark III,* US Army Research Laboratory

A low-temperature cleaning technique incorporating an ultraviolet lightozone treatment with conventional hydrogen-passivation techniques is shown to yield record-low concentrations of surface contaminants: @>=@ 0.01 monolayer (ML). An additional advantage is that no Atwater-type@footnote 1@ UHV prebaking treatments are required for substrates receiving this treatment prior to epitaxy. Low-temperature silicon molecular beam epitaxy (MBE) on such substrates is characterized by a threading dislocation density on the order of 10@super 4@/cm@super 2@ (Schimmel etching@footnote 2@) which is a reduced threading dislocation density compared to that measured from films receiving more conventional hydrogen-passivation preparation techniques: typically between 10@super 5@/cm@super 2@ and 10@super 6@/cm@super 2@.@footnote 3@ The interfacial contamination was measured before homoepitaxy by in-situ Auger electron spectroscopy (AES) and after homoepitaxy using secondary-ion-massspectroscopy (SIMS). The results of this study suggest that aqueous solutions are a significant source of surface carbon and that an ultraviolet light-ozone treatment before hydrogen passivation is particularly efficacious for removing residual carbon on the silicon surface which would otherwise contribute to the generation of threading dislocations in Si homoepitaxial films. @FootnoteText@ @footnote 1@Nikzad, S., Wong, S., Ahn, C., Smith, A., Atwater, H., Appl. Phys. Lett. Vol. 63(10) p. 1414 (1993). @footnote 2@Schimmel, D., Journ. Electrochem. Soc., Vol. 126 p. 479 (1979). @footnote 3@Eaglesham, D., Higashi, G., Cerullo, M., Appl. Phys. Lett., Vol. 59(6) p. 685 (1991).

9:40am **EM-WeM5 The Modeling of Excimer Laser Particle Removal From Silicon Surfaces***, X. Wu, E. Sacher,* ***M. Meunier,*** École Polytechnique de Montréal, Canada

The interaction of an excimer laser with a silicon surface can lead to the removal of submicrometer-sized contaminant particles. This technique is efficient, simple, fast and is chlorofluoracarbon-free, a considerable environmental advantage over standard cleaning techniques. In addition, the laser cleaning approach is compatible with cluster tools. Laser cleaning may be dry, meaning that no water was present on the sample surface during laser exposure. However, to increase removal efficiencies, the "steam" laser cleaning technique may used, where the pulsed laser beam is coupled to a liquid energy transfer medium, such as water, which is condensed on the silicon surface. We found that organic particles, such as polystyrene and carboxylate modified latices, with dimensions as low as 0.1 micrometers, can easily be removed by dry cleaning. However, inorganic particles, such as alumina and silica, of the same dimensions, can only be removed by steam cleaning. We have performed a detail analysis of the comparison between particle adhesion forces (van der Waals with deformation, capillary and chemical) and removal forces (thermoelastic, and bubble pressure when water is used) to understand laser particle removal efficiencies with respect to particle size and nature, as well as the effect of water. Our calculations show that, for organic particles during dry cleaning, the van der Waals deformation term is predominant for adhesion, and the dominant removal force is thermoelastic. However, for inorganic particles, the dominant adhesion force is that due to hydrogen bonding. Our calculations show that the presence of water greatly reduces the adhesion forces. This, coupled with the bubble pressure created by the explosive evaporation of water when exposed to the laser, leads to the higher efficiency found for steam cleaning.

10:00am **EM-WeM6 Chelating Agents for Dry Removal of Metals***,* ***A. Shah,*** *L. Ford, L. Nigg, Y. Wang, R. Masel,* University of Illinois, Urbana

We and others have found that various diketonates can be used to remove metals from a variety of surfaces under dry conditions. In this paper we use a variety of surface spectroscopic techniques to characterize the process for the removal of copper, nickel and palladium from various surfaces. We find that there are two regimes with different reactivities, a regime where the metal is (reduced) metallic and a regime where the metal is oxidized. In the oxidized regime, the rate desorption step is volatilization of the metal. In this case, the metal removal rate goes as the volatility of the metal chelate, with hexafluoropentanedione(Hhfac) showing the highest removal rate followed by trifluoropentanedione (Htfac), Hexafluorooctanedione(HFOD), 2,4 pentanedione (Hacac), Tetramethylheptanedione (TMHD). In contrast in the reduced condition, oxidation is rate determining, and the removal rate follows almost the opposite trends. We have also found some unusual effect in the intermediate oxidation conditions. For example, if we work under conditions where Cu1+ forms, we observe much lower removal rates than under conditions where Cu0 or Cu2+ forms. Htfac is the best etchant under minimal oxygen conditions. Finally, we have also discovered that some of the intermediates can polymerize and decompose on the surface, leading to carbon contamination. The main contamination pathway seems to be enhanced by impurities in the source gases. Details are still unclear, but it appears that we need purer source gases than are presently available to do clean etching.

10:20am **EM-WeM7 Process Optimization of CMP of Dielectrics for ULSI Multilevel Metallization***,* ***H.W.A. Treichel,*** OnTrak Systems, Inc.*; R. Frausto, A. Meyer, R. Morishige, S. Srivatsan, B. Withers,* Lam Research Corporation **INVITED**

The push of leading edge ULSI manufacturing technologies toward the formation of sub 0.1 µm feature sizes places extreme performance demands on the processes and equipment used. At submicron line widths, the depth-of-focus was limiting technology and CMP emerged as an essential enabling technology for feature sizes of 0.35 µm and below to meet the stringent DOF requirements for next generation devices. Thus, CMP emerged quickly and has become quite sophisticated.@footnote 1@ Current CMP systems are adaptations from existing glass and silicon polishing tools. These platforms are based on a rotating head and a circular platen. Lam Research recently introduced a new revolutionary linear track system (Aurora), an automated CMP machine which has a belt platen module that is capable of linear speeds up to 120 to 150 m/min, especially designed for planarization. This results in less pattern sensitive planarization, very high removal rates, and excellent uniformities at low head pressures. CMP is a very complex process. Its performance is determined not only by machine controlled parameters like belt speed, down force, and more, but also by consumables, pad conditioning and wear.@footnote 2,3@ In order to clarify the role of numerous factors as control parameters, extensive evaluations have been performed. This article reports on specific improvements in LPT technology. It also describes the major dependencies of machine parameters versus experimental results and finally highlights selected optimized CMP processes. @FootnoteText@ @footnote 1@R. DeJule, Semiconductor Int., 11, 15 (1996) @footnote 2@S. Sivaram, H. Bath, R. Leggett, A. Maury, K. Mennig, and R. Tolles Solid State Technology, 5, 87 (1992) @footnote 3@L.M. Cook, J.F. Wang, D.B. James, and A.R. Sethuraman Semiconductor Int., 11, 141 (1995)

11:00am **EM-WeM9 Nanoscale Corrosive Wear of Ionic Materials: A Model System for Chemical Mechanical Polishing***,* ***J.T. Dickinson,*** *L. Scudiero, S.C. Langford,* Washington State University

Fundamental studies of chemical mechanical polishing (CMP) are needed to improve and extend CMP to new applications. In CMP, surfaces experience simultaneous tribological loading and corrosive chemical exposure, which together produce high wear rates and favorable topography. We employ scanning probe microscopy (SPM) of single crystal surfaces in mildly corrosive solutions, where the SPM tip provides the mechanical stimulation in a controlled fashion. The applied normal force, the location of the contact, and lateral motion are readily controlled. For simplicity we choose model systems where the corrosive agent is water (properly buffered) and the single crystals are slightly soluble. These include calcite [CaCO@sub 3@] and brushite [CaHPO@sub 4@ 2H@sub 2@O] (a model biomaterial). Silicon nitride tips are used with applied normal loads from 0-300 nN, tip radii 30 nm and tip velocities from 1-200 µm/s. Quantitative data on the role of normal force, lateral velocity, surrounding surface topography, and solution chemistry can be obtained from images of the wear of atomic steps. The wear rate is a highly non-linear function of applied normal force (essentially exponential). Our results are interpreted in terms of stressed enhanced dissolution of steps, where double kink nucleation is the rate limiting process. We present a model which fits data for all systems examined to date. Careful analysis of step stability explain the observed sensitivity of certain step orientations to the enhanced wear induced by stress. Studies of atomically flat planarization of surfaces produced by controlled scanning are presented. This work is supported in part by the National Science Foundation under Grant CMS-9414405.

11:20am **EM-WeM10 Studies on Passivation Behavior of Tungsten in Application to Chemical Mechanical Polishing***,* ***D. Tamboli,*** *S. Seal, A. Kale, V. Desai,* University of Central Florida*; Y. Obeng, A. Maury,* Bell Laboratories, Lucent Technologies

Chemical mechanical polishing (CMP) is considered to be the enabling technology for meeting the planarization requirements in < 0.35 micron feature sized multi-level devices and interconnects in semiconductor industries. Considerable importance is given to the role played by the passive oxide film formation on the surface in CMP process.@footnote 1@ However, there are very few studies available in open literature regarding the characterization of surface reaction products in terms of chemistry and thickness of the reaction layers.@footnote 2@ In this research study, X-ray Photoelectron Spectroscopy is used to understand modification of surfaces (i.e. oxide layers) during the CMP process. Tungsten wafers are treated in static solutions with varying pH, oxidizer levels, temperature and applied potential in order to determine the effect of these parameters on the chemistry of the passive oxide layers. XPS measurements are employed to probe the chemical and stoichiometric changes (e.g. WO@sub 2@/WO@sub 3@ ratio, presence of any hydroxides, etc.) in these surface films treated under various conditions. Valence band XPS studies on W(4f) and O (2p) states are performed to determine the electronic structure of the oxide layer and its relevance to passivation. These results are compared with the electrochemical studies carried out both ex-situ and in-situ during polishing. @FootnoteText@ @Footnote 1@F.B. Kaufman, et al., J.

Electrochem. Soc., 138, 3460, 1991 @Footnote 2@E.A. Kneer , et al., J. of the Electrochem. Soc., 143, 4095, Dec 1996

11:40am **EM-WeM11 Studies of the Pad-Slurry-Surface Interactions in Chemical-Mechanical Polishing of Copper Thin Films and Patterned Structures*, J. Hernandez*,** *P. Wrschka, G.S. Oehrlein,* State University of New York, Albany*; J. King,* Cybeq Nano Technologies

Chemical mechanical polishing (CMP) of copper is a key technology for producing sub-micrometer Cu lines in multilevel metallization structures. In this work, blanket copper, tantalum and silicon dioxide thin films as well as copper damascene structures were polished using different pads and slurries. Selectivities of Cu/SiO@sub2@ as high as 200:1 were observed after polishing at low pressures and velocities utilizing slurries consisting of alumina abrasive particles. Examination of planarized Cu damascene microstructures by scanning electron microscopy allowed us to investigate critical issues in CMP such as SiO@sub2@ spacer erosion, copper line recess, corrosion of sub-micron copper lines, slurry contamination, and removal selectivity of the Ta diffusion barrier. Finally, surface chemical studies of Cu, Ta, and SiO@sub2@ thin films and the pad after CMP by x-ray photoelectron spectroscopy were undertaken to assist in the identification of the controlling factors of the CMP process.

Magnetic Interfaces and Nanostructures Technical Group
Room 324/325 - Session MI+EM-WeM

Spin-dependent Devices: Technology and Processing

Moderator: B.A. Everitt, Seagate Technology

8:20am **MI+EM-WeM1 Limiting Factors in Dense Pseudo Spin Valve and Spin Dependent Tunneling Memory Arrays*, A.V. Pohm*,** *M.C. Tondra, C.A. Nordman, J.M. Anderson,* Nonvolatile Electronics **INVITED**

For pseudo spin valve or spin dependent memory technology to persist for the coming decades, they must be able to exploit the evolving sub-micron semiconductor technology and adjust to the diminishing conductor widths. However, as pseudo spin valve and spin dependent memory arrays are scaled to 0.1 micron widths or less, a number of factors play a role in limiting ultimately the memory array densities which can be achieved. An analysis has been performed which shows that to achieve adequate stability against thermal agitation for half selected cells, the shape anisotropy in the 25 Angstrom storage layer must be at least 300 Oe for 0.1 x 0.3 micron cells. Half select fields of 100 to 150 Oe are required for the write operation. This necessitates current densities in the GMR sandwich in the 10@super 8@ A/cm@super 2@ range for the sense lines and 10@super 7@ A/cm@super 2@ in the word lines. Although GMR sandwiches can tolerate the high current densities, thin dielectrics and careful use of heat sinks are required to keep the temperature rise modest. Materials such as tungsten must be used for the word line in order to have adequate electro-migration limits. Because of the high resistance and capacitance in the spin dependent tunneling memory cells, semiconductor isolation is necessary for high performance. As a consequence, maximum array density is about ½ of that for pseudo spin valve cells.

9:00am **MI+EM-WeM3 New Aspects of GMR Spin Valves: Enhancing Specular Electron Scattering and Using Surfactants for Improved Growth*, W.F. Egelhoff, Jr.*,** National Institute of Standards and Technology

We have investigated the deposition and processing of a variety of giant magnetoresistance (GMR) spin valves with the aim of optimizing their properties. We have found that many of the magnetic and magnetoresisitive properties of spin valves are strongly influenced by surface and interface effects occurring during growth. These effects include the balance of surface and interface free energies, surface diffusion, interdiffusion at interfaces, low temperature deposition, the use of surfactants to modify growth, and specular electron scattering at surfaces. In some cases, it is possible to control these factors or to use them to manipulate the growth or improve post-growth processing of spin valves to improve their magnetic and magnetoresistive properties. For example, specular scattering is particularly important for achieving the largest possible GMR values in simple spin valves. For symmetric (or dual) spin valves GMR values as large as 24.8% have been achieved, and for simple spin valves (containing only one Cu layer) GMR values as large as 19.0% have been achieved. The best hope for someday achieving GMR values in simple spin valves as large as those reported for GMR superlattices appears to be increasing the degree of specular scattering and reducing the bulk defect scattering. The author would like to acknowledge his collaborators in this work, including P. J. Chen, C. J. Powell, M. D. Stiles, R. D. McMichael, J. H. Judy, K. Takano, A. E. Berkowitz, and J. M. Daughton.

9:20am **MI+EM-WeM4 High Temperature Pinning Properties of IrMn vs. FeMn in Spin Valves*, M.C. Tondra*,** *D. Wang,* Nonvolatile Electronics

The antiferromagnetic pinning properties of IrMn and FeMn have been observed by building spin valve samples with the structure NiFeCo / CoFe / Cu / CoFe / NiFeCo / (IrMn or FeMn) and measuring their magnetoresistive properties. The pinning strength was evaluated in terms of the break field, defined as the field applied in the direction opposite to the magnetization of the pinned layer at which the pinned layer switches. At room temperature, the break fields for both the IrMn and FeMn samples were about 250 Oe. But as the temperature increased, the break field for samples pinned with IrMn held up considerably better than for those pinned with FeMn. Specifically, the pinning of the FeMn spin valves was gone at 150°C while the pinning of the IrMn spin valves persisted to temperatures above 225°C. The IrMn spin valves performed as well as the FeMn spin valves in terms of magnetoresistance and lithographic process compatibility.

9:40am **MI+EM-WeM5 Magnetisation Reversal Studies by TEM of Continuous and Patterned GMR Films*, J.N. Chapman*,** University of Glasgow, United Kingdom **INVITED**

A highly modified transmission electron microscope has been used to study magnetisation processes in a range of GMR films suitable for application in devices. Films were deposited onto silicon nitride "window" substrates suitable for study in the TEM directly after growth or following patterning. Application of fields in-situ allowed the evolution of the magnetic domain structure to be followed in real time in both continuous films and elements. The latter frequently had dimensions in the sub-micron regime. Reversal of the free layer in spin-valve films is found to depend on the strength of coupling between free and pinned layers and the orientation of the applied field, the latter being readily under the control of the experimenter. Conditions under which quasi-coherent rotation of magnetisation takes place have been established. However, very significant changes take place as the dimensions of the films are reduced and magnetostatic energy contributions play an enhanced role. Domain nucleation at corners can lead to undesirable reversal modes and for elements with micron-sized dimensions the reversal depends critically on size, shape and the nature of the pinning layer. Examples will be given of how shape modification can change the characteristic of the reversal to suit sensing or storage application. In the case of Co/Cu multilayers reversal mechanisms quite different from those in spin-valves are observed and depend critically on the nature of the coupling between the layers. Thus films with strong biquadratic coupling tend to reverse in a relatively simple manner resembling processes in single layer films whilst films with weak antiferromagnetic coupling reverse through the formation and evolution of complex sub-micron "patch" domains. Irreversible processes are prevalent in the latter case but can be effectively suppressed in the former making films with biquadratic coupling suitable for applications where low hysteresis is essential.

10:20am **MI+EM-WeM7 Deposition and Processing of Novel GMR Structures @footnote 1@*, J.R. Childress*,** University of Florida, Gainesville **INVITED**

Optimized GMR devices may require the development of magnetic multilayer film structures combining binary and ternary alloys, composition gradients, composites, and metal/insulator interfaces. The structural and magnetic optimization of individual components within these multilayers often require specialized deposition and/or processing parameters which may be mutually incompatible, or incompatible with other necessary processing. Additionally, the interfacial structural and magnetic properties of alloys may be different from bulk, further complicating the interpretation of experimental data. Several current examples and experimental approaches will be discussed, such as the development of 100% spin-polarized magnetic films using NiMnSb and other compounds, metallic and insulating antiferromagnets for exchange biasing, and metal/insulator interfaces. @FootnoteText@ @footnote 1@ Author present address: IBM Almaden Research Center, 650 Harry Rd, San Jose, CA 95120

11:00am **MI+EM-WeM9 Direct-Measurement of Spin-Dependent Transport Across Ferromagnetic and Non-Magnetic Thin Films***, **S.K. Upadhyay**, R.N. Louie,* Cornell University*; R.A. Buhrman,* Cornell University, US

We have used superconductor-ferromagnet nanocontacts to directly measure a>spin-polarization of the current in ferromagnets (Co and Ni) and b>spin dependent transmission rates of thin ferromagnetic (Co, Ni) and non-magnetic (Cu) films. Since the size of the contact (3-10nm) is smaller than other scattering lengths in the system, our measurements can selectively probe the scattering at interfaces of dissimilar metals. We will discuss our results in the context of giant magnetoresistance in thin film magnetic multilayers and their significance in understanding the role of interfacial versus bulk scattering.

11:20am **MI+EM-WeM10 Effect of Noble Gas Addition (He,Ar,Xe) on Cl@sub 2@-Based Etching of NiFe and NiFeCo***, **K.B. Jung**, H. Cho, Y-.B. Hahn, E.S. Lambers, Y.D. Park, S.J. Pearton,* University of Florida, Gainesville*; J.R. Childress,* IBM Almaden Research Center*; M. Jenson, A.T. Hurst, Jr.,* Honeywell, Inc.

The mechanism for high rate dry etching of NiFe, NiFeCo and other components of multilayer magnetic thin film devices such as read/write heads and magnetic random access memories depends on formation of chlorinated etch products, and their efficient desorption by ion-assisted sputtering. A systematic study of the dependence of noble gas species (He, Ar, Xe) additive to high-density Inductively Coupled Plasma Cl@sub 2@ discharges has been performed. The etch rates of the NiFe and NiFeCo increase in direct proportion to the atomic weight of the noble gas species, which is the dominant factor controlling etch product desorption. Increasing the weight of the additive also leads to a decrease in residual chlorine on the etched surface, as determined by Auger Electron Spectroscopy. The effect of altering the noble gas species on etch selectivity over common mask materials (SiO@sub 2@, SiN@sub X@ and photoresist) has also been studied. Facetting of the mask edges is a particular problem with Cl@sub 2@/Xe discharges.

11:40am **MI+EM-WeM11 Magnetoresistance Properties in Granular Silicide Thin Films Formed by High Dose Iron Implantation***, **M.F. Chiah**, W.Y. Cheung, S.P. Wong, I.H. Wilson,* The Chinese University of Hong Kong, Hong Kong

High dose iron implantation into silicon wafer has been performed with a metal vapor vacuum arc ion source (MEVVA) to doses ranging from 1*10@super 16@ to 2*10@super 17@ cm@super -2@ at various beam current densities. The magnetoresistance (MR) effects in these implanted granular layers were studied at temperatures from 15K to 300K. A positive MR effect, i.e, an increase in the resistance at the presence of a magnetic field, was observed at temperatures lower than about 70K in samples prepared under appropriate implantation conditions. The magnitude of the MR effect, defined as @DELTA@R/R@sub o@ = (R(H)-R@sub o@)/R@sub o@ where R(H) and R@sub o@ denote respectively the resistance value at a magnetic field intensity H and that at zero field, was found to depend on the implantation dose, the beam current density. This is attributed to the beam heating effect during implantation which affects the formation of the microstructures. The ratio @DELTA@R/R@sub o@ was found to attain high values larger than 500% for some samples at low temperatures. The dependence of the MR effects on temperature, implantation dose, substrate dopant concentration and beam current density will be presented and discussed in conjunction with results of Transmission Electron Microscopy and Mössbauer Spectroscopy. The phase of iron silicide, composition and depth of damaged layer were determined by spreading resistance, Rutherford backscattering and XRD measurements. This work is supported in part by a grant from the Research Grants Council of Hong Kong (Ref. No.: CUHK 374/96E)

Manufacturing Science and Technology Group
Room 317 - Session MS-WeM

Advanced Process Equipment and ES&H

Moderator: G.S. Oehrlein, State University of New York, Albany

8:20am **MS-WeM1 Complete Solvent Free Stripping of via Structures using NF@sub 3@,H@sub 2@O,O@sub 2@ Ashing Chemistry***, **W. Au**, R. Solis,* VLSI Technology, Inc.*; R. Bersin, H. Xu, M. Boumerzoug,* Ulvac Technologies, Inc.

The use of TiN as a base material in submicron vias employing tungsten plugs is becoming more and more accepted. One difficulty, however, is the etching of these vias and subsequent removal of polymeric residues residing at the via base and along the vertical sidewalls. Removal of these residues prior to deposition of a Ti/TiN glue layer is most critically important to achieve low contact resistance in the vias. Resist stripping and polymer-residue-removal from submicron vias is an area of intense interest at this time. Methods employing fluorine-based plasmas to render any residues DI water soluble, thereby avoiding costly and corrosive solvent processes, are under serious investigation. In this instance of TiN based vias, however, undercutting of the TiN and resulting high via resistance have been a major obstacle. A new process has been developed which address this problem. The residues are ashed utilizing a low bias RIE plasma comprising oxygen, NF@sub 3@, and H@sub 2@O vapor in correct proportions. The presence of the fluorine renders any ash residues soluble in DI water; and the H@sub 2@O vapor addition serves to inhibit the etching of the TiN base during the stripping process. The net result is a new manufacturing process which competes directly with conventional ashing and solvent processes in product performance; and which offers substantial cost savings through total elimination of solvent processing. Details of the parametric study of process conditions to achieve good TiN selectivity, excellent contact-resistance, and elimination of any TiN undercut will be discussed. A brief description of the manufacturing equipment involved will be included.

8:40am **MS-WeM2 Studies of a New High Dissociation Inductively-Coupled Plasma Downstream Strip Module***, **W. Collison**, T. Ni, B. Berney,* Lam Research Corp.

A new inductively-coupled high dissociation plasma downstream strip source (HD@super 2@ source) was developed to meet advanced market requirements for 200mm and 300mm photoresist stripping processes. Plasma simulations were used to study the dissociation percentage of O@sub 2@ gas for different chamber designs. It shows that this source can provide higher than 20% O@sub 2@ dissociation for 1500 watts power at 1 Torr. Fluid modeling was used to design the gas-redistribution plate to optimize ashing uniformity. Detailed process results will be presented and discussed. It is shown that adding 5-10% N@sub 2@ gas can increase photoresist etch rate 2-3 times. CHARM wafer tests have demonstrated no charging or UV damage. RF bias on the bottom electrode provides added capability to remove residues and enhance etch rate. A comparison of HD@super 2@ source and microwave source will also be discussed.

9:00am **MS-WeM3 Lithography for Smaller than 0.15 Micron Silicon Technology***, **A. Ishitani**,* Association of Super-Advanced Electronics Technologies (ASET), Japan **INVITED**

Lithography for smaller than 0.15 micron silicon technology Association of Super-advanced Electronics Technologies (ASET) Akihiko Ishitani KrF laser lithography (KrF) has reached its limits in terms of resolution capabilities, and hence it has become necessary to find practical application of such technologies as ArF laser lithography (ArF), electron beam direct writing (EBDW), and proximity X-ray lithography (X-ray) to realize further downscaling of silicon devices. As a result of research and development, these technologies have attained a resolution capability that is less than 100 nm. The remaining issues to be addressed are critical dimension and position accuracy, resist and optical materials, and mask fabrication. Defect inspection and repair technologies are important issues, too. Single layer resist technology for ArF will be employed down to 130 nm. Top-surface imaging technology for ArF, or mix and match of ArF with EBDW will be used between 150 to 70 nm, and VUV or EUV lithographies should deal with 100 to 50 nm. X-ray has enough potential for between 250 to 70 nm mass production. SCALPEL and Ion Projection Lithography (IPL) are also candidates for next generation lithography. ASET is focusing on optical lithography, X-ray, and mask writers. SCALPEL and IPL are mainly depending on the United States and Europe. In the future, lithography will be adopted to suit the type of LSI devices, depending on the required field size and the depth of focus. Mask size is another critical issue for mass production. Smaller mask size has higher capability for mask accuracy. Research and development of lithography now involve very large costs and risks, and hence international cooperation and exchange of information are essential for LSI industry. This work is being performed under the management of ASET in Ministry of International Trade and Industry (MITI) and Industrial Technology Development Organization (NEDO).

9:40am **MS-WeM5 Evaluation of Chamber Liners, in TCP Metal Etchers, to Reduce the Equipment Clean Time and to Increase the Mean Time between Cleans***, **J. Sappidi**, A. Liu, D. Parks, W. Au, S. Smith,* VLSI Technology, Inc.

Implementation of in-situ clean in TCP metal etchers has decreased the defect density and increased the sort yield. However, the polymer treated with in-situ clean plasma is very difficult to remove. Soaking the chamber wall with DI water or scrubbing the chamber wall to remove polymer have disadvantages. Water absorbed by chamber walls during soaking take a long time to out gas, this increases the equipment downtime. Scrubbing the chamber is very labor intensive and extends the clean time. Scrubbing combined with reactive ion bombardment during plasma processing accelerates the erosion of the chamber walls anodization. In order to reduce the clean time and increase the life of anodization on chamber walls, a set of chamber liners were evaluated. When the machine goes down for clean, rather than cleaning the entire inside chamber wall, the dirty liners can be replaced with the clean ones. This helps in reducing the cleaning time and protects the chamber anodization from eroding. . These liners were evaluated for 0.5 µm and 0.35 µm technologies. Installation of chamber liners demonstrated less than five percent process shift in terms of etchrates and selectivities. Experiments also demonstrated the metal etch process repeatability of the liner kits installation after chamber wet clean. The metal etch related defects were monitored with and without liners. The sort yield data was also collected and analyzed. The reactor with chamber liners proved superior in terms of both cleanliness and sort yield.

10:00am **MS-WeM6 Evolution Effects of Reactor Inner Wall Surface on Fluorocarbon Plasma Parameters***, H. Oshio, M. Ogata, **T. Ichiki**, Y. Horiike,* Toyo University, Japan

SiO@sub 2@ contact hole etching using fluorocarbon plasmas cause various issues such as etch stop, relating closely to the change of plasma state due to the deposition on the reactor wall. To clarify wall effects, variations of CFx(x=1-3) radical densities, pressure and wall temperatures with the C@sub 4@F@sub 8@ discharge time were investigated. Inductively coupled plasma was generated by 13.56 MHz power supplied to an antenna wound around a 130 mm @phi@ quartz bell jar connected to a 150 mm @phi@ SUS reactor. A 130 mm @phi@ Cu barrel, whose temperature was controlled by water was inserted into the reactor. An orifice head of the appearance mass spectroscope(AMS) was set at 15 cm apart from the antenna. Etching experiments were carried out on a stage equipped with a load-locked system. At first the reactor was cleaned by ashing, then pressure evolution with discharge time was measured for different residence times,@tau@. At @tau@=100 msec the pressure once dropped, and then gradually increased after 3 min. AMS revealed the pressure increase was mainly attributed to increase in CF@sub 3@ radical. The initial decrease resulted from singnificant adsorption of radicals on the cleaned wall. The run-to-run variations were measured by repeating a cycle of 3 min discharge on and 3 min off for 20 times. The wall temperature rise reached its steady state at 50 - 80 ° after the 5th run, while the pressure kept on increasing even over the 20th run. SiO@sub 2@ and Si etch rates as well as plasma potentials decreased corresponding to these increases. In contrast, at @tau@=30 msec run-to-run variation slightly occured after the 3rd run and detailed measurements of pressure evolution with time revealed no initial drop but the rapid increase after plasma ignition, caused by the high deposition rate due to the high radical density. Furthermore, water cooling of the bell jar suppressed the increase in pressures. Consequently to adopt short residence time and control the wall temperature is important for keeping CF@sub 3@ radical density constant to achieve good reproducibility.

10:40am **MS-WeM8 Studies of 300MM Poly-Silicon Etch Processes Using A Inductively Coupled Plasma Source***, **T. Ni**, W. Collison,* Lam Research Corp.*; K. Takeshita,* Lam Research Corp., Japan, Japan.

Inductively-coupled plasma sources have been successfully applied to 200mm poly-silicon wafer etch processes. As semiconductor wafer size increases from 200mm to 300mm, scaling up sources to meet the same or even more stringent requirements is very challenging. In this study, a transformer coupled plasma (TCP) chamber is designed and studied for 300mm poly-silicon etch processes. Plasma simulation and Langmuir probe were used to investigate the effects of TCP power, chamber pressure, aspect ratio , and coil configuration on plasma uniformity. As a result, plasma uniformity is optimized from 5mTorr to 80mTorr. Effects of different gas injection schemes are carefully examined. It is found that gas injection has strong impact on etch uniformity and profile. A unique gas injector is designed to deliver gas efficiently and minimize profile microloading. A TCP coil is constructed to provide uniform plasma and uniform etch rate. Large conductance of the chamber allows high flow processes. Advanced control systems are implemented to improve process repeatability, minimize chamber-to-chamber variation, and increase throughput. Excellent etch results and wide process window were achieved. Detailed etch process results will be presented and discussed.

11:00am **MS-WeM9 Integrating Process Models and Operational Methods***, **J.W. Herrmann**, N. Chandrasekaran, R.Z. Shi, B.F. Conaghan, G.W. Rubloff,* University of Maryland

Though substantial attention is currently paid to unit process modeling/optimization and to operations/scheduling at the sector and fab levels, the relation between them has seen little exploration. This work attempts to bridge the gap between manufacturing process models and operational methods in order to systematically examine the consequences of these interactions: e.g., how the evolution of process technology will affect production, alter equipment design preferences, or suggest changes in scheduling strategies; or, what benefit to sector or factory metrics might be achieved if process or equipment improvements could be realized. The sensitivity analysis and optimization techniques in this work incorporate response surface models, which describe the manufacturing processes, and simulation and scheduling techniques, which evaluate the manufacturing system. Current work, described here, focuses on the fabrication of the tungsten plug, involving contact clean, Ti/TiN liner, and W CVD process steps carried out in a cluster tool. Response surface models for these steps are integrated in operations simulations for different cluster tool architectures (e.g., Novellus Concept II and Applied Centura) to evaluate the consequences of process-operations interactions. For each cluster tool, we describe how throughput and cycle time change as the process parameters and equipment design parameters vary. Thus, each tool's operational sensitivity is measured, which enables prediction of the impact of process changes.

11:20am **MS-WeM10 Application of an Inductively-Coupled Plasma Source to Destruction and Abatement of Fluorine-based Gases***, **L.J. Mahoney**, D.C. Carter, M.S. Amann, G.A. Roche,* Advanced Energy Industries

Recently high density plasma sources have been used to assist in the abatement of residual hydro-fluorocarbon and per-fluorocarbon gases which are used in many manufacturing processes. In this application, oxygen-containing gas mixtures are added with the exhaust gases from a vacuum process chamber within the foreline of a processing system. The mixture is then activated by a high-density plasma means in order to converted the hydro-fluorocarbon and per-fluorocarbon process gases into constituents that are more easily removed from the exhaust within an air scrubber. An economical and modular inductively-coupled plasma source has been devised to investigate the power coupling and process requirements necessary to effectively abate post-process gases by this method. The relatively high power density source is configurable to operate near 400 kHz , 2 MHz or at 13.56 MHz with more than 2 kW of delivered power. Abatement destruction efficiencies are shown for several gases including CF@sub 4@, C@sub 2@F@sub 6@, CHF@sub 3@, and SF@sub 6@ as determined by mass spectroscopy over a wide range of power, pressure, and total flow conditions and range of added oxygen/argon/nitrogen gas mixtures.

11:40am **MS-WeM11 Low Dielectric Polymer Etching with a Downstream Microwave Plasma***, **R.R.A. Callahan**, G.B. Raupp, S.P. Beaudoin,* Arizona State University

The semiconductor industry has signed a memorandum of understanding with the EPA to reduce the amount of fluorocarbon gases used. In particular, this impacts the way that silicon dioxide etching is performed. At the same time, new dielectric materials that offer lower dielectric constants than silicon dioxide are required to help reduce chip speeds. Polymer dielectrics offer reduced dielectric constants compared to silicon dioxide, and they also can be etched using oxygen, not fluorocarbon gases. We have studied the etching of parylene films using a downstream microwave oxygen plasma, and we will report on the effects of temperature on the etch rate and will provide a tentative etching mechanism.

Wednesday Morning, November 4, 1998

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+AS-WeM

Innovative Force, Near-Field Optics, and Tunneling Measurements

Moderator: H.G. Craighead, Cornell University

8:20am **NS+AS-WeM1 Recent Progress in the Functionalisation of AFM Probes using Electron-Beam Nanolithography***, H. Zhou, G.M. Mills, B.K. Chong, L. Donaldson,* ***J.M.R. Weaver,*** Glasgow University, Scotland **INVITED**

Scanned probe microscopy has greatly expanded the range of contrast mechanisms available to microscopists. Until recently, however, the only techniquees available to the non-specialist user have been those which involve either the modification of the SPM instrumentation (for example Scanning Capacitance Microscopy) or relatively simple functionalisation of the probe (for example Magnetic Force Microscopy). More complex techniques, based on the fabrication of advanced probes, have largely remained confined to a relatively small number of groups. These include the Hall Probe Microscope,@footnote 1@ The scanning Single Electron Transistor@footnote 2@ and others. Recently progress has been made towards methods whereby probes may be modified using batch fabrication techniques such as focussed ion beam deposition,@footnote 3@ controlled etching processes@footnote 4@ or direct-write electron-beam lithography.@footnote 5@ This talk describes recent work in which the last named method has been used to fabricate Near-Field Optical (SNOM), Thermal (SThM) and Magnetic sensors. Results will be presented from SNOM and SThM sensors and progress in sensor technology will also be discussed. @FootnoteText@ @footnote 1@A. Oral et. al. J. Vac. Sci. Technol. B14 (2) p.1202-5 (1996) @footnote 2@M.J. Yoo et. al. Science 276 (5312) p.579-82 (1997) @footnote 3@K. Luo et. al. Appl. Phys. Lett. 71 (12) p.1604-6 (1997) @footnote 4@E. Oesterschulze Appl. Phys. A66, S3-9 (1998) @footnote 5@H. Zhou et. al. J. Vac. Sci. Technol B16 (1) p.54-58 (1998)

9:00am **NS+AS-WeM3 Surface Derivatization of Nanoscale Tungsten Tips for Interfacial Force Microscopy***,* ***K. Griffiths****, P.R. Norton, J.F. Graham, M. Kovar, F. Ogini, O.L. Warren,* University of Western Ontario, Canada

Interfacial force microscopy (IFM) is a novel technique not only for imaging surfaces at resolutions approaching those obtainable with atomic force microscopy, but also for the quantitative determination of the mechanical properties of a material such as elastic modulus, hardness etc., with lateral resolutions of ~nm and depth resolutions ~0.1 nm. The IFM force-compensated sensor permits the acquisition of quantitative force (f) versus distance (d) curves, which through appropriate analysis yield the mechanical properties. Because of the extreme pressures that can be attained in tip-surface contact (many GPa), it is essential to passivate the chemical interactions between the probe tip and the substrate under investigation to prevent strong adhesion effects such as metal-metal bond formation. Studies on Au surfaces are feasible because of the efficacy of self-assembled thiol monolayers on Au. However, convenient and effective protective monolayers are not generally available for many substrates, and it is best to develop a general procedure of passivating the probe tip. Our present studies involve parabaloidal tungsten tips of radii 25<r<200 nm. We have shown that it is possible to use silyl coupling agents (octadecyltrichlorosilane; OTS) to derivatize tungsten surfaces. Using the same techniques we have shown that the nm-scale W-tips can also be derivatized. Measurements were made of the f-d curves for the following tip-substrate couples: underivatized W-tip against underivatized Au(111) surface, underivatized W-tip against derivatized Au(111) surface (C-18 thiol SAM) and derivatized W-tip (OTS) against underivatized Au(111). The data clearly show that the OTS derivatized tips were passivated against adhesive contact even at pressures of many GPa, demonstrating the necessary stability for use in nanoindentation experiments.

9:20am **NS+AS-WeM4 Silicon Cantilevers for Ultrahigh-Density Data Storage***,* ***A. Kikukawa****, H. Koyanagi, K. Etoh, S. Hosaka,* Hitachi Ltd., Japan

In the past few years we have been working on applying atomic force microscopy (AFM) technologies in data storage. One of the most important issues is to increase the data transfer rate (DTR). Thus, it is required to increase the cantilever resonance frequency but keeping the spring constant sufficiently small. Also, an integrated sharp tip is required for reading the small recorded marks. The smallest one we have made so far is an equilateral-triangle cantilever 7 µm long and 0.1 µm thick. Its measured resonance frequency is 6.1 MHz, which is about two magnitudes higher than most of the cantilevers used in AFM, and the calculated spring constant is 0.75 N/m. It was fabricated from a SOI (silicon on insulator) wafer using anisotropic reactive ion etching (RIE) for cantilever shape etching, isotropic RIE for the tip etching, and KOH anisotropic etching for removing excess bulk silicon on the back side and making it a freestanding cantilever. The most difficult part in making such small cantilevers was to control the variation of their dimensions. They are caused mostly by the lateral variation of the wafer thickness and the alignment error (±4 µm at maximum) between the cantilever pattern defined on the active layer and the handling piece pattern defined on the bulk side. We reduced the variation to a sufficient level not by connecting the cantilever directly to the handling piece but by connecting the cantilever via a supporting region sufficiently thicker than the cantilever and whose shape was defined from the cantilever side. We also developed new type of optical lever that can focus the incident beam spot diameter as small as 5 µm and that can be operated with a bandwidth as wide as 10 MHz. From a noise characteristic analysis, the sensitivity of the system was obtained as 4.84 µrad at 10 MHz bandwidth which corresponds to 0.48 Å when a 10 µm long cantilever is used. That is, we now have basic technologies for demonstrating a DTR of 10 Mbps.

9:40am **NS+AS-WeM5 Capacitative Force Modulation Technique in Nanoindentation***,* ***S. Asif****, K.J. Wahl, R.J. Colton,* Naval Research Laboratory*; S.G. Corcoran,* Hysitron, Inc.

The sinusoidal force modulation technique for nanoindentation has been implemented using a three-plate capacitative force/displacement transducer developed by Hysitron, Inc. The force modulation technique can be used to detect the surface of the specimen very accurately with the stiffness sensitivity of 1N/m or less. The low spring mass (243mg), spring stiffness (120N/m) and the low damping coefficient (0.007 Ns/m) of the transducer allows one to measure the damping losses in most of the materials including metals. The experimental results on indium at room temperature indicate that the damping of the material influences the modulus measurement. The technique can be used to measure the loss and storage modulus of polymer materials (e.g. poly(vinylethylene)) and thin film systems. The experimental technique will be described together with the importance of system calibration and specimen mounting.

10:00am **NS+AS-WeM6 Nanoindentation as a Probe of Stress State***,* ***K.F. Jarausch****,* North Carolina State University*; J.D. Kiely, J.E. Houston,* Sandia National Laboratories*; P.E. Russell,* North Carolina State University

A dependence of elastic response on the local stress-state of a material has been demonstrated using the interfacial force microscope (IFM). This investigation was prompted by a previous IFM survey in which the mechanical response of Au thin films was found to correlate with the films' residual stress state and not with morphology or substrate adhesion. In order to better establish the details of this relationship a concentric ring bending device was built to investigate the dependence of IFM nanoindentation measurements on applied tensile and compressive stresses. The measured elastic modulus was shown to increase to 65 +-6MPa with applied compressive stress (50 +-10MPa) and decrease to 32 +-9MPa with applied tensile stress (-50 +-10MPa). The response of the unstressed film was 47 +-6MPa throughout the measurement sequence demonstrating that this change in response is not due to any permanent change in the film. Elastic response was also found to vary as a function of work hardening, indentation position relative to morphological defects, and ion implantation dose. Results from these five experiments will be discussed in terms of possible mechanisms, in an effort to identify how stress alters the measurement process and causes the variation of Au's nano-mechanical properties. These experiments suggest that the IFM has the potential for being able to measure stress state on a very local level. 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.

10:20am **NS+AS-WeM7 Nano-scale Observations of Stress-Enhanced Dissolution in Monoclinic CaHPO@sub4@ 2H@sub 2@O: Chemical vs. Mechanical Effects***,* ***S.C. Langford****, L. Scudiero, J.T. Dickinson,* Washington State University

In several mechanical wear situations, e.g., biomaterials in hip replacements and mechanochemical polishing (used extensively in the microelectronics industry), a surface experiences simultaneous tribological loading and corrosive chemical exposure. The combination can greatly increase wear rates. We examine single crystal brushite [CaHPO@sub 4@ 2H@sub 2@O] (a model biomaterial) in buffered aqueous solutions mechanically stimulated by the tip of a Scanning Force Microscope (SFM). Quantitative data on nanometer-scale wear of single atomic layer steps are readily obtained. The (010) faces of this material are strongly anisotropic, forming trianglular etch pits bounded by three crystallographically distinct steps in aqueous solution. Stress-enhanced dissolution is readily observed along all three steps. On each step, the wear rate is a highly nonlinear (essentially exponential) function of contact force; this function dependence is modeled in terms of stress-enhanced double kink nucleation. At low contact forces, etch pit growth principally involves dissolution along [210] steps; in contrast, the [101] steps are far more vulnerable to wear at high contact forces than the other steps. Damaged regions along [101] steps are especially vulnerable to subsequent chemical dissolution. We exploit this effect to produce atomically flat surfaces many microns in dimension. We also describe the influence of tip velocity and solution chemistry on the rates of corrosive wear. This highly anisotropic material provides a useful system for isolating aspects of the crystal structure which render it vulnerable to chemical etching from those which make it vulnerable to mechanical damage. This work is supported in part by a grant from the National Science Foundation, Grant CMS-9414405.

10:40am **NS+AS-WeM8 Conductance and Force at an Atomically Defined Junction***, **G. Cross**, A. Schirmeisen, A. Stalder, P. Grütter,* McGill University, Canada*; U. Dürig,* IBM Research Division, Switzerland

We have simultaneously measured conductivity and force between an atomically defined tip and atomically flat sample in UHV. The sharp metal tips are manipulated and characterized on an atomic scale both before and after the sample approach by field ion microscopy (FIM). Conductivity over a large range is obtained by a multidecade nonlinear current amplifier,@footnote 1@ while simultaneously forces between the tip and sample are measured by an in-situ differential interferometer with sub-nN force sensitivity. We report on the conductivity and force vs. tip-sample separation relationships for specific atomic tip geometry. In particular, we have examined the precontact regime characterized by short-ranged attractive forces. In this regime, we find that for a trimer W tip approaching an Au(111) surface, the square of the force depends linearly on conductivity. This can be understood if one assumes that both tunneling and adhesion quantum mechanical exchange interactions are due to overlap of tip and sample wavefunctions.@footnote 2@ @FootnoteText@ @footnote 1@U. Dürig, L. Novotny, B. Michel, A. Stalder , Rev. Sci. Instr. 68, 3814 (1997) @footnote 2@C. Chen, J. Phys. Cond. Matter 3, 1227 (1991)

11:00am **NS+AS-WeM9 Chemical Imaging with Scanning Near Field Infrared Microscopy***, **C.A. Michaels,*** National Institute of Standards and Technology, US*; R.R. Cavanagh, S.J. Stranick, L.J. Richter,* National Institute of Standards and Technology

The development of a scanning near field microscope that utilizes infrared absorption as the optical contrast mechanism will be discussed. This instrument couples the nanoscale spatial resolution of a scanned probe with the chemical specificity of vibrational spectroscopy. This combination allows the in situ mapping of chemical functional groups with subwavelength spatial resolution. Key elements of the microscope include; an ultrafast IR light source producing pulses with a FWHM bandwidth of 150 cm@super -1@, an infrared focal plane array based spectrometer allowing parallel detection of the entire pulse bandwidth with 4 cm@super -1@ resolution, and a near field probe fabricated from fluoride glass fiber allowing single mode transmission over the range 2.2 to 4.5 µm. Factors influencing the optical and topographic resolution characteristics of this microscope will be presented. Additionally, the performance of the microscope in discriminating chemical species based on their IR optical properties will also be described.

11:20am **NS+AS-WeM10 Tapping-Mode and Nonoptical Force Sensing Near-Field Scanning Optical Microscopy***, **D.P. Tsai**, Y.Y. Lu,* National Chung Cheng University, Taiwan

We present a tapping-mode and nonoptical force sensing near-field scanning optical microscopy system. A high Q quartz tuning fork with resonance frequency of 32.768 kHz is used as a force sensing transducer. The piezoeletric current of the tuning fork is lock-in amplified and served as a signal for distance control. Excellent quality of tapping-mode sensing and imaging was obtained. The sensitivity of image is comparable to optical force sensing technique. Results show low background signal and high signal to noise (S/N)ratio for near-field optical contrast, and the elimination of possible optical excitations arising from the force sensing laser light source. Applications on the near-field optical writing and reading on the light sensitive samples show the advantages of this novel method.

11:40am **NS+AS-WeM11 Development and Application of a Dual-Probe Scanning Tunneling Microscope for Nanoscale Investigations of Materials***, **H. Grube**, M. Allgeier, J.J. Boland,* University of North Carolina, Chapel Hill

Scanning tunneling microscopy has evolved into a valuable tool for the study of the structural and electronic properties of semiconductor and metal surfaces, as well as enabling fabrication of novel nanoscopic electronic devices. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states (LDOS).@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within 100nm of the first is expected to enable measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ To this end our lab has completed construction of one of the first dual probe STMs in which tips can be placed 10-100nm apart. Each tip is mounted on an independent tube scanner with independent piezo drivers, current preamplifiers and feedback controllers. The scanners have two and three degrees of freedom for coarse motion, achieved through the use of modified commercial inertial sliders. These five degrees of freedom allow for the precise positioning of the two probes into overlapping scanning ranges of the tubes. In this DP-STM configuration it is possible to inject a current into the sample at an arbitrary location with one tip and detecting a change of the electrical environment of the sample with the other probe arbitrarily positioned close by. Therefore it is possible to probe the transport properties of the medium or three terminal nanoscale device. Our DP-STM has been characterized by using each tip to scan its local surface environment and then overlaying the images obtained to determine the inter-tip separation. @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)

Plasma Science and Technology Division
Room 318/319/320 - Session PS-WeM

Plasma Damage

Moderator: J. Werking, Sematech

8:20am **PS-WeM1 Gate Oxide Damage: Testing Approaches and Methodologies***, **C.T. Gabriel**,* VLSI Technology, Inc. **INVITED**

Plasma processing of MOS devices has the potential to induce damaging current flow through thin gate oxides. Many studies have undertaken to measure this damage, using what at first appears to be a bewildering variety of measurement techniques. A natural question to ask is, which measurement technique is best? Can't the industry standardize on a particular technique? Actually, to study gate oxide damage, a variety of complementary techniques is needed. There are two broad families of gate oxide damage measurement techniques: those that characterize the charging source independent of the gate oxide, and those that characterize the effect of the damage by examining gate oxide degradation. To study the damaging potential of the plasma itself, measurement devices include EEPROM transistors, MNOS transistors, contact potential difference, and direct measurement techniques. To study the effect that plasma damage has on gate oxide, electrical parameters are measured appropriate for capacitors and transistors, which are typically connected to large, conductive "antennas" over thick field oxide. To select the proper measurement technique, one must first have a fundamental understanding of the damage mechanism. Charging during plasma processing arises from two main sources: plasma nonuniformity and electron shading. Plasma nonuniformity is relatively independent of the wafer, so a wide variety of techniques can be used to predict or detect damage resulting from it. However, electron shading is essentially an interaction with structures on the wafer, so damage detection is critically dependent on the measurement technique. The options for measuring gate oxide damage will be reviewed and compared, leading to a selection of "application-specific" damage measurement techniques.

9:00am **PS-WeM3 Evaluation of Charging Damage Test Structures for Ion Implantation Processes***, **M.J. Goeckner**, S.B. Felch, J. Weeman, S. Mehta,* Varian Associates*; J.S. Reedholm,* Reedholm

Charging damage is a critical issue in both current and future ion implantation systems. In conventional ion implanters, plasma flood guns have been used successfully to reduce charging damage. However, the development of sub-0.18 µm devices will make control of wafer charging more important. In addition, sub-0.18 µm devices will require novel doping technologies such as ultra-low energy (ULE) ion implanters or plasma doping (PLAD). Throughput requirements for these new technologies, and other issues, might also make charging damage more prevalent. Because of these concerns, we are examining the efficacy of two charging test structures. They are Varian Research Center's (VRC) proprietary charging test structures@footnote 1@ and the test structures on CHARM-2 wafers.@footnote 2,3@ These test structures operate on two very different principles. The VRC test structures use static "antenna" MOS capacitors, while the CHARM-2 uses programmable EEPROM's. Each system has distinct limitations and advantages. For example, the CHARM-2 wafer can be used to measure the maximum induced surface voltage; however the result is influenced by the elapsed time between programming, exposure and data collection. In comparison, the VRC result is static, but the precise value of the induced surface voltage can not be measured. Both structures will be put through a series of tests on both PLAD and traditional implanters. Comparisons will be made of sensitivity, temporal and spatial variability, as well as any potential limitations or advantages each might have for examining charging in ULE and PLAD implantation environments. @FootnoteText@ @footnote 1@S.B. Felch and S. Mehta in "Materials and Process Characterization of Ion Implantation," Edited by M.I. Current and C. B. Yarling, (Ion Beam Press, Austin TX, 1997), pp 288-295. @footnote 2@W. Lukaszek in "Materials and Process Characterization of Ion Implantation," Edited by M.I. Current and C. B. Yarling, (Ion Beam Press, Austin TX, 1997), pp 296-317. @footnote 3@CHARM-2 is a registered trademark of WCM.

9:20am **PS-WeM4 SPORT Measured Electron Shading Effects 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 processed 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. This study uses SPORT wafers to measure plasma parameters and the shading effect in a commercial plasma etcher. The advantage of using a SPORT wafer is that the plasma measurements are at the wafer surface. The SPORT wafer was used as a planar floating asymmetric double probe. Ion and electron currents were collected and the electron energy distribution calculated. Measurements were also done with patterned pads of different aspect ratio features. Differences in the ion and electron current were clearly seen between a bare and shaded pad. A PIC simulation was used to predict shading effects. The simulation is able to account for charged resist structures that cause electron shading. Comparisons were made between the simulation and the experimental results.

9:40am **PS-WeM5 Suppression of Charging Damage Caused by Electron Shading Effect in Gate Etching Technology*, K. Yoshida,*** *K. Tokashiki, H. Miyamoto,* NEC Corporation, Japan

Recently, the charging damage caused by electron shading effect has become a serious problem in etching processes using high-density low-pressure plasma. This effect causes profile distortion and/or gate oxide degradation. It is expected that these problems would be enhanced in sub-quarter-micron device fabrication because of their high aspect ratios. We reported in American Vacuum Society 44th National Symposium(PS-MoM8) that the profile distortion was suppressed by applying the high pressure(@>=@20 mTorr) and low source power in HBr gas plasma to over-etching step for 0.18 µmm gate etch process. Furthermore we have studied the correlation between the profile distortion and the gate oxide degradation in order to suppress the charging damage successfully. The impact of gas chemistry (Cl@sub 2@ and HBr) and pressure on charging damage was evaluated in gate etching. Especially we focused on the just and over etch period because the charging damage takes place in this period. Thickness of gate film and that of gate oxide were 200 nm and 4.5 nm, respectively. An initial-electron-trapping-rate (IETR) method was applied to monitor the charging damage. We measured dV/dt slope under 40 mA/cm@super -2@ stress current with antenna ratios ranged from 50 to 66,700. At low pressure (2 mTorr) Cl@sub 2@ and HBr plasmas, dV/dt slope increased significantly as the antenna ratio were over 10,000. The dV/dt reached about 10 mV/sec, which means serious damage took place. However, as increasing in pressure, dV/dt slope or charging damage was effectively suppressed (dV/dt@<=@2 mV/sec at 20 mTorr). It was also found that HBr plasma more effectively suppressed the damage than Cl@sub 2@ plasma. Interestingly, these damage test results corresponded to the dependence of the profile distortion on gas chemistry and pressure. One of reasons for the different damage result between Cl@sub 2@ and HBr correlates with the different plasma characteristics between them. Electron temperature(T@sub e@) and density(N@sub e@) for Cl@sub 2@ plasma were higher than that of HBr plasma at the pressure ranged from 2 to 20 mTorr. T@sub e@ and N@sub e@ decreased with increasing pressure, 4.2 to 2.9 eV of T@sub e@ and 2.5E10 to 9.5E9 cm@super -3@ of Ne for Cl@sub 2@ plasma. In HBr plasma, T@sub e@ and N@sub e@ were lowered to 2.6 eV and 4E9 cm@super -3@ at 20 mTorr. In conclusion, the gate oxide degradation caused by electron shading effect correlates with the profile distortion. And the use of relatively high pressure(@>=@20 mTorr) HBr plasma in just and over etch period is useful to suppress the charging damage caused by electron shading effect.

10:00am **PS-WeM6 Modeling of Charging Damage during Dielectric Deposition in High-Density Plasmas***, G.S. Hwang,* ***K.P. Giapis,*** California Institute of Technology

The mechanism of charging up of interconnect metal lines during interlevel dielectric (ILD) deposition in high-density plasmas is investigated by detailed and self-consistent Monte Carlo simulations of pattern-dependent charging.@footnote 1@ The results suggest that the initial conformality of the ILD film plays a crucial role in metal line charging up and the subsequent degradation to the buried gate oxide to which the metal line is connected. Line charging occurs when the top dielectric is thick enough to prevent tunneling currents while the sidewall dielectric thickness still allows tunneling currents to flow to the metal line; the differential charging of the sidewalls, which induces the latter currents, is caused by electron shading. The simulations include a treatment of charge dissipation along the surface of the dielectric;@footnote 2@ surface currents can significantly decrease the cumulative charging damage when facile at small surface potential gradients. Charging damage during plasma-assisted ILD deposition could become a problem more serious than that occurring during plasma etching and is expected to pose additional requirements to low-k dielectrics currently sought to replace SiO@sub 2@. However, under the assumptions considered, a dramatic reduction in charging damage can be accomplished by depositing a more conformal ILD film around the metal line and/or by increasing the ability of the film surface to dissipate charge. @FootnoteText@ @footnote 1@ G. S. Hwang and K. P. Giapis, J. Appl. Phys., Vol. 84, to appear on July 1, 1998. @footnote 2@ G. S. Hwang and K. P. Giapis, Appl. Phys. Lett., Vol. 71, 458 (1997).

10:20am **PS-WeM7 Silicon Oxidation Employing Negative Ion under Transformer Coupled RF Bias*, H. Shindo,*** *T. Fujii, T. Koromogawa,* Tokai University, Japan*; Y. Horiike,* Toyo University, Japan

Directional silicon oxidation technique is highly required in various ULSI processes. Especially for trench isolation of memory cell, the oxidation should be directional but with low damage. For this purpose, a new method of negative ion assisted silicon oxidation has been experimentally studied employing a microwave O@sub 2@ plasma. A feasibility of directional silicon oxidation by negative ion was examined. 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 @super -@ and its density was more than one order higher than O @sub 2@@super -@. The oxide film quality produced was analyzed by XPS, FTIR and ellipsometer. The oxidation depth under the positive DC biases without any local discharge showed a great voltage dependence, meaning a major role of negative ion O @super -@ for oxidation. While under the negative DC biases the oxidation was rather small but the fairly large amount of the sputtering was observed at the voltage as small as 50 V, indicating the high chemical reactivity of O @super -@. In conjunction with the sputtering, however, it was observed that the sputtering became remarkable in a condition of oxidation saturation. On a basis of the oxidation depth obtained under these DC biases, directional oxidation was examined under low frequency RF bias of 100 kHz with a transformer couple to apply the net positive voltage for negative ion. This directional oxidation was made employing a Si sample of line and space with SiO@sub 2@ mask. It was demonstrated that the directional oxidation of1500A depth was possible under the RF bias of 25 W with 10 minute.

10:40am **PS-WeM8 Direct Measurement of VUV Caused Oxide Conduction during Plasma Charging*, J.P. McVittie,*** Stanford University

In a plasma the local charging voltage of a floating structure is controlled by the difference in local electron and ion fluxes, the local capacitance and the feedback of the developed voltage on the local plasma sheath, which controls the electron current. Any additional discharging current paths will also affect the charging voltage and subsequent device damage. One such current path which is poorly understood is UV induced photoconductivity in dielectrics. Among of the problems in understanding this discharging path has been the difficulty in measuring dielectric conduction in a plasma and in separating charging from UV effects. In his work a very low density plasma was used to induced charging up to 20 V while a separate high density plasma separated by a thin filter/window was used to generate the vacuum UV. For monitoring charging a bare SPORT charging probes were used, and to monitor photoconductivity oxide covered probes were used. Conductivity which deceased linearly with the UV source power was observed. In addition, the conductivity deceased with 1/ oxide thickness squared. Finally, by using different filters it was concluded that VUV near the oxide band gap of ~9 eV was causing the conductivity. All these observations are consistent classic bulk induced photoconductivity. The implications of this dielectric conductivity on charging and related damage will be discussed.

11:00am **PS-WeM9 Vacuum Ultraviolet Spectra of Metal-Etch Plasma Processing Discharges***, J.R. Woodworth, M.G. Blain, R.L. Jarecki,* Sandia National Laboratories*; T.W. Hamilton,* Sandia National Laboratories, U. S. A*; B.P. Aragon,* Sandia National Laboratories, U. S. A.

We report measurements of the absolute fluxes of vacuum ultraviolet (VUV) photons to the wafer in a commercial aluminum-etch inductively coupled plasma processing tool for discharges containing chlorine, boron trichloride and argon. Most of the VUV emissions that we observed above 8 eV in these discharges were due to spectral lines of neutral chlorine atoms. Spectra and absolute fluxes as a function of rf power, substrate type, gas mixture, and pressure will be presented. This work was supported by the United States Department of Energy Under Contract No. AC04-94AL8500, by SEMATECH, and by Applied Materials. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

11:20am **PS-WeM10 Spatial Characterization of Plasma VUV Emission in an ECR Etcher***, **C. Cismaru**, J.L. Shohet,* University of Wisconsin, Madison

In MOS (Metal-Oxide-Semiconductor) device fabrication, plasma processing plays an important role since it has many advantages in terms of process convenience, directionality and high resolution. However, because of the existence of charged particles, together with x-ray and vacuum ultraviolet emission, plasma processing enhances the possibility of damage of the processed materials. The damage potential of vacuum ultraviolet emission of processing plasmas on MOS devices is investigated. High energy photons, with energies higher than the energy band gap of SiO@sub 2@ (~9 eV) can be generated from recombination and relaxation processes in the plasma. It has been established that electron-hole pairs generated in the oxide by these photons@footnote 1@ will increase the SiO@sub 2@ bulk and Si/SiO@sub 2@ interface trapped-charge density, which will affect the device quality accordingly.@footnote 2@ In this work, emission spectra of various plasmas have been recorded in an ECR (Electron Cyclotron Resonance) etcher, at pressures ranging between 0.5 mTorr and 5 mTorr, and microwave powers between 700 W and 1000 W. The measurements were taken in the range of 20 Å to 3000 Å (600 eV to 4 eV), with a one-meter normal incidence vacuum monochromator, with a resolution of 0.2 Å. By use of a special reflection probe, the spectra were also recorded as a function of position across the wafer stage. The measurements show that most of the VUV emission of processing plasmas ranges above 9 eV, which may result in a potentially damaging effect on MOS devices. Also, a nonuniformity of the VUV photon flux impinging on the wafer surface as a function of position across the wafer has been found. This nonuniformity should be considered as having the potential for another MOS processing damaging factor. This work was supported in part by the National Science Foundation under Grant No. EEC 8721545. @FootnoteText@ @footnote 1@ R. A. Gdula, IEEE Transaction on Electron Devices 26(4), 644 (1979). @footnote 2@ R.J. Powell and G.F. Derbenwick, IEEE Transactions on Nuclear Science 18(6), 99 (1971).

Selected Energy Epitaxy Topical Conference
Room 327 - Session SE-WeM

Selected Energy Epitaxial Growth Processes

Moderator: R. Brandt

8:20am **SE-WeM1 Ab Initio Studies of the Surfaces and Growth of GaN and AlN***, **W.A. Goddard III**, R.P. Muller, B.L. Tsai,* California Institute of Technology **INVITED**

We have examined the reconstruction and growth of cubic GaN and AlN using Density Functional Theory with Generalized Gradient Approximations. We find stable surfaces for excess metal lead to a c(2x2) structure while stoichiometric leads to metal termination but a P(2x2) structure. Implications for growth will be discussed.

9:00am **SE-WeM3 Film Defects and Growth Dynamics in Wide Bandgap Epitaxy***, **F.A. Ponce**,* Xerox Palo Alto Research Center **INVITED**

The III-V nitride semiconductors have achieved a high degree of notoriety in the last few years.@footnote 1@ Light emitting devices based on double heterostructure InGaN/GaN films have been produced with light emission efficiencies exceeding incandescent lighting. Blue diode lasers with continuous operation for more than 10,000 hours using AlGaN/GaN/InGaN heterostructures have been reported and their commercial use is expected in the near future. The high optoelectronic performance of nitride semiconductors is related to an interesting microstructure, quite different from other semiconductors. Large dislocation densities are observed (~10@super 10@ cm@super -2@) and are associated with a columnar array of defect-free crystallites. The defect structure appears to play a key role in the relaxation of thermal stresses, typical in these materials, allowing the local growth of high quality heterostructures under otherwise unfavorable conditions. The nature of the substrate/thin film interfaces will be discussed, as well as the role of the buffer layer. Details of the dislocation arrangement and structure and correlation with light emitting properties will be presented for GaN thin films and for InGaN quantum wells. @FootnoteText@ @footnote 1@ F. A. Ponce and D. P. Bour, Nature Vol. 386, 351 (1997).

9:40am **SE-WeM5 Growth of Thin Film Materials with Supersonic Molecular Beams***, **W. Ho**,* Cornell University **INVITED**

Atomic and molecular beams have been used extensively to probe fundamental physical and chemical properties of atoms and molecules. A new application of molecular beams for materials synthesis is emerging. The unique properties of supersonic molecular beams which make this new application to thin film growth promising are described. Problems encountered in the implementation of supersonic jet epitaxy (SJE) as well as growth conditions favorable for the incorporation of real-time, in situ monitoring are discussed. The advantages and disadvantages of different precursors for the growth of cubic-SiC on Si are compared. The growth rate and morphology of the grown films are shown to depend on the kinetic energy of the precursors and the growth temperature. Enhancing the kinetic energy of precursors also led to lower growth temperatures for single crystal GaN and AlN thin films on silicon based substrates. Problems which remain to be solved in SJE of wide band gap semiconductors are summarized.

10:20am **SE-WeM7 Selected Energy Etching of Semiconductors by Electron-enhanced Surface Reactions***, **H.P. Gillis**, M.J. Christopher,* University of California, Los Angeles*; K.P. Martin, D.A. Choutov*,* Georgia Tech **INVITED**

It is well established that the standard ion-enhanced dry etching methods (RIE, ECR, and CAIBE) can damage the sample during etching by momentum transfer from energetic ions. The result is degradation of optical, electrical, and morphological properties of etched surfaces. We will review these energy-dependent damage mechanisms from ion-enhanced etching, and present results from an alternative approach--Low Energy Electron Enhanced Etching (LE4)--that avoids ion bombardment altogether. LE4 gives mirror smooth surfaces (RMS surface roughness 2 - 3 Angstroms) and maintains stoichiometry in compound semiconductors while giving highly anisotropic pattern transfer in micrometer and nanometer scale structures in Si, GaAs, and GaN. Special emphasis will be placed on the role of electron energy thresholds in developing selective processes and in controlling the polishing or "smoothening" of the surface during etching. @FootnoteText@ *Present address: National Semiconductors, San Jose, CA.

11:40am **SE-WeM11 Velocity, Temperature, and Chemical Composition of a dc-Arcjet Plume**, ***J.B. Jeffries***, *J. Luque, W. Juchmann,* SRI International

Laser-induced fluorescence, optical emission, and Langmuir probe measurements are used to characterize the reactive plume of a dc-arcjet reactor during diamond deposition. We find one third of the feedstock hydrogen is dissociated into atoms. Optical measurements are used to determine spatially resolved gas temperature, plume velocity, and the spatial variation of the concentrations of reactive intermediates. The atomic hydrogen concentration is not in equilibrium with the gas temperature, and finite rate chemistry controls the concentrations of the reactive intermediate species in the plume. The supersonic directed velocity of the plume produces a shock structure just above the substrate. The temperature and pressure gradient produced by this shock influences the chemical composition of the gases in the boundary layer and the transport of reactants to the surface. Supported by ARO and DARPA via the NRL.

Surface Science Division
Room 308 - Session SS1-WeM
Physics of Semiconductors

Moderator: J. Krim, North Carolina State University

8:20am **SS1-WeM1 Medard W. Welch Award Lecture - Optical Spectroscopy of Surfaces and Interfaces: Progress and Opportunities**, ***D.E. Aspnes***[1], North Carolina State University **INVITED**

9:00am **SS1-WeM3 Chemistry and Intermolecular Interactions of Nitridation and Oxidation Precursors on Si(100)-(2x1)**, ***K.T. Queeney,*** Bell Laboratories, Lucent Technologies; *A.B. Gurevich,* Columbia University; *X. Zhang, E. Garfunkel,* Rutgers University; *J. Eng, Jr., B.B. Stefanov, K. Raghavachari, Y.J. Chabal,* Bell Laboratories, Lucent Technologies

The manner in which various molecules adsorb, dissociate and interact on silicon surfaces can dramatically affect their subsequent incorporation into the silicon substrate and thus the nature of compounds formed at higher temperatures.@footnote 1@ We have studied mechanisms leading to oxidation, nitridation and oxynitridation of silicon via investigations of the structure and reactivity of H@sub 2@O, NO, NH@sub 3@ and N@sub 2@H@sub 4@ on Si(100)-(2x1). Dissociation of these molecules on a single Si-Si dimer yields well-defined structures which are identified using high-resolution infrared absorption spectroscopy in a new, sensitive transmission geometry, together with density functional cluster calculations. This powerful combination of theory and experiment also reveals subtle frequency shifts associated with the inter-dimer interactions of surface intermediates. For example, in the case of water adsorption, hydrogen bonding between two hydroxyl groups on neighboring dimers leads to splitting of all the observed vibrations (@nu@(SiO-H), @nu@(Si-H), @delta@(Si-H), @delta@(Si-OH) and @nu@(Si-O)). The magnitude of these splittings (@>=@ 10 cm@super -1@) allows definitive characterization of these interactions with infrared spectroscopy. For instance, two @nu@(OH) peaks corresponding to coupled hydroxyls appear at 3675 and 3660 cm@super -1@, well resolved from the uncoupled O-H stretch at 3684 cm@super -1@; likewise, the two @nu@(Si-O) features of coupled hydroxyl groups are split to 14 cm@super -1@ above and 12 cm@super -1@ below @nu@(Si-O) of the uncoupled species. Similar effects are observed after co-adsorption of water and ammonia. Such interactions provide a natural mechanism for local oxygen and nitrogen agglomeration during the thermal evolution of these surfaces, observed by monitoring changes in @nu@(Si-H) as well as Si-N and Si-O vibrations as atomic nitrogen and oxygen insert into Si backbonds at higher temperatures. @FootnoteText@ @footnote 1@M. K. Weldon, B. B. Stefanov, K. Raghavachari and Y. J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

9:20am **SS1-WeM4 Spectromicroscopy Evidence of Lateral Inhomogeneities for Metal-(III-VI) Semiconductor Interfaces**, ***M. Zacchigna***, *H. Berger,* Ecole Polytechnique Federale, Switzerland; *G. Lorusso, F Cerrina,* University of Wisconsin, Madison; *G. Margaritondo,* Ecole Polytechnique Federale, Switzerland

We exploited the very high lateral resolution of the MAXIMUM beamline on ALS to study microscopic lateral variations of semiconductor interface barriers. The capability to analyze the chemical properties with high lateral resolution often reveals unexpected overlayer-substratechemical reactions and links between such reactions and lateral barrier inhomogeneities. The experiment first studied lateral band bending changes in metal-semiconductor junctions for several interfaces between Au or Al and different III-VI compounds. By taking photoemission spectra on a series of microscopic spots along the interface is possible to detect the band bending with high lateral resolution. A novel way to perform this type of measurements, giving the "image" of the band bending, will be presented. The second and more interesting part of our study concerns the search for inhomogeneities in the first steps formation of metal-(III-VI) interfaces. We did discover such inhomogeneities in several prototypical interfaces, expanding and corroborating preliminary data on Au-GaSe interface. Furthermore, for the first time we did establish the sought link between barrier fluctuations and local chemical properties

9:40am **SS1-WeM5 Direct Determination of the Interplay between Gas-Surface Reactivity, Thin Film Strain and Alloy Surface Segregation: Growth of Strained Heteroepitaxial Si@sub 1-x@Ge@sub x@ Thin Films on Si(100)**, ***A.M. Lam,*** *Y.J. Zheng, J.R. Engstrom,* Cornell University

Silicon-Germanium alloys have attracted attention for more than a decade. The addition of Ge to Si epitaxial films leads to a variety of effects and phenomena, some well understood, some not. Almost untouched are phenomena related to the dissociative adsorption of the relevant thin film precursors on surfaces of the growing alloy. Knowledge of the corresponding sticking coefficients is key to developing relationships between gas phase, surface and sub-surface/bulk compositions. Concerning alloy (Ge) segregation, virtually all work conducted to date has relied on a single in situ experimental probe. We shall present here a comprehensive study of the heteroepitaxial growth of Si@sub 1-x@Ge@sub x@ alloys on Si(100) employing no less than 3 complementary in situ probes: supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS), and low-energy ion scattering spectrometry (LEISS). Our results for the first time demonstrate the importance of strain in determining gas-surface reactivity in these heteroepitaxial alloys-- the reactivity of the strained Si@sub 1-x@Ge@sub x@ overlayers is not simply an appropriate combination of pure component (bulk, relaxed) reactivities. On the other hand, use of the complementary in situ surface analyses of XPS and LEISS has allowed us to determine both the extent and nature of Ge surface segregation, and its dependence on film growth conditions. In all cases the surface Ge concentration exceeds that found in the bulk (often by an order of magnitude). A two-site model (involving surface and bulk) cannot account for both the XPS and LEISS results, rather a model invoking Ge enrichment in the subsurface layers is required to explain the data.

10:00am **SS1-WeM6 Ballistic Electron Emission Microscopy Studies of Tunneling to Surface and Bulk States on Cu (111) Thin Films**, ***W.H. Rippard***, *M.K. Weilmeier, R.A. Buhrman,* Cornell University, US

Thin bilayer films consisting of a thin Au layer and an overlayer of Cu have been grown on the surface of hydrogen passivated Si (111) and Si(100) wafers. UHV STM measurements reveal that these bilayers consist of ~10 nm grains with surfaces that are either atomically flat or transversed by only a few atomic step-edges. X-ray diffraction indicates that these films, for both substrates, consist nearly completely of (111) normal oriented grains. When ballistic electron emission microscopy (BEEM) measurements are made on these systems, a strong contrast is seen between the BEEM current when the STM tip is over a flat surface and when it is positioned at a grain boundary or step edge, with the higher BEEM current occurring in the latter case. This contrast in current can be as much as a factor of three, depending on the sharpness of the STM tip, and occurs for both (100) and (111) oriented substrates. STM spectroscopy measurements indicate the presence of pronounced surface states on the flat areas of the Cu surface and an absence of thes states at grain boundaries and steps. We conclude that the low BEEM current which occurs when the STM tip is positioned over a Cu surface mesa is the result of tunneling predominately to empty surface states, while at grain boundaries and step edges the STM tip is able to tunnel more strongly to the empty bulk states of the Cu, which enhances the BEEM signal. This observation provides a strong demonstration of the role of the metal band structure in determining the amplitude of the BEEM signal, even in the case of the noble metals, and demonstrates a new means by which the degree of coupling between bulk and surface states on the (111) normal surface of Cu, Au and Ag can be determined by BEEM.

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[1] **Medard W. Welch Award Winner**

10:20am **SS1-WeM7 Current-Voltage Measurements of Ultrathin Metal-Si(111) Sensors***, **H. Nienhaus**, H.S. Bergh, B. Gergen,* University of California, Santa Barbara*; A. Majumdar,* University of California, Berkeley*; E.W. McFarland, W.H. Weinberg,* University of California, Santa Barbara

A novel microfabricated Si-based device structure was developed in order to characterize the transport properties of thin metal films on Si(111) ranging from 10 Å to 150 Å. Metals were evaporated onto the device under ultrahigh vacuum conditions. The evaporation temperature was varied between 130 and 180 K. The design of the device allowed zero-force electrical contacts to the very thin metal films on silicon for current-voltage (I/V) measurements. The resulting I/V curves were analysed within the thermionic emission theory. The change of Schottky-barrier height, ideality factor and serial resistance was monitored as a function of film thickness and temperature. Cu, Ag and Fe films were investigated on Si(111). Generally, an improvement of the rectifying properties was observed with increasing thickness. To study the temperature dependence, Cu films of about 60 Å were annealed to room temperature. This treatment led to a significant increase of the barrier height from 0.45 to 0.65 eV and a decrease of the ideality factor from about 2.5 to values close to 1. Subsequent cooling of the annealed samples conserved the excellent rectifying properties. This finding indicates that annealing of low-temperature deposited films reduces the inhomogeneity of the contact barrier height. Further evaporation of Cu onto annealed diodes led again to lower barrier heights and larger ideality factors. First results suggest that the devices are suitable sensors for detecting hot charge carriers created by gas-surface reactions.

10:40am **SS1-WeM8 Electroless Deposition of Au onto H-Si(111)***, I. Suni, **R. Srinivasan**,* Clarkson University

Electroless deposition of Au from aqueous HF onto p-type H-Si(111) has been studied by electrochemical methods, atomic force microscopy (AFM), Rutherford backscattering (RBS), and surface second harmonic generation (SHG). The H-terminated Si(111) surface is prepared by HF etching prior to Au deposition. We have found evidence that Au deposition occurs by a two-step process, where initial deposition of AuCN is rate-limited by diffusion, while subsequent reduction of Au is rate-limited by surface reaction involving a fluoride-containing species. The growth of Au nanoclusters can be monitored by SHG through the development of the surface plasmon resonance, which occurs above a threshold cluster size of about 2 nm. The SH signal goes through a temporal maximum and then declines again due to interdiffusion of Au and Si. Surface kinetics can then be analyzed by manipulating the solution phase equilibria and following the effects on Au reduction by SHG. This analysis reveals that HF, not HF@sub 2@@super -@, is the mechanistically important species and that Au reduction is half-order in HF.

11:00am **SS1-WeM9 Growth of Si@sub 1-x@Ge@sub x@ on Si(011): Kinetics, Surface Structure, and Morphological Evolution***, **N. Taylor**, H. Kim, T. Spila, P. Desjardins, J.E. Greene,* University of Illinois, Urbana-Champaign

Strained Si@sub 1-x@Ge@sub x@/Si(011) heterostructures provide additional degrees of freedom over the more common Si@sub 1-x@Ge@sub x@/Si(001) system for bandgap engineering. The maximum film/substrate conduction band offset is predicted to be substantially larger, the optical bandgap decreases more rapidly with increasing x, and optical selection rules allow hole-intersubband transitions to be excited by light parallel to multiple quantum well layers. In this investigation, Si@sub 1-x@Ge@sub x@ layers with x @<=@ 0.35 were grown on Si(011) by gas-source molecular beam epitaxy (GS-MBE) using Si@sub 2@H@sub 6@ and Ge@sub 2@H@sub 6@ at T = 400-950 °C. The growth kinetics are a function of the following complex surface reconstructions: 16x2 at x < x@sub c@ and 2x8 at x > x@sub c@. The critical Ge concentration x@sub c@ ranges from 0.10 at T = 475 °C to 0.06 at T = 650 °C. As the temperature is raised from 650 to 725 °C, the surface gradually transforms to a 1x1 reconstruction for all x. Temperature-programmed desorption (TPD) measurements show that the 16x2 unit cell consists of 16 adatoms and 8 pi-bonded dimers, resulting in 32 dangling bonds compared to 64 for the 1x1 surface. In the surface-reaction-limited growth mode at T < 500 °C, the rate-limiting growth step is hydrogen desorption from the Si and/or Ge monohydride. The surface structure consists of uniformly-sized terraces, according to atomic force microscopy (AFM) measurements. In the flux-limited regime at T = 500-650 °C, the growth rate is limited by the surface-dependent reactive sticking coefficient and the morphology is characterized by extensive faceted pitting. At T > 650 °C, the growth rate rises with temperature as the dangling bond coverage increases with the surface transformation to a 1x1 reconstruction. At these high temperatures, the surface morphology consists of long ridges oriented along the [100] direction.

11:20am **SS1-WeM10 Surface Structural Study of Ultra-Thin Si (111) on SiO@sub 2@***, **M. Noh**,* University of Tennessee and ORNL*; A.P. Baddorf,* Oak Ridge National Laboratory*; H.H. Weitering,* University of Tennessee and ORNL

Si on insulator (SOI) material is important for extension of metal-oxide silicon (MOS) technology development in the next generation of microelectronics. Technological requirements have led to interest in very thin SOI layers. The surface structure of ultra-thin layers of (111) oriented SOI has been investigated for the first time, using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). SOI samples were prepared using the Separation by Implanted Oxygen (SIMOX) method, then characterized by Rutherford backscattering spectrometry (RBS) to determine the thickness and quality of the Si overlayer. LEED observations from a 2000 Å thick Si layer on 5000 Å SiO@sub 2@ reveal a sharp 7x7 diffraction pattern, well known for bulk Si (111) surfaces. STM images of the same surface show nearly defect free 7x7 surface reconstructions with terrace lengths exceeding 1000 Å. These observations reveal that the surface of a thin Si (111) film on SiO@sub 2@ can be fabricated with a comparable degree of structural perfection as the (111) surface of bulk Si. The quality of the (111) SOI surface was monitored as a function of Si top layer thickness after thinning by dry oxidation and stripping. Results are compared to previous images of (100) SOI surfaces.@footnote 1,2@ @FootnoteText@ @footnote 1@K.C. Lin, O.W. Holland, L.C. Feldman, and H.H Weitering, Appl. Phys. Lett. 72 (1998) 2313. @footnote 2@Oak Ridge National Laboratory (ORNL) is managed by Lockheed Martin Energy Research Corp. for the U. S. DOE under contract number DE-AC05-96OR22464.

11:40am **SS1-WeM11 Reconstructed Oxide Structures Stable in Air: Monolayer Silicate on Hexagonal SiC Surfaces***, **U. Starke**, J. Schardt, J. Bernhardt, K. Heinz,* University of Erlangen-Nuernberg, Germany

Ultrathin oxide layers on hexagonal SiC surfaces were studied using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). SiC(0001) and SiC(000-1) samples were ex situ prepared using thermal hydrogen etching or microwave powered hydrogen plasma treatment. A well ordered (@sr@3x@sr@3)R30° reconstructed surface is observed by LEED immediately upon introduction into vacuum. The samples contain oxygen of approximately one layer equivalent bonded to Si atoms as indicated by AES. By a full dynamical LEED structure analysis carried out for the SiC(000-1) surface the crystallographic structure is determined: The silicon oxide is arranged as a silicate (Si@sub 2@O@sub 3@) layer ontop of the SiC substrate forming rings of the (@sr@3x@sr@3)R30° periodicity with twofold coordinated oxygen atoms in the topmost position. The oxygen incorporation into the surface is presumably caused by a rapid oxidation in air of the well ordered topmost substrate bilayer. The extreme stability of the resulting surface reconstruction is caused by the absence of dangling bonds in the surface terminating silicate layer. Similar results are indicated for the SiC(0001) surface by preliminary LEED calculations.

Surface Science Division
Room 309 - Session SS2-WeM

Gas-Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS2-WeM1 Monte-Carlo Simulation of the Adsorption and Desoption of CF@sub 4@ on Cu/CuO(110)***, **M. Hohage**,* University of Wisconsin, Madison*; V. Diercks,* Forschungszentrum Jülich, Germany*; P. Zeppenfeld,* Universität Linz, Austria*; M.G. Lagally,* University of Wisconsin, Madison

The unique adsorption and desorption dynamics of CF@sub 4@ on the Cu/CuO(110) stripe phase is reproduced by a Monte-Carlo simulation to reveal the underlying processes on the molecular scale. As observed by means of thermal energy atom scattering (TEAS), at temperatures above 20K CF@sub 4@ adsorbs preferentially on the CuO stripes.@footnote 1,2@ A comparison of these adsorption measurements with a Monte-Carlo simulation is used to determine the parameters of the CF@sub 4@ diffusion on Cu and on CuO. With the knowledge of these diffusion parameters the more complicated desorption of CF@sub 4@ is analyzed. TEAS and TDS measurements show that annealing the sample with a rate of 1K/s leads to desorption between 55K and 70K@sub 2@. Two well-separated peaks occur. The peak at lower temperature is related to the desorption from the Cu stripes, whereas the peak at higher temperatures is related to the desorption from the CuO stripes. This desorption behavior as well as shifts of the desorption peaks in dependence of the composition of the surface (amount of O on the surface) is reproduced by a Monte-Carlo simulation including the previously determined diffusion parameters as a fixed input. The different features of the desorption spectra, i.e. peak positions, peak shifts, and peak shapes, are assigned to binding energies and diffusion barriers on the molecular scale. This allows the development of a consistent model of the CF@sub 4@ adsorption and desorption dynamics. *Supported by NSF and by the Alexander von Humboldt-Stiftung @FootnoteText@ @Footnote 1@P. Zeppenfeld, V. Diercks, Ch. Tölkes, R. David, and M. A. Krzykowski, Appl. Surf. Sci. (1998) in print. @Footnote 2@V. Diercks, Ph.D. thesis, Bonn 98

8:40am **SS2-WeM2 Adsorption, Absorption, and Abstraction of Hydrogen on Cu(111) Surfaces***, Th. Kammler, **J. Küppers**,* Universität Bayreuth, Germany

The interaction of H(D) with Cu(111) surfaces and the abstraction of D adsorbed on Cu(111) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H atoms were produced in a W tube heated at 2000 K. H atoms directed at clean Cu(111) surfaces at 85 lead to H adsorption with an initial sticking coefficient of 0.19. After completion of the adsorbed layer with a saturation coverage of 0.25, further H uptake leads to H absorption. Adsorbed H desorbs as H@sub 2@ via a second order process in the temperature range 250 to 400 K. Absorbed H desorbs as H@sub 2@ starting at 150 K and peaking around 200 K in a first order process. The interaction of H atoms with a saturated D layer, @THETA@=0.25, at 85 K leads to the formation of gas phase HD and D@sub 2@. The kinetics of HD formation as a function of H atom fluence follows a strict Eley-Rideal-type phenomenology: a HD rate jump at reaction start and a subsequent exponential decay of the HD rate. However, the D@sub 2@ product suggests that the reaction mechanism is not of an Eley-Rideal but of hot atom type. An analysis of the abstraction kinetics in terms of hot-atom mechanisms reveals that on Cu(111) the reaction probability of hot atoms is of the same magnitude as their sticking probability at empty surface sites. About 1% of the adsorbed D appears in the D@sub 2@ reaction channel. The abstraction cross section towards HD is 2.3 Å@super 2@. The HD yields and rate steps scale with the D coverage at reaction start, the D@sub 2@ yields and rate steps scale with the square of the D coverage. Absorbed D cannot be abstracted by gas phase H. The kinetics of HD formation is independent of the H flux.

9:00am **SS2-WeM3 A Comparison of State-Resolved Studies of Reaction and Inelastic Scattering for H@sub 2@ with Palladium and Copper Surfaces***, E. Watts,* University of Texas, Austin*; M. Gostein,* Massachusetts Institute of Technology*; **G.O. Sitz**,* University of Texas, Austin **INVITED**

We report results of molecular beam experiments of hydrogen scattering from single crystal palladium and copper surfaces. These two materials represent a reactive and unreactive substrate, respectively, for hydrogen dissociation at low (50-70 meV) incident energy. Because the reaction has strong geometrical and dynamical requirements, features of the potential energy surface are evidenced in the inelastic scattering of those molecules which do not react. This will be demonstrated by comparing scattering distributions for the two surfaces. In addition we have observed efficient loss of initially vibrationally excited H@sub 2@, and have measured the probability that this loss occurs via relaxation into the ground vibrational state for selected final rotation states. For scattering from Pd, an energy balance for the H@sub 2@ degrees-of-freedom indicates that a substantial amount of energy is lost to the surface during the relaxation.

9:40am **SS2-WeM5 Energy Dependent Al(111) Oxidation Kinetics***, H. Ternow, **I. Zori@aa c@**, M. Zäch, B. Kasemo,* Chalmers University of Technology, Sweden

We have investigated the oxidation kinetics of the Al(111) surface at different O@sub 2@ kinetic energies, using molecular beam technique, Auger electron spectroscopy, AES, and surface plasmon spectroscopy. The central issue we concentrate in this report is how the oxide growth kinetics depends on kinetic energy of the impinging O@sub 2@ molecules. A series of oxygen uptake experiments, a la King and Wells, were performed for two oxygen beam energies yielding low (0.8) initial dissociative sticking probabilities. The total coverage (chemisorbed plus oxidic oxygen) was increased in steps of 0.1 ML until the surface was saturated with oxygen. Between each step the surface was analyzed by AES and surface plasmon measurements. Al(LVV) transitions influenced by oxygen chemisorption and oxide formation were measured as a function of the total amount of oxygen on (in) the sample for different oxygen beam energies. We find the appearance of oxide in a submonolayer regime at a threshold coverage which depends on oxygen beam energy. Furthermore, the growth kinetics of the oxidic phase is also energy dependent. We attribute the latter to energy and coverage dependent dissociation dynamics, resulting in an energy dependent distribution of oxygen atoms among available adsorption sites. Surface plasmon spectroscopy (plasmon energy and lifetime dependence on total oxygen coverage) also reflects the existence of the well defined threshold for oxide appearance as well as heterogeneous distribution of chemisorbed and oxidic phases on the surface. A simple kinetic model which accounts for these observations is presented.

10:00am **SS2-WeM6 Initial Stages of Al(111) Oxidation by Oxygen - Temperature and Surface Morphology Effects***, **V. Zhukov**, I. Popova, J.T. Yates, Jr.,* University of Pittsburgh

The mechanism of oxygen chemisorption and the oxidation of aluminum is again of interest in the light of recent STM studies on Al(111).@footnote 1,2@ We have used X-Ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS) to carefully examine the temperature dependence of the Al(111) oxidation kinetics in the range 95-773 K. The onset of oxide formation was detected near 473 K at the low oxygen coverages investigated here. Both activated and non-activated adsorption channels have being found depending on surface temperature and the degree of oxide formation, causing nonmonotonic behavior of the sticking coefficient versus temperature. These results are discussed in terms of a one-dimensional potential energy diagram. Surface defects along with the presence of the oxide structures have been found to influence the kinetics of O@sub 2@ adsorption. The importance of careful surface preparation and smooth surface morphology for the reproducible adsorption measurements are demonstrated in this work. Coverage sensitive HREELS measurements are highly dependent upon surface conditions, and these results may rationalize contradictions present in the literature. Work supported by AFOSR. @FootnoteText@ @footnote 1@H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, R.J. Behm, J. Chem. Phys., 99 (1993) 2128. @footnote 2@J. Trost, H. Brune, J. Wintterlin, R.J. Behm, G. Ertl, J. Chem. Phys., 108 (1998)1740.

10:40am **SS2-WeM8 Comparison of Chemical Selectivity and Kinetic Energy Release in Si@sub (s)@ + ICl@sub (g)@ and H@sub (g)@ + ICl@sub (g)@***, **K.A. Pettus**, T. Ahmadi, E. Lanzendorf, A.C. Kummel,* University of California, San Diego

The chemisorption of ICl on the Si(111)-7x7 surface is comparable to the gas reaction of ICl and hydrogen. ICl chemisorbs onto Si(111)-7x7 by two mechanisms: dissociative chemisorption and abstractive chemisorption. Abstractive chemisorption, in which one halogen atom of ICl bonds to the silicon surface while the other is ejected into the gas phase, is the dominant chemisorption mechanism for ICl/Si(111)-7x7. 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 34 +/- 4 :1. Furthermore, the chemical selectivity of ICl + Si(111)-7x7 is greater than the chemical selectivity of the gas phase reaction of H +ICl where the ratio of formation of HI to HCl is 4:1.@footnote 1@ In both reactions, the iodine atom of ICl molecules is more reactive than the chlorine atom because the pi @sub x,y@ @super *@ antibonding orbital (the orbital that reacts with any other species) consists primarily of atomic iodine orbitals.@footnote 2@ The difference in the chemical selectivities of the silicon surface and gaseous hydrogen reactions with ICl is due to the ability of the silicon surface to rotationally steer ICl molecules and the inability of silicon to migrate between the iodine and chlorine atoms in ICl . The median translational energies of the abstracted halogen atoms were determined to be 0.18 +/- 0.04 eV for chlorine atoms and 0.53 +/-0.27 eV for iodine atoms which are a small fraction (14% for ejected iodine atoms and 9% for ejected chlorine atoms) of the total reaction exothermicities. The low translational energy of ejected atoms is due to the fact that the iodine-chlorine bond of ICl lengthens as the Si-I bond contracts and there is little repulsion energy attributed to the Si-I-Cl transition state. @FootnoteText@ @footnote 1@J.C. Polanyi, Chemica Scripta, 27, 229 (1986) @footnote 2@J.D. McDonald, P.R. LeBreton, Y.T. Lee, and D.R. Herschbach, J. Chem. Phys., 56, 769 (1972)

11:00am **SS2-WeM9 Hydrogen Atom Induced Decomposition of Water Adsorbed on Si(100)***, **L.M. Struck**,* National Institute of Standards and Technology, US*; S.A. Buntin,* National Institute of Standards and Technology

The reaction of incident atomic hydrogen with water adsorbed on Si(100) is investigated using multiple internal reflection infrared (IR) spectroscopy.

The clean Si(100) surface is exposed to water forming a half monolayer of both SiH and SiOH surface species. Atomic hydrogen is generated by hot filament decomposition of molecular hydrogen. The evolution of the adlayer is probed with IR spectroscopy by following the silicon hydride and hydroxyl stretch features as a function of atomic hydrogen exposure for different isotopic reaction combinations (e.g., incident D atoms on adsorbed H@sub 2@O). The results show a concomitant decrease in the Si-H and O-H stretch features with increasing D atom exposure, indicating the involvement of both the surface hydride and hydroxyl species in the initial adlayer decomposition. The implications of these results with regard to the reaction mechanism will be discussed.

11:20am **SS2-WeM10 Nonthermal Effects of Photon Illumination on Surface Diffusion**, *E.G. Seebauer,* ***D. Llera-Rodriguez,*** University of Illinois, Urbana

The presence of an energy bandgap in semiconductors together with their ability to support significant separations in charge offer the potential to observe surface phenomena not seen on metals. For example, several years ago this laboratory predicted the possibility of photon-influenced surface diffusion on semiconducors by nonthermal mechanisms. The present work reports the first experimental confirmation of this prediction for Ge, In, and Sb diffusion on Si(111), using second harmonic microscopy as the measurement probe. At modest illumination intensities of 2 W/cm@super 2@ or less, we have observed substantial changes in diffusional activation energy E@sub diff@ and prefactor D@sub o@. For all the adsorbates on p-type Si, illumination increases E@sub diff@ by about 0.3 eV (out of 2.4) and increases D@sub o@ by nearly two orders of magnitude. However, use of n-type substrates causes decreases of the same magnitude. All effects remain independent of illumination wavelength as long as the photon energy remains higher than the substrate bandgap energy. We can explain most of these effects by extending our adatom-vacancy model for surface diffusion at the experimental temperatures (400 to 1000 C) to incorporate charging of the surface vacancies, in direct analogy with vacancy behavior in bulk semiconductors. Charging of the vacancies requires electron transfer to or from surface quasi-fermi levels, whose positions are modified by illumination as in surface photovoltage spectroscopy. Our results have significant implications for semiconductor manufacturing steps performed by the lamp illumination of rapid thermal processing.

11:40am **SS2-WeM11 The Role of Surface Reconstruction in the Photofragmentation Dynamics of Oriented Methyl Bromide Adsorbed on GaAs**, ***K.A. Khan***, *N. Camillone III, R.M. Osgood Jr.,* Columbia University*; J.A. Yarmoff,* University of California, Riverside

Our previous work has detailed the UV-initiated dissociation of CH@sub 3@Br physisorbed on GaAs(110), both by numerous experimental techniques and theoretical calculations. The substrate-electron-mediated dissociation yields energetic (1.4eV) methyl fragments whose dynamics are governed by surface-alignment forces acting on the adsorbate. The anisotropic angular distribution of the methyl fragments reflects the surface corrugation of the 1x1 reconstruction of GaAs(110). In this paper we demonstrate that significant changes are observed in the fragment dynamics upon modifying the surface reconstruction via well-controlled surface preparation protocols. Specifically, to further explore and understand the role played by the surface morphology in fragmentation dynamics, we have compared the photodissociation of methyl bromide on two different surface reconstructions of the (100) face of GaAs. In contrast to the (110) surface, mass and angle-resolved time-of-flight measurements show the ejection of methyl fragments from the (100) surface to be symmetrical about the surface normal. Photoinduced fragmentation of monolayers of methyl bromide on c(8x2)-reconstructed Ga-rich and c(2x8)-reconstructed As-rich GaAs(100) surfaces also reveals a striking difference between these two surface structures. On the Ga-terminated surface we observe desorption of intact CH@sub 3@Br as well as methyl fragments formed by photoinduced dissociation. Only methyl fragments are detected leaving the (110) surface and the As-terminated (100) surface. As in the (110) case, the mechanism for C-Br bond cleavage in the (100) cases is photo-initiated electron attachment from the surface to the molecule. However, the energetics of the methyl fragments are quite different on the three surfaces suggesting site-specific dissociation. Therefore, the energetics of the methyl fragments will be discussed in terms of the surface texture and stoichiometry of the three surfaces.

Surface Science Division
Room 314/315 - Session SS3-WeM

Surface Dynamics and Roughening

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

8:20am **SS3-WeM1 The Atomic Steps of Oxygen Adsorption on Pt(110)-(1x2)**, *S. Helveg, S. Horch, I. Stensgaard, E. Laegsgaard,* ***F. Besenbacher***, Aarhus University, Denmark

The dissociative adsorption of Oxygen on the Pt(110)-(1x2) surface is studied using a variable-temperature, fast Scanning Tunneling Microscope. The dynamic information extracted from the STM movies direct reveal how the O structures develop as function of O coverage. A variety of new and novel O structures are observed on the atomic scale. These initial structures develop at higher O coverage into [110] oriented stripes which self organize into highly regular and periodic bands. From an interplay between these STM results and theoretical GGA calculations a new and coherent picture evolves for O adsorption on Pt(110). This picture deviates significantly from previously proposed structural models but we can within the new picture explain all previous experimentally obtained results.

8:40am **SS3-WeM2 Etching of the Si(001) Surface with Molecular Oxygen**, ***J.B. Hannon***, *M.C. Bartelt, N.C. Bartelt, G.L. Kellogg,* Sandia National Laboratories

We have investigated the growth and decay of two-dimensional pits, or vacancy islands, at the Si(001) surface using low-energy electron microscopy (LEEM). The vacancy islands nucleate near the centers of large (10 micron diameter) terraces when the surface is exposed to molecular oxygen at elevated substrate temperature. At sample temperatures above about 1000 K, oxygen does not accumulate on the surface, but desorbs in the form of SiO, leading to a net removal of Si from the surface. In our experiments, the vacancy islands grow monotonically during oxygen exposure. The growth rates of the individual vacancy islands depend on the distribution of neighboring islands and steps. We quantify this dependence using both Monte Carlo simulations and a diffusion equation analysis. The vacancy-island growth rates can be described using a simple model of the etching process: during oxygen exposure, Si atoms are removed from the surface at a temperature-dependent rate, leaving behind surface vacancies. The vacancies diffuse on the terrace until they encounter an island edge, where they are irreversibly incorporated. The sensitivity of the vacancy-island growth rates to the island configuration is a consequence of the fact that vacancy terrace diffusion is slow compared to vacancy incorporation at steps. By measuring the growth rates as a function of temperature and oxygen pressure, we are able to determine both the mechanisms by which oxygen etches the surface as well as the activation energy associated with the etch rate. We find that the temperature dependence of the etch rate, at constant oxygen pressure, obeys an Arrhenius form with an activation energy of about 2.0 eV. This work was performed at Sandia National Laboratories, 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 **SS3-WeM3 Surface Morphology Induced on Metal Surfaces by Ion Sputtering**, *S. Rusponi, G. Costantini, C. Boragno,* ***U. Valbusa***, University of Genova, Italy

Ion sputtering can be used not only to clean or to analyse a surface, but also to construct regular patterns on amorphous, semiconductor and metals surfaces. We studied the formation of these patterns in different metal single crystals by using a variable temperature UHV STM. By accurately dosing the ion energy, flux and fluence and by selecting the appropriate crystal temperature, we can tune the final morphology, changing the shape of holes and islands, their density and thickness. Different examples will be reported: on Ag(110)@footnote 1@ and Cu(110)@footnote 2@ a ripple structure can be induced, with an orientation respect to the surface directions depending mainly on the temperature, while on Ag(001)@footnote 3@ a checkerboard morphology with a square simmetry has been found. It has been found that many properties of the sputtered surfaces follow simple scaling laws. A general model, based on the competitive role of surface diffusion and erosion can well explain the reported results. @FootnoteText@ @footnote 1@S. Rusponi et al., Phys. Rev. Lett. 78 (1997) 2795 @footnote 2@S. Rusponi et al., Phys. Rev. Lett., submitted @footnote 3@S. Rusponi et al., Surf. Sci., submitted

9:20am **SS3-WeM4 Direct Observation of Etching Mechanisms of Cu Surfaces with STM**, *C.Y. Nakakura, **E.I. Altman**,* Yale University

Scanning tunneling microscopy movies of the halogenation and subsequent etching of Cu(100) and Cu(11 1 0) were recorded. Adsorption of both Br@sub 2@ and Cl@sub 2@ resulted in a c(2x2) structure on the Cu(100) terraces. As the adsorbate coverage approached saturation, the substrate steps faceted to align along the close-packed directions of the adlayer. The faceted steps were the Cu atom source for subsequent halide formation and etching. For Cl@sub 2@, the reaction was initiated at facet corners and proceeded by stripping away rows of atoms parallel to the steps. In contrast, Br@sub 2@ could also react perpendicular to the step edge creating channels etched into the terraces. For both Cl@sub 2@ and Br@sub 2@, the halide formed by reaction diffused across the surface, nucleating and growing halide clusters independently of the reaction step. At room temperature, three-fold symmetric CuBr(111) islands were observed that grew by addition of CuBr units to island edges. Remarkably, the presence of these islands did not block further reaction of the underlying Cu surface. The CuBr islands formed at room temperature roughened either with time or annealing. At temperatures above 440 K, the halide formed by reaction sublimes resulting in etching. Under these conditions, a new CuBr morphology was observed: four-fold symmetric islands. These square islands nucleated at step edges and then sublimed at rates far in excess of those of similar sized three-dimensional clusters, suggesting that controlling the morphology of the CuBr can lead to reductions in etching temperatures.

9:40am **SS3-WeM5 How Predictable Is Surface Morphology?**, ***N.C. Bartelt,*** Sandia National Laboratories **INVITED**

One way people are beginning to probe the mechanisms of surface dynamics is to compare the histories of particular surface configurations obtained using microscopy with predictions from simulations. An advantage of this technique over the usual method of studying the time dependence of quantities averaged over the surface is that it allows the direct determination of how individual surface defects (such as steps) move in response to their local environment. A fundamental question about this approach is how well, and for how long, can one expect to account for the evolution of the complicated surface configurations which are typically observed in experiments. At small enough length scales, unpredictable thermal fluctuations begin to play a role. In this talk I discuss the basic theory and implications of the breakdown of deterministic equations of motion of surface morphology caused by these fluctuations. I will illustrate the issues involved. for several systems: First, given a configuration of surface steps, I will discuss how well one can predict where, and in what sequence, islands nucleate during epitaxial growth. I will compare theory with experiments of vacancy island nucleation during O etching of Si(001) which show that nucleation gets less predictable as the temperature (and critical nucleus size) gets smaller. Second, I will discuss how long one can in principle expect to account for the structure of adsorbed layers during domain coarsening and for island configurations during ripening. I will give theoretical and experimental examples of how sensitive histories of such complicated structures are to chance events and the knowledge of initial conditions.

10:20am **SS3-WeM7 Restructuring of Non-Square Vacancy and Adatom Clusters and of Indentations and Protrusions at Step Edges for Ag/Ag(100)**, ***C.R. Stoldt**, A.M. Cadilhe, C.J. Jenks, J.W. Evans, P.A. Thiel,* Iowa State University

During metal(100) homoepitaxy, near-square 2D islands (which are nucleated on broad terraces) first grow and merge, forming rectangular and dumbbell shaped clusters. Approaching a coverage of one monolayer, vacancy regions remain in the first layer which display a variety of unusual compact and worm-like shapes. Also, any extended step edges advance during deposition, incorporating islands in the process, and acquiring an irregular structure with many protrusions and indentations. The rearrangement of these non-equilibrium structures, if sufficiently rapid, can significantly influence multilayer growth. Thus, we present room-temperature STM studies for Ag/Ag(100) adlayers which provide a comprehensive characterization of the restructuring dynamics: (i) for adatom and vacancy clusters with rectangular and dumbbell shapes, and for worm-like vacancy regions; and (ii) for square, triangular, and other shapes of protrusions and indentations at extended step edges. In particular, we assess the dependence of restructuring rates on feature size and shape (or on local step edge orientation), and compare behavior for "mirror-image" adatom and vacancy structures. Behavior is elucidated by comparison with theoretical studies of "perimeter diffusion" models for step edge evolution.

10:40am **SS3-WeM8 Evolution and Structure of the Stripe Phase Reconstruction of Cu/Ru(0001)**, ***H. Zajonz**, D. Gibbs,* Brookhaven National Laboratory*; A.P. Baddorf, D.M. Zehner,* Oak Ridge National Laboratory

X-ray scattering studies of the structure of Cu layers deposited on Ru(0001) substrates during growth and versus substrate temperature have been initiated. The nearest-neighbor spacing in bulk fcc Cu is 5.8% smaller than that in hcp Ru. Earlier STM studies,@footnote 1@ established that the first layer of Cu on Ru(0001) adopts a pseudomorphic structure, but that the two-layer film exhibits a stripe-phase reconstruction which consists of an uniaxial modulation of Cu chains along [100]. Measured x-ray intensities provide evidence that the first layer does not remain pseudomorphic in the stripe phase. Our experiments also involve characterizing the appearance and evolution of the stripe-phase reconstruction peak as a function of Cu coverage and substrate temperature. At 720 K, x-ray scattering confirms a pseudomorphic Cu structure for coverages up to about one monolayer, followed by the growth of a stripe-phase reconstruction between one and two layers. In the stripe phase, the average Cu spacing along the rows is that of Cu bulk, however between rows the spacing is equivalent to that of Ru. At two monolayers coverage, there is an abrupt contraction of the average Cu spacing by an additional ~0.5% which can be attributed to an increase in the amplitude of the transverse modulations with layer completion. This phenomenon has not been observed previously for an interfacial reconstruction. ORNL is managed by Lockheed Martin Energy Research Corp. under U.S. Department of Energy contract DE-AC05-96OR22464. Work at BNL is supported by DOE, under contract DE-AC02-98CH10886. @FootnoteText@ @footnote 1@ C. Günther et al., Phys. Rev. Lett. 74, 754 (1995)

11:00am **SS3-WeM9 Dynamics of the Striped Nanostructure of the Oxidized Cu(110) Surface: A Momentum-Resolved ESDIAD Study**, ***D. Mocuta**, J.W. Ahner, J.-G. Lee, S. Denev, J.T. Yates, Jr.,* University of Pittsburgh

The striped structure of the partially oxidized Cu(110) surface has been studied using a novel technique, Momentum-Resolved ESDIAD. Long ...O-Cu-O... strings oriented in the direction and exhibiting attractive interactions with each other form periodically arranged stripes with widths in the nanometer range.@footnote 1,2@ Two different oxygen sites were detected, leading to a two-fold symmetrical four beam O@super +@ ESDIAD pattern with tilting of the beams of 22° in the azimuth (A) and 8° in the azimuth (B) directions. The relative intensities of the four beams have been compared for a wide range of oxygen coverages leading to a model in which the A beams correspond to O@super +@ ions desorbing from the edges of the stripes and the B beams from the internal regions of the stripes. This model is confirmed by studying the effect of the coadsorption of Ar at 32 K on the oxidized structure. The dynamical motion of the one-dimensional ...O-Cu-O... oscillator chains situated at the edges of the stripes has been studied by Momentum-Resolved ESDIAD measurements over a broad range of temperatures (70 K- 650 K). In addition, this striped surface has been used as a template for the adsorption of other species, whose interactions with the ...O-Cu-O... chains are revealed. @FootnoteText@ @footnote 1@D. J. Coulman, J. Wintterlin, R. J. Behm, G. Ertl, Phys. Rev. Lett. 64 (1990) 1761. @footnote 2@K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. George, G. Comsa, Phys. Rev. Lett. 67 (1991) 855.

11:20am **SS3-WeM10 Evidence and a Model for a Chemically Mediated Roughness Transition**, ***E.A. Irene**, C. Zhao, Q. Liu,* University of North Carolina, Chapel Hill

In our previous research we have followed the changes effected by oxidation on purposely roughened and initially smooth Si surfaces via atomic force microscopy (AFM) and spectroscopic ellipsometry (SE) and a new technique called spectroscopic immersion ellipsometry (SIE).@footnote 1,2@ For initially rough surfaces both thermal and plasma oxidation yield smoother surfaces and this can be understood from the changes in the local free energy at asperities, viz. the Kelvin equation. What was surprising was that initially smooth Si surfaces roughen upon oxidation. These results are not contradictory, since the roughness magnitudes do not cross, but these results strongly suggest a limiting roughness. Furthermore, a chemically mediated roughening transition explains the observations although this mechanism is not yet proven. The experimental and modeling results will be presented. @FootnoteText@ @footnote 1@Q. Liu, L. Spanos, C. Zhao and E.A. Irene, J. Vac. Sci. Technol. A, 13, 1977 (1995). @footnote 2@C. Zhao, Y.Z. Hu, T. Labayen, L. Lai and E.A. Irene, J. Vac. Sci. Technol. A, 16, 57, (1998).

11:40am **SS3-WeM11 Reconstruction of Bimetallic Systems: Ultrathin Films of Rh, Pt and Pd on W(211)**, ***K. Pelhos,*** *I.M. Abdelrehim, C.H. Nien, T.E. Madey,* Rutgers University

The (211) face of tungsten is found to undergo an (nx1) reconstruction when covered with a thin film of Rh, Pt or Pd, followed by annealing. A combination of low energy electron diffraction, Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) experiments indicate that the reconstruction occurs within a very narrow coverage range, between 0.5 and 1 physical monolayer, and only when the annealing temperature exceeds a threshold value of ~900 K (Rh and Pt) or ~500 K (Pd) (1 physical monolayer corresponds to 1.63 x 10@super 15@ atoms/cm@super 2@, sufficient to cover completely all of the exposed W atoms in the W(211) rows and troughs). The reconstruction is almost exclusively (3x1) for Rh and Pt, and (~12x1) for Pd. Scanning tunneling microscopy (STM) investigations of the Rh/W(211) system reveal that the atomic structure of the (3x1) reconstruction is due to very long (up to 1000 Angstroms) double rows of Rh separated by missing rows; the troughs of the W(211) surface presumably are filled with Rh atoms. Similarly, the atomic structure of the Pd/W(211) (~12x1) reconstruction is due to the W(211) surface being covered by the Pd overlayer, except for equally spaced missing rows of overlayer atoms. Furthermore, evidence for two phase coexistence and domain growth (distinct (1x1) and (3x1) regions) is found in STM of Rh/W(211) near one physical monolayer coverage.TPD experiments performed at very high temperatures (up to 2400 K) provide insight into the adsorption energetics of these metallic overlayers. Our results are discussed in the context of previous experiments: the faceting of W(111) surface into nanoscale three-sided pyramids with (211) facets, induced by metal overlayers.

Thin Films Division
Room 310 - Session TF-WeM
ULSI Metalization and Interconnects

Moderator: J. Hopwood, Northeastern University

8:20am **TF-WeM1 ULSI Metallization and Interconnects**, ***C.B. Whitman,*** CVC, Inc. **INVITED**

The performance of advanced IC chips is limited by the interconnect propagation delays, dispersion, and cross-talk within the Al/SiO@sub 2@ system. The combination of Cu and low-k dielectrics enables a reduction of the interconnect levels and improved reliability. Various deposition methods (MOCVD, PVD, and plating) have been evaluated for Cu. Vacuum-integrated clustering of single-wafer process modules offers advantages for advanced metallization applications. The capability to integrate the pre-clean process with the copper (seed and/or fill) and barrier layers in a vacuum cluster tool prevents atmospheric exposure of the sensitive metallization interfaces, resulting in improved process repeatability and reduced via resistance. A vacuum-integrated MOCVD metallization technology has been developed and demonstrated for formation of high-performance Cu plugs/lines for 0.18 - 0.13 µm IC manufacturing. MOCVD copper seed and gap-fill processes have been integrated with soft plasma clean and barrier deposition processes in a vacuum cluster tool. The MOCVD-Cu process is capable of void-free filling of high-aspect-ratio (up to 8:1) features with low-resistivity (@<=@2 micro-ohm.cm) Cu layers. Excellent copper layer adhesion and copper/barrier microstructure properties have been achieved. The films have shown negligible impurities and large (0.5 - 0.8 µm) grains with texturing. Deposition rates in the range of 400 to 3000 Å/min have been achieved. Inlaid MOCVD copper lines and vias have been fabricated with TiN and TaN barrier layers using CMP damascene processing. MOCVD-Cu offers performance advantages for fabrication of void-free inlaid lines/plugs for all the interconnect levels, including the lower levels with narrower and larger aspect-ratio lines and the upper interconnect levels with wider/thicker and smaller aspect-ratio lines. We have also demonstrated successful process integration of copper electroplating via/trench filling with MOCVD cluster tool barrier and seed formation.

9:00am **TF-WeM3 Pinhole Formation in Solid Phase Epitaxial Film of CoSi@sub 2@ on Si(111)**, ***L. Ruan,*** *D.M. Chen,* The Rowland Institute for Science

We have revisited the long-standing pinhole problem in solid phase epitaxial growth of a CoSi@sub 2@ film on Si(111) with in situ scanning tunneling microscopy.@footnote 1@ While the as-deposited film with 5 Å of Co at room temperature shows a smooth granular texture with original substrate terraces remaining intact, annealing at 580ºC produces an epitaxial CoSi@sub 2@ film with large pinholes enclosed by a thin ring CoSi@sub 2@, exhibiting a volcano feature. Quantitative analysis shows that the formation of pinholes is a result of rapid Si outward diffusion from bulk to surface, and of the subsequent Si reaction with Co on the outer surface. Evidence suggests that inhibiting the Si diffusion channels during the thermal annealing process is the key to solving the pinhole problem. @FootnoteText@ @footnote 1@Like Ruan and D. M.Chen, Apply. Phys. Lett. in press.

9:20am **TF-WeM4 Investigation of the Structural and Chemical Stability of Advanced Metal Gate and Ultra-Thin Gate Dielectric Interfaces**, ***B. Claflin,*** *G. Lucovsky,* North Carolina State University

Aggressive scaling of MOS device features to 0.1 µm and below will require the introduction of novel materials and new, low-thermal-budget processes. For example, in front end-of-the-line processing, alternative gate dielectrics such as ultra-thin SiO@sub 2@/Si@sub 3@N@sub 4@ stacks and/or high dielectric constant (K) materials such as Ta@sub 2@O@sub 5@ will be required to scale down the oxide equivalent thickness, t@sub ox@, and limit leakage current to acceptable levels. Likewise, replacements for heavily doped polycrystalline Si (poly-Si) gate electrodes such as simple or compound metals will be needed to prevent i) poly-depletion and ii) boron out-diffusion and dielectric penetration effects. However, the compatibility of these new materials under device processing conditions must be demonstrated. For example, many transition metals chemically react@footnote 1,2@ with SiO@sub 2@ at temperatures above 650@degree@C, and as such can not be used in gate stacks. In addition, the effects of thin film microstructure or phase transitions can dramatically alter the electronic and mechanical properties of these materials, and their interfaces, degrading both device performance and reliability. Recent studies@footnote 3,4@ indicate that TiN@sub x@ and WN@sub x@ composite metal gates are compatible with ultra-thin remote plasma-enhanced chemical-vapor deposited (RPECVD) SiO@sub 2@ and stacked SiO@sub 2@/Si@sub 3@N@sub 4@ gate dielectrics that are subjected to rapid thermal annealing (RTA); i.e., they perform well as metal gate electrode in MOS device structures. In this work, the structural integrity of these metal/dielectric interfaces subjected to RTA is investigated by SEM, TEM, and X-ray diffraction. These structural characterizations are correlated with the chemical stability of these interfaces determined by Auger electron spectroscopy (AES). Supported by NSF, SRC, and ONR. @FootnoteText@ @footnote 1@ S. Q. Wang and J. W. Mayer, J. Appl. Phys. 64, 4711 (1988). @footnote 2@ R. Pretorius, J. M. Harris, M-A. Nicolet, Solid State Electron. 21, 667 (1978). @footnote 3@ B. Claflin, M. Binger, and G. Lucovsky, J. Vac. Sci. Technol. A 16 (1998), in press. @footnote 4@ B. Claflin, M. Binger, and G. Lucovsky, Mat. Res. Soc. Symp. Proc. (1998), in press.

9:40am **TF-WeM5 Low Temperature Deposition of Zirconium Diboride, A Candidate Diffusion Barrier, Using Remote Plasma CVD**, ***J.H. Sung,*** *D.M. Goedde, G.S. Girolami, J.R. Abelson,* University of Illinois, Urbana-Champaign

Zirconium diboride is potentially suitable as an advanced diffusion barrier in ULSI circuits because of its low electrical resistivity, 10 micro-ohm-cm in bulk form, very high melting temperature, ~ 3000 C, and resistance to air oxidation and reaction with metals. However, the CVD of ZrB2 from conventional halide/hydrogen source gases requires a relatively high temperature of ~ 900 °C. We showed that zirconium tetrahydroborate, Zr(BH@sub 4@)@sub 4@, is an attractive precursor which has high vapor pressure and can be thermolyzed at < 300 °C to produce ZrB2 films with resistivity ~ 120 µm@OMEGA@-cm. In this work, we report the use of remote plasma CVD to further reduce the ZrB2 deposition temperature and improve the film properties. Atomic hydrogen is generated by a microwave plasma source and mixed downstream with Zr(BH@sub 4@)@sub 4@ to produce high quality films at only 150 °C. The films have resistivity ~ 60 µm@OMEGA@-cm, and low carbon and oxygen contamination. XPS data indicate that the plasma-deposited films are single phase ZrB2. Based on in-situ mass spectroscopy data, we will present a preliminary analysis of the chemical reaction pathways associated with the remote plasma growth process.

10:00am **TF-WeM6 A Parameter Free Model for the Simulation of Trench Filling Profiles under Al PVD and Al IPVD Conditions**, ***A. Kersch,*** Siemens Ag, Germany; *U.P. Hansen,* Technical University Munich, Germany

Simulation results are presented for microscopic profile evolution of deposited Al metal films in trench structures. The model for the simulation is derived from atomistic, molecular dynamics calculations using a previously developed Al-Al interaction model.@footnote 1@ The essential elements are: (1) an angular and energy dependent non unity sticking coefficient resulting in specular reflection of the impinging Al atoms, (2) an energy and angular dependent sputter yield. The parameters of the model are obtained from the molecular dynamics results, surface diffusion is so far neglected. We study the surface evolution and sidewall coverage for different PVD and IPVD conditions for trench structures of different aspect ratios and clarify the influence of the model elements on the deposition process. The predictions of the model agree with the results of a published model@footnote 2@ in some range of process conditions. Finally results are compared to experimental data. @FootnoteText@ @footnote 1@U. Hansen, Molecular Dynamics Study of Al PVD Processes @footnote 2@S. Hamaguchi and S.M. Rossnagel, J. Vac. Sci. Technol. B13 (1995) 183

10:20am **TF-WeM7 Energy Dependent Atomistic Simulations of Trench-filling*, Y.G. Yang*,** *X.W. Zhou, H.N.G. Wadley,* University of Virginia

A comprehensive atomistic analysis of incident kinetic energy effects during vapor deposition has been conducted and the results integrated into a kinetic Monte Carlo simulation of physical vapor deposition. Interactions of hyperthermal atoms with substrate that resulted in biased diffusion, atomic reflection, resputtering and local thermal spikes were incorporated in a simulation model that also included normal, thermally driven multipath diffusional processes. Results are presented for the vapor phase deposition of metal interconnects by the dual damascene process. This involves the filling of increasingly narrow trenches with copper and other metals. Filling of these trenches has been studied as a function of the substrate temperature, the deposition rate, trench geometric parameters, incident atom flux energy and angular distributions.

10:40am **TF-WeM8 Sputtered Copper Seedlayer Processing Issues*, E.C. Cooney III,*** *D.C. Strippe, J.W. Korejwa, A.H. Simon, C. Uzoh,* IBM Microelectronics

One method to produce reliable Copper interconnects for advanced logic chip technology utilizes sputtered Copper seedlayers which are subsequently electroplated. However, experimental results indicate that good film step coverage as well as conformality are necessary to promote complete filling of the feature. Current trench dimensions and dual damascene aspect ratios are such that traditional sputter processes cannot adequately cover these structures. In addition, Copper tends to dewet from the substrate when thermal aspects of the process, such as sputter energy and deposition temperature, become too great. This can lead to a discontinuous film causing void formation during electrodeposition. We have investigated collimation of Copper films to improve the conformality in aggressive single and dual damascene structures. Collimation filters of various aspect ratio were used to deposit Copper seedlayers which were then filled using electrodeposition. In addition, thermal effects were examined through experimentation with lower DC magnetron powers coupled with special platen cooling considerations to reduce the heat load within the film. Electrical opens-yield and resistance data was then measured. Failure analysis was also performed to observe the plating fill.

11:00am **TF-WeM9 The Effect of Sputter Process and Target Pass-Through Flux on Sputter Deposition of Co Thin Film for Cobalt Silicide Metallization*, H. Zhang*,** *J. Poole, R. Eller, M. Keefe,* Tosoh SMD, Inc.

CoSi@sub 2@ is considered an alternative to TiSi@sub 2@ for use as a contact in ULSI due to its low resistivity, excellent chemical stability and lower formation temperature. Sputter deposition of Co thin film is one of the crucial steps in salicide (self-aligned silicide) process. One major problem with sputter deposition of Co thin film, however, is that Co is a ferromagnetic material, which can be difficult to sputter. Magnetic field strength has been found to be the key parameter in sputtering magnetic films. In magnetron sputtering of Co, high magnetic field strength can be obtained by using a high pass-through flux (PTF) target that allows maximum magnetic flux from the magnets to permeate through the magnets. A high PTF target also allows efficient sputtering and uniform target erosion. The effects of target PTF and sputtering process parameters such as Ar pressure, sputtering power, target to substrate spacing and substrate temperature on the sputter process and film properties were studied. Co targets with PTF of 65% (high PTF), 55% (medium PFT) and 35% (low PTF) were sputtered. Co thin films ranging from 16 nm to 500 nm in thickness were deposited on 200 mm (100) Si wafers. Sputter deposition rate, I-V characteristics, film sheet resistance and film uniformity was measured under various sputter conditions. It is indicated that the I-V characteristics of different PFT targets followed the normal I=KV* relationship of DC planar magnetron sputtering. The exponents in the equation, n, increased with increasing target PTF, indicating the higher the PTF, the lower the impedance. The target having the highest PFT demonstrated the best film uniformity. Rapid thermal processing was carried out to form cobalt silicides at temperatures between 300°C to 850°C in Ar ambient for various times. The sheet resistance of the Co and cobalt silicide films was monitored by four-point probe before and after the RTP. Phases and microstructure of the films were characterized using XRD, SEM and SIMS. The sheet resistance decreased significantly after annealing at 600°C and 700°C due to formation of CoSi@sub 2@, which has lower resistivity. The significant increase in sheet resistance after annealing at 400°C and 500°C was attributed to formation of CoSi phase. For the 16 nm thick Co film, sheet resistance of 3.2 @OMEGA@/sq was obtained after RTP at 600°C and 700°C.

11:20am **TF-WeM10 Improvement of Morphological Stability of Ag Thin on TiN Layer*, C.-Y. Hong,*** Massachusetts Institute of Technology*; Y.-C. Peng, L.-J. Chen,* National Tsing-Hua University, Republic of China*; W.-Y. Hsieh,* United Microelectronic Corporation, Republic of China

Owing to the need to increase the packing density in ULSI, thermally stable low-resistive contact and metallization technologies are important. Numerous studies of noble-metal-semiconductor processes have been conducted to obtain a better understanding of the interface structure and other properties. Ag is the most conductive materials and has been considered to be a candidate materials for interconnection in ULCI fabrication. Since fast interdiffusion occursbetween Ag and Si substrate, advanced metallization technologies of Ag for ULSI require a highly comformal barrier layer to prevent the interdiffusion between Ag and Si substrate. Among various kinds of diffusion barriers, titanium nitride (TiN) thin films have been widely used in ULSI fabrication due to its relatively low electrical resistivity and high thermal stability. In a previous study, Ag islands were found to form on TiN layers after annealing at 100 °C for 30 min. Owing to the poor morphological stability of the Ag/TiN interface, the utilization of thin Au and Ti layers between Ag and TiN layers has been explored to overcome the island formation problem in this study. The presence of interposing Au and Ti layers was found to increase the morphological stability temperature of Ag thin films on TiN layer from 100 °C to 450 °C and 350 °C, respectively.

Vacuum Technology Division
Room 329 - Session VT-WeM

Vacuum Microelectronics

Moderator: J.W. Weed, Sandia National Laboratories

9:00am **VT-WeM3 Electron Beam Degradation of Sulfide-Based Thin Film Phosphors for Field Emission Flat Panel Displays*, B.L. Abrams,*** University of Florida, Gainesville*; T.A. Trottier,* Motorola*; H.C. Swart,* University of the Orange Free State, Republic of South Africa*; E.S. Lambers, P.H. Holloway,* University of Florida, Gainesville

The change in cathodoluminescence (CL) brightness and changes in surface chemistry of the thin film phosphor, SrS:Ce, have been investigated using a scanning Auger electron spectrometer and an Orial optical spectrometer. The data for SrS:Ce were compared to ZnS:Cu,Cl,Au and Y@sub 2@O@sub 2@S:Eu powders all collected in a stainless steel UHV chamber with gas pressures of 10@super -6@ Torr O@sub 2@. In the presence of a 2kV primary electron beam, the amounts of C and S on the surface decreased while the oxygen concentration increased. As a result, ZnO, Y@sub 2@O@sub 3@ and preumably SrO@sub x@ formed. This change in surface chemistry coincided with a decrease in CL brightness. SrS degraded much faster than ZnS of Y@sub 2@O@sub 2@S. The model for this degradatin process suggests that the primary electron beam dissociated physisorbed molecules to reactive atomic species. These atomic species reacted with surface S and C, carrying them away and leaving behind an increasingly more impenetrable layer. Threshold voltage experiments were conducted to reveal where it becomes possible to measure the CL. This threshold voltage should be affected by the oxide layer discussed above. The implications for vacuums in an FED FPD will be discussed. This work was supported by Darpa grant MDA 972-93-1-0030 through the Phosphor Technology Center of Excellence

9:20am **VT-WeM4 Current Status of Field Emission Displays (FED's)*, B.E. Gnade,*** Defense Advanced Research Projects Agency **INVITED**

Over 12 years have passed since the first field emission display (FED) prototype was built by LETI, France; this was a 5Ó diagonal, 1/4 VGA monochrome screen. At present, commercially available screens of similar design are beginning to emerge. These displays, manufactured by PixTech Inc., are based on a low-anode-voltage (<1kV) concept and are geared primarily for instrumentation applications. However, FED screens of superior image quality, including brightness and color purity, must be produced in order to challenge AMLCDs and ultimately the CRT beyond niche applications. To this end, Motorola adopted a high-anode-voltage approach to FED design that results in full-color, sun-light readable FED prototypes. In my presentation, I will address some of the challenges faced in producing a high-anode-voltage FED. In addition, I will describe some of the ongoing efforts at Motorola to produce still more readily affordable and reliable displays, such as those based on carbon cathodes.

10:00am **VT-WeM6 Thin Film and Powder Phosphors for Field Emission Flat Panel Displays***, **P.H. Holloway**, S. Jones, T.A. Trottier, J. Sebastian, B.L. Abrams, J. Thomes,* University of Florida, Gainesville*; H.C. Swart,* University of the Orange Free State, Republic of South Africa **INVITED**

Field emission displays (FEDs) are now available in the market place as monochrome product, and full color displays are available for engineering evaluation. Critical to the success of the full color display will be the performance and lifetime of the red, green and blue phosphors. The effects of operating voltage, current density, residual vacuum and phosphor, tip interactions will be discussed. The critical parameters are the phosphor brightness, efficiency, and lifetime, which are impacted by numerous factors. Reduced saturation effects have been demonstrated in FED phosphors by reducing the luminescent lifetime so that luminescent centers may be excited multiple times during one writing cycle. Charging of phosphors, especially at low voltages, has been studied and new models developed which may lead to better control through processing. Considerable progress has been achieved in understanding the limited lifetime and the phosphor/tip interaction. The surface chemistry of the phosphors is critical to brightness and efficiency, and electron beam stimulated surface chemical reactions with residual vacuum gases have been shown to dominate the evolution of surface chemistry. This is particulary true for sulfur-containing phosphors, but also true for oxide-based phosphors as well. This mechanism will be reviewed in detail, and the effects on FED phosphors will be discussed.

10:40am **VT-WeM8 A Poor Vacuum Tolerant, Low-Voltage, Scalable, Thin-Film-Edge Dispenser Field Emitter Array***, **D.S.Y. Hsu**, H.F. Gray,* Naval Research Laboratory **INVITED**

A new low-voltage, poor-vacuum-tolerant, area-scalable, field emitter array (FEA) electron source has been developed for field emitter displays (FEDs). The new FEA cell has a horizontal gate to minimize capacitance and a vertically oriented multi-layer thin-film-edge dispenser field emitter. This multilayer thin-film emitter is made with alternating high work function and low work function metal thin films with a total thickness in the range of 60-75 nm. The FEA cell aperture diameter is about 400 nm and the height of the emitter is about 0.5 micrometers. Spacing between the gate aperture edge and the emitter film is about 75-90 nm. This new FEA, based on chemical beam deposition, is fundamentally self aligned and should not depend on high resolution lithography. All dimensions are totally independent; that is, the FEA cell aperture diameter, spacing between gate edge and emitter, emitter height, insulator thickness, gate thickness, number of multi-layers, thickness of multi-layers, etc. can be independently designed without effecting the other dimensions. The number of processing steps is less than 1/3 the number required for other FEAs. We have measured single FEA cell emission of about 5-10 microamps using an extraction voltage of 60 volts and about 10 nanoamps with 30 volts. We have also observed no emission degradation after repeated cycling from 10@super -8@ to 10@super -6@ torr of room air. No activation procedures are required and exposure to atmosphere has no measurable effect.

11:20am **VT-WeM10 Diamond Coated Silicon Field Emitter Array***, S. Albin, **W. Fu**,* Old Dominion University*; G.R. Myneni,* Thomas Jefferson National Accelerator Facility

Diamond coated silicon tip arrays, with and without a self-aligned gate, were fabricated and their I-V characteristics were measured. Sharp silicon tips were prepared by a wet etching technique. For samples without the gate, the silicon array was selectively nucleated at the tip region using ultrasonic agitation in a 10-nm diamond suspension. CVD diamond films were grown uniformly on the tips with a negative bias on the substrate to enhance the diamond growth. The arrays were tested for current emission under a vacuum of 10@super -6@ torr. A piece of polished silicon was used as anode with a 2-@micron@ thermal oxide spacer. An emission current of 50 @mu@A was obtained at 5 V from an array of 400 tips. The I-V curve of the diamond coated silicon arrays showed typical diode characteristic under forward and reverse bias. To fabricate the self-aligned gate structure, 1-@micron@ thermal oxide was grown on the etched samples followed by deposition of 0.2 @micron@ tungsten as a gate metal using RF sputtering. After planarization by etch back, the exposed gate metal and oxide were removed from the tips. Diamond films were grown selectively on the silicon tips. A copper anode was placed 200 @micron@ away from the array surface with an applied voltage of 400 V. The turn-on gate voltage was found to be 40 V for the gate aperture of about 1.5 @micron@. An emission current of 3 @mu@A was obtained from an array of 400 tips at a gate voltage of 80 V. Our technique shows the potential for development of diamond based low voltage vacuum electronic devices and field emission based micro sensors.

11:40am **VT-WeM11 Field Emission Characteristics of SiC Capped Si Tip Array by Ion Beam Synthesis***, D. Chen, **W.Y. Cheung**, S.P. Wong, Y.M. Fung,* The Chinese University of Hong Kong, Hong Kong*; J.B. Xu,* The Chinese University of Hong Kong, China*; I.H. Wilson,* The Chinese University of Hong Kong, Hong Kong*; R.W.M. Kwok,* The Chinese University of Hong Kong, China

High dose carbon implantation into Si tip array and Si wafer using a high beam current density Metal Vapor Vacuum Arc ion source were performed to synthesis SiC/Si heterostructure tip array. Silicon tip array were prepared by anisotropic chemical etching. An implantation energy of 35keV was used to a dose of 1.0*10@super18@ ions/cm@super2@ were performed and subsequent annealing in argon ambient at 1200@supero@C for various time were performed to form SiC capping layer. Scanning Electron Microscopy (SEM) revealed the Si are sharp and uniformly arranged. X-ray photoelectron showed that a thin surface SiC layer has been formed. Electron Field Emission characteristics have been measured using a diode structure by using a spacer in an ultra-high vacuum chamber with a base pressure better than 2*10@super-8@ torr. Results shown that electron emission properties depend on the processes conditions of the these samples. Typical turn-on field and emission current density are about 2.5 V/mm and 1mA/cm@super2@, respectively. These results were compared with that of planar structure prepared by ion implantation into Si wafer. The dependence of the electron emission mechanism on the surface morphology and the structure of the samples will be presented and discussed. This work is supported in part by the Research Grants Council of Hong Kong (Ref. No. CUHK513/95E)

Applied Surface Science Division
Room 307 - Session AS-WeA

Polymer Surfaces, Films and Interfaces

Moderator: D.G. Castner, University of Washington

2:00pm **AS-WeA1 Changes in the Band Structure Across the Surface Ferroelectric Phase Transition in the Crystalline Ferroelectric Copolymer P(VDF-TrFE)**, ***J. Choi**, P.A. Dowben, A.V. Bune, S. Ducharme,* University of Nebraska, Lincoln*; V.M. Fridkin, S.P. Palto, N. Petukhova,* The Russian Academy of Sciences, Russia

Recently, the ferroelectric copolymer poly(VDF-TrFE, 70:30) LB films have been attracted because of the new surface ferroelectric phase transition and correlation of the surface ferroelectric transition with the electronic structure.@Footnote 1,2@ The relationship between the electronic structural and the conformational structural change of the crystalline 5 ML films of poly(VDF-TrFE, 70:30) has been studied in detail using several methods angle resolved inverse photoemission spectroscopy, low energy electron diffraction, angle resolved X-ray photoemission, and work function across the surface ferroelectric transition. Their results indicate that the Brillouin zone size is doubled across the surface ferroelectric transition. These is a C-F bond reorientation across the ferroelectric phase transition. Most profound are the change in the unoccupied (conduction band) band structure. @FootnoteText@ @footnote 1@A. V. Bune, V. M. Fridkin, Stephen Ducharme, L. M. Blinov, S. P. Palto, A. Sorokin, S. G. Yudin, and A. Zlatkin, Nature (London) (to be published) @footnote 2@Jaewu Choi, P. A. Dowben, Shawn Pebley, A. V. Bune, Stephen Ducharme, V. M. Fridkin, S. P. Palto, and N. Petukhova, Phys. Rev. Lett. 80, 1328(1998)

2:20pm **AS-WeA2 UV Photopolymerization of Methyl Methacrylate and Acrylic Acid on Pt(110) Using Time-Resolved FT-IRAS**, *J. Yan, K. Green, T. Jachimowski, **J. Lauterbach**,* Purdue University

The adsorption and polymerization characteristics of methyl methacrylate (MMA) and acrylic acid on platinum were studied under varying conditions using time-resolved Fourier-transform IR reflection-absorption spectroscopy (FT-IRAS). Methyl methacrylate adsorbs physically on Pt(110) at 100 K, while acrylic acid likely chemically adsorbs. Adsorption of these monomers results in broadening of features, peak shifts, and changes in the intensity ratios of different peaks in the vibrational spectra, as compared to their liquid phase values. The most significant observation in the FT-IRAS spectrum of adsorbed MMA is the absence of the vibrational bending mode of the @alpha@-CH3 group of the monomer in the adsorbed films. The FT-IRAS spectrum of acrylic acid shows that it adsorbs in both the cis and trans forms showing a relative increase in the cis form with coverage. The UV-initiated photopolymerization of MMA and acrylic acid were examined by monitoring the disappearance/appearance of characteristic absorption bands as the monomer was converted to polymer. MMA polymerization results in the expected decrease in intensity of the C=C bond of the monomer and also a decrease in the intensity of the carbonyl group of the monomer. Associated with the decrease in intensity of the carbonyl group is the observation of surface bonded CO. The most significant result of the photopolymerization of acrylic acid is the appearance of CO@sub 2@ on the surface as the polymerization proceeds. In contrast with MMA we did not observe large changes in the intensities of the carbonyl and C=C peaks indicating that although polymerization was occurring, decarboxylation was more likely.

2:40pm **AS-WeA3 Correlations of the Structure and Mechanical Properties of Polymer Surfaces: Combined Sum Frequency Generation-Surface Vibrational Spectroscopy and Atomic Force Microscopy Studies**, ***G.A. Somorjai**, D. Gracias, D. Zhang,* University of California, Berkeley **INVITED**

Vibrational spectroscopy by sum frequency generation (SFG) is a non-linear optical technique that is totally monolayer sensitive and can be employed for studies of solid-liquid, solid-solid, and solid-gas interfaces. It provides information about the surface structure and orientation of molecules at the interface. Atomic force microscopy permits measurements of the elastic moduli and the friction coefficient of interfaces with excellent spatial resolution. We utilized both techniques to investigate polyethylene (low and high density), polypropylene (atactic, isotactic) surfaces, and a polymer blend, Biospan-S, in air and in liquids and as a function of temperature. The structure and orientation of CH@sub 2@ and CH@sub 3@ groups at the interface readily identify polyethylene and polypropylene types. Structural changes that occur near and at the glass transition temperatures are detectable. The friction coefficients and elastic moduli correlate well with changes of surface structure. Biospan-S undergoes structural changes when placed in an aqueous solution from air resulting in the migration of the hydrophilic polymer components to the surface. Good correlations of these changes with variations of contact angle were found. AFM detects phase segregation as the composition of the polymer blend is altered.

3:20pm **AS-WeA5 Hydrolysis Degradation of Biodegradable Polymers A Time-of-Flight Secondary Ion Mass Spectrometry Study**, *J.A. Gardella, Jr., **J. Chen**[1],* State University of New York, Buffalo

Biodegradable polymers have found many applications such as controlled release for drug delivery and as wound healing devices. The characteristics of surface hydrolysis as a degradation mechanism for biodegradable polymers are crucial to the application. Time-of-flight secondary ion mass spectrometry (ToF SIMS) makes it possible to observe the in-vitro hydrolysis products directly as intact low molecular weight oligomers. In this study, we have investigated the hydrolysis degradation of important biodegradable polymers, in particular, polyesters such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA), the copolymer poly(lactic-co-glycolic acid) (PLG) and various polyanhydrides. The in-vitro hydrolysis reaction is conducted on polymer disc samples at 37 @super 0@C in a physiological buffer for a range of hydrolysis periods from one to twelve hours. The hydrolysis products are observed in ToF SIMS spectra as peaks assigned to intact molecular ions. The molecular weight distribution of hydrolysis products is then obtained. The capability of using ToF SIMS in direct characterization of surface degradation kinetics of biodegradable polymers is demonstrated.

3:40pm **AS-WeA6 Effect of PDMS Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion**, *J. Zhao,* State University of New York, Buffalo*; S.R. Rojstaczer,* Occidental Chemical Corporation*; J.A. Gardella, **J. Chen**,* State University of New York, Buffalo

Polyimidesiloxane (SIM) copolymers are becoming increasingly important materials in the microelectronics industry in applications, such as die attach adhesives, due to their attractive properties, such as good adhesion, low dielectric constant and low stress. In this study, a series of SIM copolymers, based on @alpha@,@omega@-aminopropylpoly(dimethylsiloxane)(PDMS), 2,2-bis(4-[4-aminophenoxyl]phenyl)propane(BAPP) and 4,4'-oxydiphthalic-anhydride(ODPA) was synthesized in our laboratories. We investigated the effect of siloxane segment length on the surface composition of the SIM copolymers and its role in adhesion. The aim is to elucidate the correlation between polymer structure, surface composition, and the adhesion strength, as evaluated by peel tests. In-depth compositional profiles of the near surface region to approximately 100Å depth were simulated from the results of angle-dependent Electron Spectroscopy for Chemical Analysis (ESCA) experiments by using a deconvolution computer program. The simulated in-depth compositional profiles show that the topmost surface of the air (free) surface of the 75µm thick SIM copolymer film consists of a siloxane-rich layer, even with the shortest siloxane segment. For a given siloxane bulk content, a longer siloxane segment gives a surface richer in siloxane. The adhesion strength was determined by peel testing of SIM copolymers-Fe/Ni Alloy-42 laminates. The peel strength decreases exponentially with increasing thickness of the surface siloxane-rich layer, which corresponds to a longer siloxane segment length. However, all values of adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results that both siloxane and polyimide are essential components to rendering the high adhesion strength. The siloxane component provides a good diffusive ability, while the polyimide component interacts with the substrate to give rise to adhesion strength. Longer siloxane segments in the SIM copolymers are found to be detrimental to adhesion strength by way of interference with the polyimide-metal interaction.

4:00pm **AS-WeA7 Interface Characterization with Combined XPS and TOF-SIMS An Application to the Metallization of Plasma Modified Polymer Surfaces**, ***D. Wolany**, T. Fladung, Th. Gantenfort, L. Wiedmann, A. Benninghoven,* Universität Münster, Germany

In recent years, the combination of time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) has gained considerable importance for the analysis of technologically relevant surfaces and interfaces, e. g. for device technology or for surface modification of organic substances. The polymer-metal interface is of particular interest, because such compound materials are used e. g. for compact disks or flexible electronic circuit boards. The polymer-metal

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interface itself, however, is not accessible by surface analytical techniques except in the case of adhesion failure. The combination of TOF-SIMS and XPS can help in this situation by characterization of the original polymer substrate, the surface of the plasma modified polymer, and the initial stages of metal deposition. In this way, one can obtain valuable insights into the interaction mechanisms between the metal and the substrate. We present results for Cu on polyimide modified in an oxygen plasma, and Al on polycarbonate modified in oxygen, argon and SF@sub 6@ plasmas, respectively. In both cases, XPS shows, after plasma modification, the occurrence of additional binding states within the polymer. In the initial stages of metallization, metal-substrate bonds can be identified which are characteristic for adhesion of the metal. The TOF-SIMS fragmentation patterns both after plasma treatment and after metallization allow the identification of specific interaction mechanisms between the polymer and the metal. In addition, standard technical adhesion tests (peel test, twist-off test) were applied to similar samples with thick metallic overlayers.@footnote 1@ In this way we established correlations between the plasma parameters used for substrate modification, the chemical and physical properties of the modified substrate and the polymer-metal interface, and the adhesion strength of the compound material. @FootnoteText@ @footnote 1@Federal Institute for Materials Research and Testing (BAM), Berlin, 12200, Germany

4:20pm **AS-WeA8 XPS Evidence of Redox Chemistry Between Cold Rolled Steel and Polyaniline**, ***B.C. Beard**, P. Spellane,* Akzo Nobel Chemicals, Inc.

The electrochemical response of polyaniline (PANI) in its undoped intermediate (emeraldine base, EB) oxidation state coated on cold rolled steel (CRS) or glass substrates has been evaluated by xray photoelectron spectroscopy (XPS). The oxidation state of the polymer was determined from the ratio of amine to imine nitrogen chemical states observed in the N(1s) photoelectron spectrum. A room temperture air dried PANI coating cast from NMP solution onto CRS was found to be reduced relative to its as-synthesized, air stable state. Heating the PANI coated on CRS in the absence of air (165°C, in ultra high vacuum) produced an even deeper reduction, resulting from the transfer of electronic charge to the polymer from the metal substrate. Subsequent brief exposure of this reduced PANI coating to air at elevated temperature (165°C) reoxidized the PANI to the EB state. Analogous treatment of a PANI coating on glass caused no such change in oxidation state of the polymer. Unlike steel which provides a redox couple with PANI, glass is electro-inactive.

4:40pm **AS-WeA9 Evaluation of the Degradation Mechanism(s) Associated with Acid Rain Exposure of Acrylic Melamine Based Automotive Clearcoats**, ***P.J. Schmitz**, J.W. Holubka, L.F. Xu,* Ford Motor Company

Environmental exposure of clearcoats to ambient conditions of low pH can result in visible surface pitting. The degradation phenomenon associated with this localized loss of material is thought to occur primarily through crosslink hydrolysis as a result of acid rain exposure. Although this phenomenon has been studied quite extensively, limited chemical data has been presented that confirms the mechanism(s) of the degradation process. Most conclusions that have been made are largely based on empirical considerations involving observations that degradation is most prevalent in areas having low pH rain, and the results of field exposure studies that indicate the sensitivity of a particular coating to environmental degradation is directly associated with the ease of hydrolysis of the crosslink. In this study, we have used XPS to monitor changes occurring at the clearcoat surface as a result of field exposure, to attempt to more clearly define degradation products, and therefore the mechanism(s) associated with the degradation phenomenon. Changes were observed in the N, C, and O core level spectra after field exposure, and were found to be consistent with the modification of melamine crosslinkers following laboratory acid treatment. Bulk elemental analysis and XPS core level results, obtained from sulfuric acid treated crosslinkers, were found to be consistent with melamine salt (sulfate) formation. The confirmation of residual melamine sulfate on the clear coat surface following field exposure, strongly suggests that the prominent degradation pathway is acid rain induced crosslink hydrolysis. The identification of degradation products associated with environmental exposure could prove useful in the development of laboratory testing for the evaluation of clearcoat hydrolysis resistance, to verify that exposure conditions reproduce field degradation pathways.

5:00pm **AS-WeA10 Optical Characterization of FEP Teflon: Pristine and from Hubble Space Telescope@footnote 1@**, ***C.L. Bungay,*** Univeristy of Nebraska, Lincoln*; J.N. Hilfiker,* J. A. Woollam Co., Inc.*; J.A. Woollam,* University of Nebraska, Lincoln

Polymers used on spacecraft are often susceptible to environmental degradation in Low Earth Orbit (LEO). Therefore, the behavior of materials used on spacecraft such as the International Space Station and Hubble Space Telescope (Hubble) must be well characterized to ensure long term survivability of the spacecraft. Optical methods are favorable to study space application materials because they are non-contact and non-destructive. However, polymer films are often biaxially anisotropic and this anisotropy is usually not accounted for when optical measurements are acquired. In this work FEP Teflon (pristine and exposed to the LEO environment on Hubble) are studied using various optical measurements, including transmission ellipsometry, reflection ellipsometry and transmission intensity. By acquiring a series of different optical measurements the optical constants in three orthogonal directions and their optical axis orientations were determined. The optical data were also studied to help determine the extent of degradation of aluminized FEP returned from the first and second Hubble servicing missions. @FootnoteText@ @footnote 1@Research funded by NASA Lewis contract #NAG3-2086 and NASA Epscor contract #NCC5-169

Electronic Materials and Processing Division
Room 314/315 - Session EM1-WeA

Si Surface Chemistry

Moderator: M.K. Weldon, Bell Laboratories, Lucent Technologies

2:00pm **EM1-WeA1 Understanding the Evolution of Surface Morphology during Chemical Etching**, ***M.A. Hines,*** Cornell University*; J. Flidr, Y.-C. Huang, T.A. Newton,* Cornell University, US **INVITED**

In this talk, I will discuss the evolution of surface morphology during the etching of Si(111) by NH@sub 4@F(aq). By combining STM measurements of surface morphology with kinetic Monte Carlo simulations of the etching process, we are able to obtain microscopic information on surface reaction mechanisms. We find that long-range surface roughness can be suppressed by a low density of monolayer-deep etch pits on an otherwise "perfect" surface. On surfaces miscut in the direction, Si(111) etches via a step-flow mechanism that is nucleated by slow etching into the step and then propagated by rapid etching of the nucleated kinks -- the steps "unzip" in a direction parallel to the step. Without terrace etching, individual steps would etch independently, and the long-range surface roughness, which is reflected in the terrace width distribution, would be comparable to that expected of an equilibrium surface. If there is a small probability of terrace etching, the steps repel one another through a kinetic feedback effect that we term dynamic step-step repulsion. This effect is mediated by the anisotropic distribution of terrace pits -- wide terraces have a higher density of pits than narrow terraces. We also find that steps can self-pin during etching. This type of pinning is independent of contamination and is due to the formation of a relatively unreactive structure on the etching step. Once formed, this structure reacts slowly and acts as a self-propagating pinning site to further etching. Self-pinning can drive a morphological transition that leads to chemically induced step facetting. In spite of this pinning, the steps still etch by step-flow.

2:40pm **EM1-WeA3 Structure of a Passivated Ge Surface Prepared from Aqueous Solution**, ***P.F. Lyman,*** Northwestern University*; D.T. Keane,* Northwestern University and DND CAT*; D.L. Marasco, T.-L. Lee,* Northwestern University*; M.J. Bedzyk,* Northwestern University and Argonne National Lab

We investigated the local structure and order of a aqueously sulfided Ge(001) surface using x-ray standing waves. The adsorption of a group VI element on the Ge(001) surface could satisfy all of the substrate dangling bonds by occupying a bridge site. Such a surface would be expected to be both chemically and electronically passivated, perhaps suppressing surface carrier recombination. In the present study, S/Ge(001) surfaces prepared in aqueous (NH@sub 4@)@sub 2@S solution (diammonium sulfide) exhibited a S coherent position P@sub 004@ of 0.90 ± 0.01, implying that the S adsorption height is 1.27 Å ± 0.01 Å. This closely corresponds to the expected adsorption height for S residing in a bridge site. This finding supports the local geometry inferred for aqueously sulfided Ge(001) by previous workers.@footnote 1@ That study concluded that a single atomic layer of S binds to the surface, residing in the a (1x1) bridge-bonded configuration. However, the present studies showed a low, repeatable value of 0.15 for the coherent fraction. The simplest explanation for these observations is that, in addition to an ordered S monolayer at the interface, a ~5 ML sulfided Ge layer is formed during the chemical passivation treatment. Although this model conflicts with the conclusions of Ref. 1, such an interface is not unlike the native oxide of Si, where several atomic layers of passivating silicon oxide readily form. We are presently conducting other tests of the S/Ge(001) surface to determine the nature of this interface more completely. @FootnoteText@ @footnote 1@G. W. Anderson, et al., Appl. Phys. Lett. 66, 1123 (1995).

3:00pm **EM1-WeA4 Reflectance Difference Spectroscopy of Ge / Si(001)**, ***V. Zielasek***, *S.G. Jaloviar, M.G. Lagally,* University of Wisconsin, Madison

Reflectance difference spectroscopy (RDS) has proven to be an easy-to-use tool to monitor semiconductor epitaxy, especially of III-V systems. The origins of the surface optical anisotropy, however, are not yet fully understood. Several calculations for dimerized Si(001) terraces and lately for Ge / Si(001) have been reported and compared with experimental RD spectra from highly vicinal surfaces with the conclusion that steps do not produce an RD signal.@footnote 1@ Recent experiments, however, demonstrate that on vicinal Si(001) with miscut angles even as low as 1° the steps contribute significantly to the RD signal.@footnote 2@ From this, we expect that other morphological features, such as dimer vacancy lines formed during the epitaxy of Ge on Si(001), leave their fingerprint in RD spectra as well. We present a combined RDS and scanning tunneling microscopy (STM) study of Ge / Si(001) using both vicinal and superflat wafers as substrates. STM provides an accurate measure of step density and step structure. A macroscopic anisotropy of the superflat Si(001) surface is obtained by applying uniaxial elastic strain to the sample, leading to step movement and favoring domains with dimer rows oriented in the direction of lowest external compression. We find a shift in energy of RD spectral features with increasing Ge coverage in the sub-monolayer regime. Reversal of the surface stress anisotropy with increasing Ge coverage around 1 monolayer leads to a reversal in sign of the RD signal in the 2 - 4 eV range after applying external strain. For superflat and vicinal Si(001) 4° [110] with similar Ge coverages and annealing temperatures both the RD spectra and the morphologies of the growing films differ. We discuss the relationship of stress induced by Ge adsorption and external strain effects, focussing on their influence on the RD spectra. Supported by NSF, ONR, and Alexander von Humboldt-Stiftung (V.Z.) @FootnoteText@ @footnote 1@J.R. Power et al., Phys. Rev. Lett. 80 (1998) 3133. @footnote 2@S.G. Jaloviar, J.-L. Lin, M.G. Lagally, submitted.

3:20pm **EM1-WeA5 Second Harmonic Study of Ge/Si(100) and Si@sub 1-x@Ge@sub x@(100) Films**, ***P.S. Parkinson***, *D.E. Brown, M.C. Downer, J.G. Ekerdt,* University of Texas, Austin

Second harmonic generation (SHG) allows real-time, in-situ measurement of hydrogen coverage on intrinsic silicon. Thus, SHG has been used by this group to perform hydrogen desorption measurements and growth rate calculations on intrinsic silicon.@footnote 1@ Our current challenge is to develop SHG as a tool to study the Si@sub 1-x@Ge@sub x@(100) alloy surface. We present studies of the SiGe/Si(100) and the Ge/Si(100) systems in vacuum around the E@sub 1@ critical point using SHG. In Ge@sub 2@H@sub 6@ atomic layer epitaxy (ALE) on Si(100), the SH intensity increases linearly with Ge coverage; below 5 ALE cycles (approximately 1.5 ML). Further deposition causes a continuous decrease in the signal intensity and a blue shift in the spectra. Hydrogen passivation of the surface leads to substantial quenching of the signal which reveals the sensitivity of the SH response to the near-surface Ge composition. Monitoring the growth of Si@sub 1-x@Ge@sub x@(100) films, with SHG we observed an initial rise in the SH intensity and then a decrease as the films became rougher and thicker. The time constant for the initial rise became shorter with increasing Ge film composition. Spectra of strained smooth SiGe films showed that the SH intensity at the peak maxima increased with increasing Ge film composition. Also, hydrogen saturation of the film surfaces led to an order of magnitude decrease in the SH response, similar to the Ge/Si(100) system. Thus, the initial rise in SH intensity during growth may correspond to the development of the near-surface Ge composition profile at the leading edge of growth. SH intensity decreased with increasing atomic hydrogen coverages on the SiGe/Si(100) surface; the same trend observed on intrinsic Si(100). Therefore, the SH response to hydrogen coverage in the alloy system might be explainable within the framework of models proposed for the H/Si(100) system.@footnote 2@ @FootnoteText@ @footnote 1@ Xu et al., Appl. Phys. Lett., 71, 1376,(1997). @footnote 2@ Dadap et. al., Phys. Rev. B, 56, 1, (1997).

3:40pm **EM1-WeA6 Silicon Epoxide: Fundamental Intermediate in Si(100) Oxidation**, *A.B. Gurevich,* Columbia University*; M.K. Weldon,* ***Y.J. Chabal***, *B.B. Stefanov, K. Raghavachari,* Bell Laboratories, Lucent Technologies

Understanding the growth and formation of thin oxides is critical to the development of high quality gate oxides. However, obtaining a detailed structural picture of interfacial SiO@sub 2@ poses a formidable scientific challenge due to the lack of long-range order and the critical dependence on processing parameters. We have therefore investigated with infrared absorption spectroscopy the water-induced oxidation of Si(100)-(2x1) under ultra-high vacuum conditions, as a prototypical silicon-oxide system: the water is initially dissociated into H and OH on each surface dimer; as the temperature is increased to 675K, the Si-Si dimer becomes the first target for oxygen insertion into the surface, facilitating in turn the subsequent incorporation of O into the Si backbonds.@footnote 1@ We show here that, upon dehydrogenation at higher temperatures (900K), a surprising structure is formed. The combination of high resoluton IR spectroscopy and density functional cluster calculations can, for the first time, identify this triangular SiOSi sub-unit, termed silicon epoxide, based on subtantially lower Si-O stretch frequencies (780-990 cm@super -1@) and smaller isotopic shifts (20-30 cm@super -1@) compared to those of known oxide structures. These silicon epoxides are similar to COC structures well-known in organic chemistry and characterized by a shorter Si-Si bond (2.4Å). We demonstrate that epoxides are the thermodynamically favored product upon dehydrogenation when three or more oxygen atoms are agglomerated. These epoxide structures are stable at intermediate annealing temperatures (800-1000K) and are observed upon pure oxygen exposure as well. They therefore constitute a metastable intermediate in the growth of thermal gate oxides, and are expected to be preferentially formed both in small molecules and at silica interfaces. @FootnoteText@ @footnote 1@ M.K. Weldon, B.B. Stefanov, K. Raghavachari and Y.J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

4:00pm **EM1-WeA7 Structure of Ultrathin Silicon Oxide - Silicon Interfaces Studied by Ultraviolet Photoelectron Spectroscopy**, ***J.W. Keister***, *J.E. Rowe,* North Carolina State University*; J.J. Kolodziej,* Rutgers University*; H. Niimi,* North Carolina State University*; T.E. Madey,* Rutgers University*; G. Lucovsky,* North Carolina State University

Device-grade ultrathin (9-18 Å) films of silicon dioxide, prepared from crystalline silicon by remote-plasma oxidation, are studied by the surface-sensitive method of ultraviolet photoelectron spectroscopy. The 2p core-level spectra for silicon (at ~100 eV binding energy) show evidence of five distinct states of Si. These peaks are attributed to the five oxidation states of silicon between 0 (the Si substrate) and +4 (the thin SiO@sub 2@ film), although the precise configuration has recently been called into question.@footnote 1@ We find that the peaks for Si@super 1+@ through Si@super 4+@ are shifted relative to the Si@super 0@ bulk peak to higher binding energy by 0.92 eV, 1.90 eV, 2.51 eV and 3.86 eV. The relatively weaker signal found for the three intermediate states (+1, +2, and +3) is attributed to silicon atoms at the interface between these two materials. Estimates of the interface thickness from the intermediate valence signal agree with the value reported earlier of 3-5 Å (~ 2 ML).@footnote 2,3@ In this work, the position and intensity of the five peaks are measured as a function of post-growth annealing temperature (700 - 900 °C), crystal orientation, and incorporation of N@sub 2@ in the reactant gas flow. One result we have found is that annealing produces more abrupt interfaces, but never more abrupt than about one or two monolayers. This comes from the observation of a sudden drop in the interface thickness (in particular the Si@super 2+@ peak intensity) upon reaching 800-900 °C annealing temperature. A more complete and quantitative analysis will be presented which explores the effects of the other sample parameters and takes advantage of nonlinear least-squares fitting routines. @FootnoteText@ @footnote 1@McFeely, Zhang, Banaszak-Holl, Lee, Bender J. Vac. Sci. Tech. B 14(4), 2824-2831 (1996). @footnote 2@Himpsel, McFeely, Taleb-Ibrahimi, Yarmoff, Hollinger, Phys. Rev. B 38, 6084-6096 (1988). @footnote 3@Himpsel, Meyerson, McFeely, Morar, Taleb-Ibrahimi, Yarmoff Core Level Spectroscopy at Silicon Surfaces and Interfaces, in Campagna and Rosei, eds. Photoemission and Absorption of Solids and Interfaces with Syncrotron Radiation (Proceedings of the International School of Physics "Enrico Fermi", Course CVIII, Varenna, Italy. 1988.) North-Holland/Elsevier Science Publishers: 1990, pp. 203-236.

4:20pm **EM1-WeA8 Influence of Rapid Thermal Annealing on Vicinal Si(111)/SiO@sub 2@ Interfaces Investigated by Optical Second Harmonic Generation.***, **J.F.T. Wang**, G.D. Powell, D.J. Stephens, R.S. Johnson, B.R. Solazzo, Y. Wu, D.E. Aspnes, G. Lucovsky,* North Carolina State University

We have studied optical Second Harmonic Generation, SHG, from Si/SiO@sub 2@ interfaces formed by 800°C thermal oxidation of vicinal Si(111) surfaces off-cut approximately 5 degrees in the 112bar direction. Changes in the rotational anisotropy of the SHG were observed when interfaces were annealed at temperatures between about 800 and 1000°C. We have analyzed the rotational anisotropy by including harmonic functions that reflect the C@sub 1v@ and C@sub 3v@ symmetry of the vicinal Si(111) surface corresponding respectively to steps and terraces of the vicinal surfaces. The relative phase difference, @phi@@sub 13@, between the C@sub 1v@ and C@sub 3v@ harmonic contributions is strongly influenced by the Rapid Thermal Annealing, RTA, temperature. In this paper we compare our results with an incident wavelength of 800 nm (or 1.55 eV) from a Ti:sapphire laser to previous reported work with incident wavelength of 1053 nm (or 1.17eV) using a Nd:YLF laser. The largest change in @delta@@phi@@sub 13@, ~72 degrees, using the 1.55 eV laser source is between 800°C and 900°C which is consistent with the previously reported studies using the Nd:YLF laser.@footnote 1@ However, @delta@@phi@@sub 13@ is larger for a pump beam of 800 nm compared to that of 1053 nm, ~72° compared to ~38°. These results are consistent with the anharmonic oscillator model if the laser energy is less than about one-half of the resonance energy of the anharmonic oscillator.@footnote 2@ Finally, it is important to note that annealing at 900°C has been shown to reduce sub-oxide interfacial bonding introduced at the Si/SiO@sub 2@ interface during thermal and plasma-assisted oxidation processes@footnote 3@ suggesting that changes in @delta@@phi@@sub 13@ between 800 and 900°C anneals in the SHG response are associated with changes in interface bonding that include a reduction of the extent of transition regions with the sub-oxide bonding arrangements. @FootnoteText@ @footnote 1@C. H. Bjorkman, C. E. Shearon, Jr., Y. Ma, T. Yasuda, G. Lucovsky, U. Emmerichs, C. Meyer, K. Leo, and H. Kurz, J. Vac. Sci. Technol. A11(4), 964 (1993) @footnote 2@Y. R. Shen, The Principles of Nonlinear Optics (John Willey & Sons, New York, 1984) @footnote 3@G. Lucovsky, A. Banerjee, B. Hinds, C. Claflin, K. Koh and H. Yang, J. Vac. Sci. Technol. B15, 1074 (1997), and references therein.

4:40pm **EM1-WeA9 The Initial Stages of Si(100) Oxynitridation by NO: An Infrared Study***, **J. Eng, Jr.**, K.T. Queeney, Y.J. Chabal, B.B. Stefanov, K. Raghavachari,* Bell Laboratories, Lucent Technologies*; X. Zhang, E. Garfunkel,* Rutgers University

The oxynitridation of Si(100) by N@sub 2@O has been studied extensively because the electrical properties of thin silicon oxynitride films are superior to those of silicon oxide films with the same thickness. Although the oxynitridation mechanism is not completely understood, it is generally believed that N@sub 2@O decomposes to form NO under industrial processing conditions, and that NO is the species ultimately responsible for oxynitridation. On this basis, we have chosen to study the initial reaction of NO with clean Si(100) by using infrared spectroscopy, Auger electron spectroscopy, and low energy electron diffraction. We conclusively show that NO dissociatively adsorbs on Si(100) at room temperature, thereby resolving an existing debate in the literature.@footnote 1@ Heating the NO/Si(100) surface to 650 @degree@C causes the formation of SiO@sub x@N@sub y@ structures which have strong characteristic modes at 858, 989, and 1057 cm@super -1@. These modes have been assigned based on isotopic labeling studies involving @super 15@N@super 16@O and @super 14@N@super 18@O, as well as ab-initio density functional calculations. Auger studies show that heating to 850 @degree@C removes oxygen, but the nitrogen 379 eV KLL feature is not attenuated. However, the Si-H vibrational features observed in H atom post-dosing experiments designed to probe the surface after heating to 850 @degree@C are similar to those obtained by exposing clean Si(100) to H atoms, indicating that the N atoms reside in subsurface sites. Additional information about the Si-N modes is obtained by studying the adsorption and thermal decomposition of ammonia on Si(100) surfaces. @FootnoteText@ @footnote 1@ Y. Taguchi, M. Fujisawa, and M. Nishijima, Surf. Sci. Lett., 233 (1990) L251-252

5:00pm **EM1-WeA10 Growth and Analyses of Silicon Nitride Thin Films on Si(111) and Si(100)***, **X.-S. Wang**,* Hong Kong University of Science & Technology, China*; N. Cue,* Hong Kong University of Science & Technology, China, Hong Kong, China

Silicon nitride is attractive for applications as dielectric and wide bandgap semiconductor materials. Using LEED, SPM, AES and XPS, we have analyzed geometric, thermodynamic and electronic properties of silicon nitride thin films grown on Si(111) and Si(100) substrates. The nitride films are prepared in two ways: (a) nitridation of Si substrates, i.e., by exposing clean Si samples to NH@sub 3@ or NO of various dosage and at substrate temperatures about 1150 K; (b) Si deposition under a flux of NH@sub 3@ or NO. In the second method, the substrate temperature can be kept significantly lower than 1150 K. On Si(111), the nitride thin films show a clear 8/3x8/3 superstructure. On nitrided Si(100), LEED shows a weak 1x2 + 2x1 pattern sometimes. Analysis of lattice structure of Si@sub 3@N@sub 4@ indicates that crystalline Si@sub 3@N@sub 4@ film epitaxy on Si(111) is feasible, while on Si(100) this is much more difficult. The nitride films show a remarkable thermal stability in comparison with silicon oxide films. Desorption of oxide films starts at about 1075 K, whereas the nitride films remain stable at a substrate temperature as high as 1350 K. Furthermore, surface crystalline order of the nitride films is preserved after air exposure and even after going through system baking. The implication of these results on application of nitride, oxide and oxynitride thin films in microelectronics will be discussed.

Electronic Materials and Processing Division
Room 316 - Session EM2-WeA

Application of Scanning Probes to Electronic Materials

Moderator: A. Smith, Ohio University

2:00pm **EM2-WeA1 Oscillating Contrasts Surrounding Charged Defects and Dopant Atoms in (110) Surfaces of III-V Semiconductor at Room-Temperature***, **Ph. Ebert**, C. Domke, M. Heinrich, K. Urban,* Forschungszentrum Jülich, Germany

Positively and negatively charged defects and dopant atoms in n-doped GaAs(110) surfaces give rise, at room temperature, in occupied-state scanning tunneling microscope images to a bright elevation, which is surrounded by a dark depression ring. This oscillating contrast is not observed in empty-state images. A similar effect is found on n-doped GaP(110) surfaces. In order to explain the origin of this contrast behavior we simulated the spatial variation of the tunnel current as a function of the tunneling voltage, the polarity of the charge, and the doping of the material. The calculation of the tunnel current takes into account the tip-induced band bending, the local potential change induced by the screening of the charge, and the extension of the Tersoff-Hamann model for larger voltages. The results suggest that the oscillation in room-temperature STM images can be explained as the image of the local potential change (screened Coulomb potential) induced by the presence of the charge on (110) surfaces of III-V semiconductors. It is found that the oscillating contrast behavior occurs only if competing contributions to the tunnel current from the valence and conduction bands exist. The simulation also reproduces qualitatively all presently known contrast features of charged defects and dopant atoms on III-V and II-VI compound semiconductor cleavage surfaces in STM images.

2:20pm **EM2-WeA2 Two-Dimensional Carrier Profiling of III-V Structures using Scanning Spreading Resistance Microscopy***, P. De Wolf, T. Hantschel,* IMEC, Belgium*; M. Geva, C.L. Reynolds,* Bell Laboratories, Lucent Technologies*; **W. Vandervorst**,* IMEC, Belgium*; F. Bylsma,* Bell Laboratories, Lucent Technologies

Scanning Spreading Resistance Microscopy (SSRM) is a powerful tool originally developed for measuring two-dimensional (2D) carrier distributions in Si device structures with nm-spatial resolution.@footnote 1@ It is in essence based on an Atomic Force Microscope equipped with a conductive tip that is biased relative to the sample. From the current flowing through the tip one deduces the local spreading resistance value. The spreading resistance value is determined primarily by the resistivity of the material in the small semi-hemispherical volume at the surface region where the tip contacts it. The resistivity is closely related to the local carrier concentration (and mobility) in this surface region. The spatial resolution thus mainly depends on the tip radius and pressure. Since SSRM measures resistance, a material property that depends upon carrier concentration, rather than detecting the carriers directly, it is capable of producing images of both high spatial resolution and wide dynamic range of carrier concentration. We have demonstrated spatial resolution values as small as 20 nm, and dynamic ranges of 10@super 15@-10@super 20@ atoms/Cm@super -3@ in analyses of Si devices.@footnote 1@ Whereas its application has been explored in detail on Si structures,@footnote 1@ we report here for the first time on the application of SSRM for the analysis of III-V semiconductor structures, and in particular MOCVD-grown InP-based structures. We found that the application of SSRM to InP-based structures is much simpler than to Si. A minimal surface preparation is required in the cross sectioning process, much lower tip forces are needed, and metal tips instead of diamond tips can be used. When imaging complex multilayer epi-structures (containing p, n, and semi-insulating layers), close agreement between the SSRM profile and SIMS profiles can be obtained. More importantly is the capability of SSRM to image and determine 2D structures in actual devices, such as mesas and trenches common in semiconductor laser devices. SSRM also proved very valuable in characterizing with high spatial resolution 2D dopant and implant distributions. In this presentation we will present SSRM analysis of lateral Zn-diffusion into a semi-insulation layer in a mesa-like InP structure. @FootnoteText@ @footnote 1@P. De Wolf, T. Clarysse, W. Vandervorst, L. Hellemans, Ph. Niedermann, and W. Hänni, J. Vac. Sci. Technol. B16, 355 (1998).

2:40pm **EM2-WeA3 The Structure of InAs/AlSb/InAs Surfaces and Interfaces Grown by MBE***, **B.Z. Nosho**, W.H. Weinberg,* University of California, Santa Barbara*; B.V. Shanabrook, B.R. Bennett, W. Barvosa-Carter, L.J. Whitman,* Naval Research Laboratory

We have used in-situ plan-view scanning tunneling microscopy to study the surfaces and interfaces within an InAs/AlSb/InAs resonant tunneling diode-like structure grown by molecular beam epitaxy. The nanometer and atomic-scale morphologies of the surfaces have been characterized following a number of different growth procedures. When InAs(001)-(2x4) is exposed to Sb@sub 2@ a bilayer surface is produced, with one monolayer-deep (3 Å) vacancy islands covering approximately 25% of the surface. Both layers exhibit a (1x3)-like reconstruction characteristic of an InSb-like surface terminated with >1 ML Sb, indicating that there is a significant amount of Sb on the surface. When 5 ML of AlSb is deposited on an Sb-terminated InAs surface, the number of layers observed on each terrace increases to three. Growth of an additional 22 ML of InAs onto the AlSb layer, followed by a 30 s interrupt under Sb@sub 2@, further increases the number of surface layers observed. The rms roughness is found to increase at each subsequent interface; however, on all the surfaces the roughness is @<=@2 Å. The surface roughness is attributed to a combination of factors, including reconstruction-related stoichiometry differences and kinetically-limited diffusion during growth. To begin to elucidate these various factors and help distinguish between kinetic and thermodynamic effects, we have examined the initial stages of Sb@sub 2@ deposition on InAs(001)-(2x4) under various growth conditions. Possible methods to reduce the roughness of the interfaces will be discussed.

3:00pm **EM2-WeA4 In-Situ STM of MBE Growth Quality for GaAs(001) and InP(001)****, G. Lengel**, F.G. Johnson, W.T. Beard, R.J. Phaneuf,* Laboratory for Physical Sciences*; E.D. Williams,* University of Maryland

As heterostructure-based devices continue to shrink in size, the roughness of the interface between two materials plays a larger role in determining the performance of the final product. Characterization of the lateral length scales of the roughness as well as the root-mean-square roughness is important for understanding the impact of interface quality on device performance, To address this problem, In-Situ Scanning Tunneling Microscopy (STM) has been used to study the geometry of freshly prepared MBE samples. The evolution of roughness as a function of the initial condition of the surface before growth, the thickness of the buffer layer, as well as the role of the growth temperature on both GaAs and InP will be presented. The relative quality of these surfaces has been quantified by calculation of the height- height correlation function from the measured images. The physical significance of the measured parameters, and their usefulness as criteria for judging growth quality will be discussed. @FootnoteText@ *This work has been supported by the Laboratory for Physical Sciences.

3:20pm **EM2-WeA5 Structural and Morphological Studies of GaN Heteroepitaxy on SiC(0001)***, **V. Ramachandran**, A.R. Smith, R.M. Feenstra, D.W. Greve,* Carnegie Mellon University

Heteroepitaxial growth of GaN on SiC has been studied using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and high resolution x-ray diffraction. Growth was performed by molecular beam epitaxy (MBE) on hydrogen etched SiC(0001) substrates that show a @sr@3x@sr@3 R-30° reconstruction. Significant differences are seen in the growth morphology in different growth temperature regimes, both at low and high film thicknesses. At a coverage of a few monolayers, STM observation of GaN grown at temperatures around 550°C shows layer-by-layer growth. Terraces show sub-Å corrugation corresponding to the formation of misfit dislocations at the heterointerface, indicating that the film has relaxed. Films grown at around 650°C with a similar thickness show columnar, flat-topped islands of uneven heights with deep crevices between them. This difference in morphology may be understood in terms of the different strain relaxation mechanisms in the two temperature regimes. At higher temperature, films prefer to relieve strain by forming 3-D islands, which can be distorted to relieve strain. Alternatively, at lower temperature, the films remain pseudomorphic and grow in a layer-by-layer manner both before and after the formation of misfit dislocations. AFM measurements also show remarkable morphological differences between thicker (200 nm) films grown in the two temperature regimes mentioned above. Films grown at 550°C show a large number of spiral growth fronts while films grown at 650°C show a stepped layer-by-layer structure. Based on the growth model outlined above, it is apparent that in the low temperature 2-D growth mode, misfit dislocations at the interface are associated with screw dislocations which extend upto the surface and act as a source for the spiral growth. In 3-D growth, misfit dislocations can form at the edges of islands without the need for as many screw dislocations. X-ray rocking curve measurements on GaN films 200-400 nm thick show decreasing FWHM with increasing growth temperature. This would agree with the above model, where, as the growth temperature rises, the film requires fewer screw dislocations in order to create the necessary number of misfit dislocations at the interface.

3:40pm **EM2-WeA6 Impact of Deposition Method on the Microstructural and Electrical Properties of Thin Film Silica Aerogels***, **C. Caragianis-Broadbridge**, L. Carmona, M. Farag, M. Guillorn, F. Stellabotte,* Trinity College

Aerogels are nanoporous materials with unique optical, thermal and electrical properties. Silica thin film aerogels demonstrate great potential as low dielectric constant insulators for interlevel dielectric applications. The focus of this research is the fabrication of thin film silica aerogels through a sol-gel process in conjunction with low-temperature supercritical extraction of CO@sub 2@. The microstructural and electrical properties of the aerogel were studied as a function of deposition method, using non-contact atomic force microscopy (nc-AFM), scanning and transmission electron microscopy (SEM and TEM) and capacitance-voltage (C-V) instrumentation. Alcogels, aerogel precursors, were prepared by hydrolysis and condensation of metal alkoxide, tetraethyothrosilicate, and were catalyzed by both acids and bases, according to a standard reaction. Before gelation, the solution was deposited on two substrates (bare Si and SiO@sub 2@ coated Si) by two techniques (dipping and spin coating). After supercritical extraction of the CO@sub 2@, the resulting aerogels were characterized using AFM, SEM and TEM to obtain film uniformity, thickness and pore size. C-V data were acquired from metal insulator semiconductor (MIS) capacitors fabricated using the aerogel-coated wafers. This study reveals a correlation between deposition technique and uniformity of the aerogel. Thin films deposited by the spinning technique yield consistently smaller pore sizes, ranging between 150 and 440nm while producing a more uniform film thickness. C-V characterization of the aerogel MIS devices (for both substrates) indicates a high quality dielectric with minimal mobile, fixed and interface state charge. These measurements also reveal that these aerogel MIS capacitors possess a substantially lower dielectric constant (1.5-3.5 vs. 3.9) when compared with standard control SiO2 MOS devices.

4:00pm **EM2-WeA7 UHV STM Nanofabrication and the Giant Deuterium Isotope Effect: Applications to CMOS Technology***, **J.W. Lyding**, M.C. Hersam, G.C. Abeln, E.T. Foley, J. Lee, Z. Chen, D.S. Thompson, J.S. Moore, S.-T. Hwang, H. Choi, K. Hess,* University of Illinois, Urbana-Champaign **INVITED**

The use of the UHV STM to selectively desorb hydrogen with atomic scale precision from Si(100)-2x1:H surfaces@footnote 1@ has opened new opportunities for creating nanoelectronic device structures. The chemical contrast between H-passivated and clean Si has enabled the development of nanoscale selective chemical schemes including oxidation,@footnote 1@ nitridation,@footnote 2@ and molecular functionalization.@footnote 3@ Using a high temperature STM these schemes are also being extended to include nanoscale metallization by UHV chemical vapor deposition. A key aspect of this work is the establishment of an electronic interface between nanoelectronic device structures and macroscopic contacts to enable testing. We will report on several schemes that are being developed for this purpose. In a parallel set of experiments it was found that the desorption of deuterium from Si(100)-2x1:D surfaces is much more difficult than hydrogen desorption.@footnote 4@ Using this as a basis, we discovered that deuterium treatment can dramatically prolong the lifetime of CMOS transistors by factors of 10 to 50.@footnote 5@ Recent low temperature STM desorption experiments@footnote 6@ have shed additional light on the CMOS degradation problem and the giant isotope effect. @FootnoteText@ @footnote 1@J.W. Lyding, T.-C. Shen, J.S. Hubacek, J.R. Tucker, and G.C. Abeln, Appl. Phys. Lett. 64, 2010 (1994). @footnote 2@J.W. Lyding, T.-C. Shen, G.C. Abeln, C. Wang, E.T. Foley, and J.R. Tucker, Mat. Res. Soc. Symp. Proc. 380, 187 (1995). @footnote 3@G. C. Abeln, S. Y. Lee, J. W. Lyding, D. S. Thompson, and J. S. Moore, Appl. Phys. Lett. 70, 2747 (1997). @footnote 4@Ph. Avouris, R.E. Walkup, A.R. Rossi, T.-C. Shen, G.C. Abeln, J.R. Tucker, and J.W. Lyding, Chem. Phys. Lett. 257, 148 (1996). @footnote 5@J.W. Lyding, K. Hess, and I.C. Kizilyalli, Appl. Phys. Lett. 68, 2526 (1996). @footnote 6@E. T. Foley, A. F. Kam, J. W. Lyding, and Ph. Avouris, Phys. Rev. Lett. 80, 1336 (1998).

4:40pm **EM2-WeA9 Scanning Probe Microscopy Imaging of IC Cross Sections***, **K.-J. Chao**, R.J. Plano, J.R. Kingsley, X. Lu, I. Ward,* Charles Evans & Associates

Various Scanning Probe Microscopy (SPM) techniques have been applied to investigate the cross sections of modern integrated circuit (IC) devices. The IC devices were prepared by polishing using common Scanning Electron Microscope (SEM) sample preparation methods. Some of the samples were further etched to delineate the various oxides. Atomic force microscope (AFM) was used to simultaneously acquire both topography and phase images of these surfaces. The topography images reveal height information about the sample while the phase images are sensitive to material differences and show edges clearly. Different metal layers and device structures are clearly resolved. To verify the results, these samples were coated with a thin layer of metal and then imaged with an SEM. AFM and SEM results show a close agreement, with the AFM topography image having additional height information and the phase image showing sharper detail than the SEM images. Also, the doping regions of IC devices were investigated by the scanning capacitance microscope (SCM) and low voltage SEM. A detail comparison will be presented.

5:00pm **EM2-WeA10 Silicon Nitride Islands as Oxidation Masks for the Formation of Silicon Nano-Pillars***, **J.S. Ha**, K.-H. Park, W.S. Yun, E.-H. Lee,* ETRI, Republic of Korea

We have used nanometer-scale silicon nitride islands as oxidation masks for the formation of silicon nano-pillars. For the growth of silicon nitride islands on Si(111)-7x7 surface, two different methods were used; N @sub 2@ exposure at temperatures between 700 and 800 ° C and 100 eV N @sub 2@ @super +@ ion exposure at room temperature followed by subsequent post-annealing at 980 ° C. Scanning tunneling microscope (STM) images taken from the two differently prepared surfaces showed a submonolayer coverage of nanometer-sized silicon nitride islands. On these surfaces, O @sub 2@ was exposed at high temperatures where silicon etching was dominant over oxide formation. It was found that N @sub 2@ @super +@ ion induced silicon nitride islands work as successful oxidation masks to form silicon nano-pillars as high as several nanometers via selective oxygen etching of silicon. On the other hand, oxygen exposure to the silicon surface covered with N @sub 2@ - induced silicon nitride islands resulted in the increase of lateral size and density of pillars, compared to the initially formed islands. Such difference can be explained in terms of the segregation of extra nitrogen species which had migrated into subsurface region when N @sub 2@ had been exposed at high temperatures. Optimum conditions for the formation of silicon nano-pillars could be obtained by controlling the nitridation temperature, annealing time, and oxidation temperature. In this paper, we will propose a successful way to form silicon nano-structures using silicon nitride islands and also discuss underlying mechanisms of the island growth.

Magnetic Interfaces and Nanostructures Technical Group Room 324/325 - Session MI+NS-WeA

Nanoscale Magnetics: Imaging and Fabrication

Moderator: S. Foss, Seagate Technology

2:00pm **MI+NS-WeA1 Using the Magnetic Force Microscope as a Quantitative Micromagnetic Probe***, **R. Proksch**,* Digital Instruments **INVITED**

The Magnetic Force Microscope (MFM) has developed into a popular tool for nanometer scale resolution imaging of a wide variety of magnetic samples. The routine <50nm spatial resolution rivals and sometimes exceeds electron based microscopies while not requiring operation in a vacuum or special sample preparation. Since the MFM is sensitive to the external magnetic field gradients of a sample, however, it does not directly yield quantitative values of either the external field or a sample's magnetization. A recent advance@footnote 1@ has allowed quantitative imaging of the localized field from a sample. It based on a magnetically soft tip that acts as a fluxgate sensor. An external field is applied to the MFM tip and sample until the response of the MFM is zeroed. This zeroing occurs when the external field cancels the local field at the MFM tip. The resulting quantitative images have the same spatial resolution of the MFM. Another recent development in MFM was the realization that the energy dissipated by an oscillating cantilever was quantifiable.@footnote 2,3@ Measurements of the energy dissipated by the MFM tip have been quantitatively compared to micromagnetic models.@footnote 4@ Measurements of other fundamental quantities such as the moment of a single magnetic particle and nucleation volumes in relaxing domain structures through dissipation observations will be presented. @FootnoteText@ @footnote 1@R. Proksch, G. Skidmore et al., Appl. Phys. Lett. 69, 2599 (1996). @footnote 2@P. Grutter, Y. Liu, P. LeBlanc, and U. Durig, Appl. Phys. Lett. 71, 279 (1997). @footnote 3@J. P. Cleveland et al., Appl. Phys. Lett. in press (1998). @footnote 4@Y. Liu, B. Ellman and P. Grutter, Appl. Phys. Lett. 71, 1418 (1997).

2:40pm **MI+NS-WeA3 Imaging Current Flow in Polycrystalline Bi2Sr2CaCu2Ox Superconductors by Magnetic Force Microscopy***, **F. Král**, D. Perednis,* ETH Zürich, Switzerland*; D.A. Bonnell,* The University of Pennsylvania, US*; G. Kostorz, L.J. Gauckler,* ETH Zürich, Switzerland

The measurement of magnetic fields induced by current flow can be used to visualize current transport paths in complex microstructures. Magnitudes of fields induced by currents typical of metallic conductors and of superconductors are within the range accessible by magnetic force microscopy. Finite element calculations indicate that conducting grains separated by as little as a hundred nm will be distinguished. The fields emanating from current in the complex textured microstructure of a Bi2Sr2CaCu2Ox based thick film in the superconducting state at temperatures below 60 K were clearly delineated. Magnetic field variations with the size and orientation of the textured grains that carry current were quantified. Obstructions to current flow are imaged.These measurements were accomplished on a commercial instrument modified to connect to a He cryostat and operate in medium vacuum.

3:00pm **MI+NS-WeA4 Imaging Magnetic Domains by Spin-Polarized Scanning Tunneling Spectroscopy***, **M. Bode**, M. Getzlaff, R. Wiesendanger,* University of Hamburg, Germany

The concept of spin-polarized scanning tunneling spectroscopy (SP-STS) promises the unique capability of magnetic imaging with a resolution down to atomic scales. We will show that the (0001)-surface of Gadolinium, which has a bulk Curie-temperature T@sub C@ = 293K, is ideally suited for the realization of SP-STS since Gd(0001) exhibits a d@sub z@@super 2@-like surface state. This surface state is exchange split in an occupied majority (spin-up) and an empty minority (spin-down) spin-part below T@sub C@. Already in a previous publication we have shown that both spin-parts appear as a double-peak structure in the tunneling spectra.@footnote 1@ Here we report on our experiments with magnetic thin film probe tips. In accordance with the spin-valve effect@footnote 2@ we found characteristic variations in the tunneling spectra which correlate with the direction of the external field, i.e. the differential conductivity of the particular spin-part of the surface state being parallel with the tip is enhanced on the expense of the counterpart being antiparallel. This allows the imaging of magnetic domains with the STM. The resolution obtained so far is approximately 20nm. The measured spin-asymmetry of approximately 40% (20%) at the majority (minority) part of the surface state is in good agreement with former spin-resolved (inverse) photoemission experiments. We will show that the application of thick Fe-coatings on the tip leads to a sudden contrast reversal probably caused by a switching of sample domains due to the strong magnetic interaction between tip and sample. @FootnoteText@ @footnote 1@R. Pascal, Ch. Zarnitz, M. Bode, M. Bode, and R. Wiesendanger, Appl Phys A 65, 603 (1997). @footnote 2@M. Julliere, Phys. Lett. A 54, 225 (1975).

3:20pm **MI+NS-WeA5 Imaging Magnetization in Fe and Layered Fe/Co Films Using an Element-Specific Scanning Transmission X-Ray Microscope***, **J.B. Kortright**, S.-K. Kim, T. Warwick, G. Meigs,* Lawrence Berkeley National Laboratory

Magnetization distributions in demagnetized polycrystalline Fe films and in the individual Fe and Co layers of layered films were imaged with a scanning transmission x-ray microscope and circular polarizing filters using the strong magnetic circular dichroism at the Fe and Co 2p3/2 levels. Transmission images were obtained at roughly 200 nm resolution with high contrast that was reversed by reversing the saturated magnetization in the polarizing filters. Large, regular 180 degree domains dominate Fe films 20-30 nm thick. Smaller magnetization features (swirls, ripples, etc.) are observed at grain boundaries and near the tip of needle-shaped domains growing into or being consumed by larger domains. In layered films consisting of Fe and Co layers separated by a 2 nm SiC spacer the magnetization in each layer is entirely different from the single Fe film, revealing significant interaction between the two different layers in the demagnetizing process. Large 180 degree domains are absent, and are replaced by much smaller, more irregular magnetization distributions having characteristic dimensions of several microns and somewhat resembling stripe domains. The domains in the Fe and Co layers show some degree of spatial correlation, and some degree of antiferromagnetic alignment. These first imaging studies using a scanning transmission x-ray microscope in conjunction with a high resolution grating monochromator complement other recently demonstrated imaging techniques using x-rays, and point to new opportunities to quantitatively study magnetization distributions in a variety of samples. Technical aspects underlying these new capabilities will be reviewed. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

3:40pm **MI+NS-WeA6 Substrate and Growth Related Nanostructural and Magnetic Properties in La@sub 0.67@SR@sub 0.33@MnO@sub 3@ Thin Films***, **M.E. Hawley**, G.W. Brown, C. Kwon, Q.X. Jia,* Los Alamos National Laboratory

Beyond achieving a target chemical composition, optimization of metal oxide thin film properties depends on a number of growth-determined factors: microstructure, defects, and stress. For CMR materials, these factors can lead to low Curie temperature, non-ideal temperature-dependent magnetization, undesirable domain structures, higher coercivity, and magnetic anisotropy. In particular, growth of these materials, which possess fairly large positive magnetostrictive constants, on lattice-mismatched substrates can result in residual stress-induced maze-like domains. This type of domain was observed by magnetic force microscopy (MFM) for some La@sub 0.67@Sr@sub 0.33@MnO@sub 3@ films grown on LaAlO@sub 3@ (compressive mismatch) and tied to substrate-induced stress and film thickness. Stress-induced elongation of the out-of-plane lattice parameter may be necessary but is not sufficient to produce these domains. Their existence has also not been correlated with processing parameters. To address some of these issues, we have grown films over a range of temperatures by pulsed-laser deposition on LaAlO@sub 3@ and SrTiO@sub 3@ (tensile mismatch) to determine the correspondence of lattice-induced strain and degree of granularity to magnetic properties. Nanostructure characterization (STM, AFM, and MFM) magnetization, and coercivity will be presented to show the relationship between growth and properties. Maze-like domain structures, with 150 to 200 nm separations, were observed for thicker films grown at 800@degree@C on LaAlO@sub 3@ versus weak diffuse domains for thin films and all films grown on SrTiO@sub 3@. Application of an increasing in-plane external magnetic field converted the maze-domains first into stripe domains with decreased spacing (with reduced out-of-plane magnetization) and then into diffuse in-plane structures. Field orientation versus magnetic structures will be included.

4:00pm **MI+NS-WeA7 Monodisperse Cobalt Nanocrystals and Their Assembly into Nanocrystal Superlattices: Building with Magnetic Artificial Atoms***, **C.B. Murray**, S. Sun,* IBM T.J. Watson Research Center **INVITED**

We present chemical methods which yield cobalt nanocrystals uniform in size to + or - one lattice constant while simultaneously controlling crystal shape, structure and surface passivation. We use high temperature (200 - 300° C solution phase synthesis and size selective processing to produce organically passivated nanocrystals with size distributions less than 5%. These monodisperse transition metal nanocrystals self-organize during controlled evaporation to produce three dimensional superlattices (colloidal crystals, opals). The cobalt nanocrystals resemble "artificial atoms" sitting on regular close-packed superlattice sites, each separated by a selected organic spacer. The superlattices retain and enhance many of the desirable mesoscopic properties of individual cobalt nanocrystals and provide a model system for studies the electronic coupling of neighboring particles. The inter-particle spacing can be varied from intimate contact up to 40 Å separation. Superlattices can be prepared as either faceted colloidal crystals or as ordered nanocrystal thin films on a variety of optically and electronic addressable substrates (sapphire, silicon, etc.). Structural and magentic investigations of both dispersed and assembled nanocrystal systems will be presented.

4:40pm **MI+NS-WeA9 Fabrication and Characterisation of Micron Scale Magnetic Features***, **C.N. Borca**, P.A. Dowben,* University of Nebraska, Lincoln

Different methods can be adopted to fabricate patterned thin films with features spatially restricted in the micron-scale regime. We are studying ferromagnetic films of cobalt and cobalt - palladium heterostructures fabricated by selective area deposition from organometalic compounds. We have developed this one-step deposition technique sufficiently to deposit pure metal features with excellent spatial resolution and in multilayer geometries. From the comparison between the continuous and patterned films we can conclude that the patterning of the films into arrays of discrete micron-scale features has a greater influence on the magnetic properties of the films than changes microstructure and film growth. We propose that this organometallic chemical vapor deposition (CVD) method represent a new approach for novel devices fabrication.

5:00pm **MI+NS-WeA10 Domain Behavior in Magnetic Nanostructures as Revealed by MOIF Observations***, **R.D. Shull**, A.J. Shapiro,* National Institute of Standards and Technology*; V.I. Nikitenko, V.S. Gornakov,* Institute of Solid State Physics RAS, Russia

A magneto-optical indicator film (MOIF) technique has been used for imaging magnetic domains and applied to magnetic nanostructures, including granular metals, magnetic multilayers, and antiferromagnet (AF)/ferromagnet (FM) bilayers. In this technique, the sample domains are imaged by their effect on a garnet film with in-plane magnetization located immediately above the sample. In addition to static domain structures, dynamic information has been obtained by monitoring the domain pattern evolution upon the application of an external magnetic field. Fractal type domain walls were observed in Co/Ag granular metals with a two-step remagnetization process, non-homogeneous nucleation processes were observed in AF/FM bilayers with remagnetization behavior dependent upon field direction, and non-collinear spin configurations were detected in Cu/Co multilayers (electrodeposited on Si substrates) displaying giant magnetoresistance (GMR) effects during the remagnetization process. In these latter samples, the GMR magnitude was correlated with the spin reorientation mechanism. In all samples the effects of crystal lattice defects on the remagnetization process was documented, and found to be significant. The MOIF technique was also found to be capable of detecting not only the domain structure of the surface layer, but also that of subsurface layers in a multilayer morphology. In this presentation, a review of the domain statics and dynamics which have been observed in a variety of nanostructured material types will be discussed. Particular attention will be given to the origin of enhanced coercivity in a bilayer system with unidirectional anisotropy.

Manufacturing Science and Technology Group
Room 317 - Session MS-WeA

Process Control and Yield from Tool to Factory

Moderator: S. Shankar, Intel Corporation

2:00pm **MS-WeA1 Factory Implementation of Process Control: Technical or Cultural Challenge?***, **K.G. Vickers,*** Texas Instruments **INVITED**

The use of systematic, company wide process control techniques in integrated circuit manufacturing factories (known as wafer fabs) have been low since the inception of the industry in the 1960s. Reasons for this low implementation of process control methods have included both technical and cultural barriers to implementation. The technical barriers that have hampered process control implementation in wafer fabs originated from both the unique nature of IC fabrication processing and the rapidly changing equipment sets needed to build ever advanced technology node integrated circuits. These technical barriers included the simultaneous continuous flow and discrete event nature of most processes, the high number of equipment types/processes in an IC product flow, the significant changes in required process output from run to run, and the lack of computing power to handle a large diversified data stream. In recent years these technical barriers been reduced to the point that the size of the cultural barriers have become obvious as the major obstacle to successful systematic implementation. These cultural barriers originated in early wafer fabs whose technical population was strongly focused on device characteristics rather than process stability, whose reward and recognition system was based on local problem solutions rather than systematic solutions, and whose manufacturing methods were created locally rather than through company wide standardization. Over the last fifteen years Texas Instruments has achieved some success in overcoming first the technical barriers and then the cultural barriers for systematic implementation of advanced process control techniques in all TI world wide wafer fabs. This presentation will highlight the necessary technical changes that were put in place, and a key set of cultural changes that were implemented, to gain the benefits of systematic process control in a world wide manufacturing environment.

2:40pm **MS-WeA3 Advanced Process Control and Sensor Requirements for Reducing Non-Product Wafer Usage and to Increase Tool OEE in 300mm Manufacturing*, M.L. Passow*,** *J. Pace,* IBM Corporation **INVITED**

To maintain productivity in leading edge manufacturing, shrinking feature sizes and increases in equipment productivity are necessary. The shift from 200mm diameter wafers to 300mm diameter wafers is required, but not sufficient. Improvements in equipment OEE and reductions in the usage of non-product (NP) wafers and SAHD wafers must be made as the cost of using conventional methods of control in new, fully automated 300mm fabs is too high. Based on learning gained by understanding NP wafer usage in 200mm development and manufacturing lines, areas with the highest potential benefit from various reduction strategies will be identified. Process tool suppliers will be requested to incorporate Advanced Process Control (APC) strategies where possible. Adherence to standards will be required to facilitate the adaptation of new sensor, APC, data collection, and line management strategies to meet these needs. Particular recommendations will be presented.

3:20pm **MS-WeA5 Process Module Control Technology for 300mm Plasma Processing*, F. Kaveh*,** *B. McMillin, W. Collison,* Lam Research Corporation **INVITED**

In order to meet the challenge posed by the processing of the 300mm wafers, and the move toward sub quarter micron feature sizes, a new hybrid etch tool control architecture has been devised. This new architecture, based on TI's ControlWORKS environment, has enabled close coupling of a number of feedback loops for control of equipment level parameters, as well as control of stand alone remote sub-systems. Through the use of VME based direct I/O, for fast loops, and LonWorks network for less time critical loops, effective partitioning and optimization of the control functions has been achieved . Through the digitization and integration of a number of the process control loops such as the match and pressure controllers, measurable improvements in the overall operation of the tool has been realized. Further, a structure has been put in place that allows further integration of the aforementioned loops, and implementation of outer loops, for plasma state control applications. The new architecture is highly flexible, and as such, has enabled the integration of various sensors, such as an optical emission spectrometer, and a low cost RGA. These sensors are being used for detailed characterization of the chamber and the plasma, and are expected to result in significant gains in tool productivity and performance.

4:00pm **MS-WeA7 Using Wafermap Data for Automated Yield Analysis@footnote 1@*, K.W. Tobin*,** *T.P. Karnowski, S.S. Gleason,* Oak Ridge National Laboratory*; D. Jensen, F. Lakhani, C. Long,* SEMATECH **INVITED**

To be productive and profitable in a modern semiconductor fabrication environment, it is required that large amounts of manufacturing data be collected and maintained. This includes data collected from in-line and off-line wafer inspection systems and from the process equipment itself. This data is increasingly being relied upon to design new processes, control and maintain tools, and to provide the information needed for rapid yield learning and prediction. Because of increasing device complexity, the amount of data being generated is outstripping the yield engineer's ability to effectively monitor and correct unexpected trends and excursions. The 1997 SIA National Technology Roadmap for Semiconductors highlights a need to address these issues through "automated data reduction algorithms to source defects from multiple data sources and to reduce defect sourcing time." In this paper, we will discuss the current state of yield management automation and the role that SEMATECH and the Oak Ridge National Laboratory@footnote 2@ are taking in directing and developing new technologies that will provide the yield engineer with higher levels of automated data reduction and analysis. Yield management systems have been evolving over the past decade from a primary role of database storage and retrieval to systems that provide timely insight into the current state of manufacturing. The evolutionary process can be described in terms of five fundamental steps: (1) infrastructure and database management; (2) processes that add context to the data, i.e., that add information; (3) the use of data and context to find patterns, i.e., extract information; (4) methods of interpreting patterns, i.e., extracting knowledge; (5) and the automated application of process knowledge to yield management. In this paper we will focus on step (2), technologies which add context to data. In particular, we will discuss ORNL's contributions to the fields of automatic defect classification (ADC) and whole-wafer spatial signature analysis (SSA) for optical and electrical test data. We will also discuss preliminary results in the field of manufacturing-specific, content-based image retrieval (MSCBIR). MSCBIR is an image-based datamining technology that allows engineers to search a large image repository using an image of a semiconductor defect event as a query to locate other images that are similar in appearance. This exciting new technology is valuable due to the highly image-oriented approach taken by the yield engineer in problem solving, and the vast quantities of images stored in yield-management databases (approximately 70% of the total data). The ability to automatically extract content from raw manufacturing data will be a key factor for automating the discovery of knowledge in the dynamic semiconductor manufacturing environment. The current state of the art in yield management is only now beginning to comprehend these capabilities. Potential future applications of this knowledge in areas such as auto-sourcing statistical process control, condition-based maintenance of process tools, and yield prediction will also be briefly presented. @FootnoteText@ @footnote 1@K.W.T. (Correspondence): E-mail tobinkwjr@ornl.gov; WWW: http://www-ismv.ic.ornl.gov; Telephone: (423) 574-8521; Fax: (423) 574-6663. @footnote 2@Work Performed for SEMATECH, Austin Texas, under Contract No. ERD-95-1340 and prepared by OAK RIDGE NATIONAL LABORATORY, Oak Ridge, Tennessee, 37831-6285, managed by LOCKHEED MARTIN ENERGY RESARCH CORP. for the U.S. DEPARTMENT OF ENERGY under contract DE-AC05-96OR22464. @footnote 3@ K.W. Tobin, S.S. Gleason, F. Lakhani, and M.H. Bennett, "Automated Analysis for Rapid Defect Sourcing and Yield Learning", Future Fab International, Issue 4, Vol. 1, Technology Publishing Ltd., London 1997, p. 313.

4:40pm **MS-WeA9 Visual Data Mining of Defectivity Data using Parallel Coordinates*, A. Chatterjee*,** IBM Research **INVITED**

Defectivity data from a 4MB DRAM manufacturing process was analyzed using a visual data mining methodology based on Parallel Coordinates. Parallel Coordinates provides an interactive framework for analyzing multi-variate data graphically using 2-D graphs that can be colored using visual queries. These graphs provide a unique mapping of multivariate data to 2-D without any loss of information. Using this methodology, some defects were found that were actually "beneficial" and in small quantities improved the yield and speed performance (access time) of the wafer. While using conventional methods, the yield on the wafers couldn't be improved beyond a plateau and hence had led the engineers to think of redisgning the chip, the process window discovered using the Parallel Coordinate methodology provided some insights that helped in improving the yield of the process significantly. This technique is extremely useful in yield analysis and improvement, process control and design of experiments.

Plasma Science and Technology Division
Room 318/319/320 - Session PS-WeA

Plasma-Surface Interactions I

Moderator: V.M. Donnelly, Bell Laboratories, Lucent Technologies

2:00pm **PS-WeA1 Surface Reactions and Hydrogen Coverage on Plasma Deposited Hydrogenated Amorphous Silicon and Nanocrystalline Silicon Surfaces*, D.C. Marra*[1]**, *S. Ramalingam, E. Edelberg, D. Maroudas, E.S. Aydil,* University of California, Santa Barbara

In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to study the H bonding on surfaces of amorphous hydrogenated silicon (a-Si:H) and nanocrystalline (nc-Si:H) films during plasma enhanced chemical vapor deposition (PECVD) from SiH@sub 4@/H@sub 2@/Ar containing discharges. During the deposition of a-Si:H films using SiH@sub 4@ without H@sub 2@ dilution, the surface coverage was primarily di- and trihydrides, and there were very few dangling bonds on the surface. In contrast, during the deposition of nc-Si:H using SiH@sub 4@ diluted with H@sub 2@, the amount of di- and trihydrides on the surface was drastically reduced and monohydrides dominated the surface. Furthermore, the vibrational frequencies of the monohydrides on nc-Si:H film match well with the resonant frequencies of monohydrides on H-terminated Si(111) and Si(001) surfaces. The decrease of higher hydrides upon H@sub 2@ dilution is attributed to an enhanced dissociation rate of

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

tri- and di-hydrides on the surface through dangling bonds created by increased rate of H abstraction from the surface. The mechanism of hydrogen loss from the surface is thought to be abstraction by H and/or SiH@sub 3@ radicals. Simultaneously with the experiments, we have been using molecular dynamics (MD) simulations of radical-surface interactions occurring during PECVD of Si films. The MD simulations aim at the direct examination of chemical reactions, such as H abstraction by SiH@sub 3@ and by H as suggested by the analysis of the ATR-FTIR experiments. For example, using the MD simulations of deposition through SiH@sub 3@ impingement on the surface, we have observed that the dominant mechanism of H removal from the surface is through abstraction by SiH@sub 3@ radicals, which return subsequently to the gas phase in the form of silane. Atomistic simulation results will be presented together with experimental evidence for reactions that are thought to play key roles in plasma deposition of Si films.

2:20pm **PS-WeA2 Gas Phase and Surface Kinetics in Plasma Enhanced Deposition of Silicon Nitride: Effect of Gas Dilution on Electron Energy Distribution, Radical Generation, and Film Composition***, **T.M. Klein**, C.S. Yang, A.I. Chowdhury, G.N. Parsons,* North Carolina State University

Gas diluents, including N@sub@2, He, H@sub 2@, Ar, etc., are often used in silicon nitride plasma CVD to improve film density and electronic properties. We have formed silicon nitride films by parallel plate rf PECVD using SiH@sub 4@/NH@sub 3@ and SiH@sub 4@/N@sub 2@ source gases, and studied the effects of H@sub 2@, He, and N@sub 2@ dilution with substrate temperatures between 350 and 25°C. The plasma was characterized using optical emission and mass spectroscopy, and the thin films were characterized using infrared transmission, IV and CV measurements. We find that dilution can control the Si-H and N-H bond concentrations, and can improve the electrical performance in silicon nitride formed at very low temperature (35 at. %) at low temperature, resulting in high etch rates. Using SiH@sub 4@ and N@sub 2@ source gases, N/Si ratios > 1.3 can be achieved with hydrogen content < 20 at.%. However, optimized N/Si in the film is not obtained by simply increasing N@sub 2@ in the gas phase. At 12W and 250°C, increasing the N@sub 2@ gas fraction from 16% to 37%, leads to a decrease the N/Si in the film from 1.37 to 1.27. Using mass spectroscopy, the silane consumption fraction is greater than 90%, and significant change in silicon incorporation is not expected with N@sub 2@ dilution. We have modeled the effect of N@sub 2@ dilution on the electron energy distribution in the plasma using available software to solve the Boltzmann equation, and developed a simple gas kinetic model to estimate relative N and SiH@sub x@ radical concentrations. The model shows the high energy (>10eV) electron density decreases with N@sub 2@ dilution, consistent with the experiments. The model can predict the effects of gas residence time and He and N@sub 2@ dilution during nitride deposition from SiH@sub 4@/NH@sub 3@ mixtures. These results demonstrate a detailed understanding of gas dilution effects in plasma deposition, and indicate that optimized material properties can be predicted from detailed gas reaction analysis.

2:40pm **PS-WeA3 Atomistic Simulation of Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon Films***, **S. Ramalingam**, D. Maroudas, E.S. Aydil,* University of California, Santa Barbara

Hydrogenated amorphous Si (a-Si:H) and microcrystalline Si grown by plasma deposition through SiH@sub 4@ containing discharges are widely used in solar cells and thin film transistors for flat panel displays. Developing deposition strategies for improving film quality requires a better fundamental understanding of the radical-surface interaction mechanisms. Atomic-scale computer simulations of the deposition process allow monitoring of the events that occur on the surface on a microscopic scale and help elucidate reaction mechanisms that lead to film deposition, defect formation and H incorporation. We present a systematic atomic scale analysis of the interactions of SiH@sub x@ (1@<=@x@<=@) radicals with pristine and H-terminated Si(001)-(2x1) surfaces as well as a-Si:H surfaces with varying H coverage. Hydrogen coverage of the surface is the key factor that controls both the surface reaction mechanism and the reaction probability. The radicals are most reactive when they impinge on pristine c-Si surfaces or surfaces of a-Si:H films with low H concentration, which have high density of Si dangling bonds. In contrast, they are less reactive on H-terminated c-Si and on a-Si:H films with high H coverage. Deposition of a-Si:H from SiH@sub 3@ radicals has also been simulated by repeatedly impinging SiH@sub 3@ radicals onto Si (001)-(2x1) surfaces. The key reactions that occur on the surface during the deposition can be grouped into three classes: (i) SiH@sub 3@ adsorption, (ii) H abstraction, and (iii) disilane formation. We have observed that the dominant mechanism of H removal from the surface is through abstraction by SiH@sub 3@ radicals, which return subsequently to the gas phase in the form of silane and leave behind a dangling bond. The dangling bond created upon H abstraction becomes an adsorption site for the SiH@sub 3@ radicals impinging at this location and the film grows by repeated abstraction and adsorption events which bring Si to surface and remove H.

3:00pm **PS-WeA4 The Ion-assisted Etching and Profile Development of Silicon in Molecular and Atomic Chlorine: Experiment, Modeling, and Simulation***, **J.A. Levinson**, E.S.G. Shaqfeh,* Stanford University*; M. Balooch, A.V. Hamza,* Lawrence Livermore National Laboratory

We report on 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. 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. 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 lag as caused by neutral starvation and/or atomic to molecular chlorine recombination. 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. The dependence of the yield on the ion angle of incidence was also incorporated into the simulation and was found to have a significant impact on profile evolution as a function of the ion to neutral flux ratio. 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.

3:20pm **PS-WeA5 The Role of Etching Products on the Chemical Composition and Thickness of the Chlorinated Surface Layer That Forms During Etching of Silicon in a Chlorine Plasma***, **K.H.A. Bogart**, V.M. Donnelly,* Bell Laboratories, Lucent Technologies

The influence of etching products on the surface layer formed during chlorine (Cl@sub 2@) plasma etching of unmasked and silicon dioxide (SiO@sub 2@) masked p-type Si (100) was investigated using vacuum-sample-transfer and angle-resolved x-ray photoelectron spectroscopy (XPS). The etch product concentration was controlled by varying the Cl@sub 2@ flow rate from 0.5 to 10.0 sccm at constant pressure. Gas phase Si, Cl, Cl@sub 2@, SiCl, SiCl@sub 2@, and SiCl@sub 3@ were monitored by optical emission spectroscopy (OES). The Si etching rate increased linearly with Cl@sub 2@ flow from 1917 Å/min at 0.5 sccm to 2848 Å/min at 10 sccm. From these rates, mass balance, and the Si area (4.62 cm@super 2@), the product-to-etchant ratio, defined as SiCl@sub x@(g)/(Cl(g) + Cl@sub 2@(g)) varied from 3.64 to 0.027 between 0.5 and 10.0 sccm, respectively, and was qualitatively confirmed by OES. On unmasked substrates, Cl was present as SiCl@sub x@ (x = 1-3) at XPS Si2p@sub 3/2@ binding energies of 99.9, 101.0, and 102.0 eV, respectively, relative to Si at 99.1 eV. Surprisingly, the amounts of the three components and the total Cl (also derived from its 2p peak) were nearly independent of the product-to-etchant flux ratio. Depth profiles were obtained from an inversion of the observed take-off angle dependencies of the XPS signals. The chlorinated layer was approximately 20 Å thick, with Cl falling off in a graded fashion. The Cl areal density was 2.5 x 10@super 15@ Cl/cm@super 2@ and the average stoichiometry was [SiCl]:[SiCl@sub 2@]:[SiCl@sub 3@] = 1.0:0.25:0.20. SiCl@sub 2@ and SiCl@sub 3@ were in the top 75% of the layer, while SiCl was throughout the layer. On SiO@sub 2@ masked samples, less SiCl@sub x@ was found on exposed Si sidewalls, as well as on trench bottoms, than on unmasked samples. SiCl@sub x@ coverage in the features was also independent of the product-to-etchant flux ratio, suggesting that redeposition of SiCl@sub x@ plays no role in etched profile evolution.

3:40pm **PS-WeA6 Reactive Ion Etching of Si by Cl, Cl@sub 2@, and Ar Ions: Molecular Dynamics Simulations with Comparisons to Experiment***, **D.E. Hanson**, J.D. Kress, A.F. Voter,* Los Alamos National Laboratory

We will present results of molecular dynamics simulations of reactive ion etching (RIE) of a reconstructed Si(100)(2x1) surface. The existing Stillinger-Weber Si/Cl interatomic potential has been modified by correcting the Si-Si bond strength for a SiClx moiety bound to a Si surface as a function of the number of Cl atoms, x. This potential has been used to study RIE of Si by Cl, Cl@sub 2@ and Ar ions to characterize the Si yield, product stoichiometry, and the stoichiometry of the chlorosilyl surface layer as a function of ion energy and species. Such results, suitably parameterized, can be used as fundamental input to device feature scale topography simulations. We have also simulated the dissociative chemisorption of Cl@sub 2@ on Si(100)(2x1) and find that it is in reasonable agreement with experiment. We will discuss an important area of disagreement between theory and experiment, the effect of neutral to ion ratio on the Si yield. Where possible, we will present comparisons of our results with experiment. @FootnoteText@ Work partially supported by Cooperative Research and Development Agreement between the US Department of Energy and the Semiconductor Research Corporation.

4:00pm **PS-WeA7 Investigation of Si-poly Etch Process for 0.1 µm Gate Patterning and Beyond***, **L. Vallier,*** France Telecom-CNET, France*; L. Desvoivres, M. Bonvalot,* France Telecom-CNET*; O. Joubert,* France Telecom-CNET, France*; S. Tedesco, B. Dal'Zotto,* CEA-LETI, France

The etching of dense and isolated 0.1µm gate structures has been studied in a high density plasma helicon source capable of processing 200 mm diameter wafers. The gate stack consists of 150 nm thick amorphous silicon film on a 2 nm thick gate oxide, covered with 50 nm thick SiO@sub 2@ patterns obtained using e-beam direct writing. HBr/O@sub 2@ gas chemistry is used for the etching; a 2 steps etching recipe using 2 RF bias regimes was developped in order to obtain anisotropic etching profiles without any etching anomalie(trenching, bowing, notching) while keeping a high selectivity on the very thin gate oxide. Real time ellipsometry was used either to measure etching rates or to monitor the arrival on the thin gate oxide. XPS analysis of the etched wafer is performed in an ultra high vacuum chamber after transfer under vacuum ; XPS data were obtained on dedicated structures with different aspect ratio allowing the gate oxide comsumption as well as sidewall passivation thickness to be precisely measured in dense areas. Attempts to measure CD variation due to the etch process and profiles anomalies related to the etching parameters will also be presented. @FootnoteText@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

4:20pm **PS-WeA8 Mechansims in High Aspect Ratio Oxide Feature Etching using Inductively Coupled Fluorocarbon Plasmas***, **M. Schaepkens,** G.S. Oehrlein,* State University of New York, Albany*; K.G. Donohoe,* Micron Technology, Inc.*; J.M. Cook,* Lam Research Corporation

Mechanisms controlling SiO@sub 2@ etching in high aspect ratio features have been studied using an inductively coupled plasma (ICP) source fed with trifluoromethane (CHF@sub 3@) gas. The behavior of the transition from fluorocarbon deposition to SiO@sub 2@ etching with increasing self-bias voltage has been determined in features with aspect ratios ranging from 0.8 to 6. Both the fluorocarbon deposition rate on the feature bottom at 0 W bias and the SiO@sub 2@ etching rate at highly negative self-bias voltages decrease with increasing aspect ratio. The SiO@sub 2@ etch rate reduction can be explained by a differential charging mechanism, for which experimental evidence is provided. Surface chemistry results obtained in microstructures are compared with unpatterned surfaces, and their significance for the etching process is discussed.

4:40pm **PS-WeA9 Surface Reactivity of CF and CF@sub 2@ Radicals Measured Using Laser-Induced Fluorescence and CHF@sub 3@ Plasma Molecular Beams***, **N.E. Capps,** N.M. Mackie, E.R. Fisher,* Colorado State University

Fluorocarbon discharges have been widely studied because of their ability to promote etching of a variety of substrates and to deposit a wide range of fluorinated polymeric films. CF and CF@sub 2@ radicals are important species in fluorocarbon pla smas and are postulated to contribute both to plasma polymerization and to selective etching of Si and SiO@sub 2@. The surface reactivity of CF and CF@sub 2@ radicals during the plasma processing of a variety of substrates using the Imaging of Radicals I nteracting with Surfaces (IRIS) technique is reported. IRIS combines spatially-resolved laser-induced fluorescence with molecular beam and plasma techniques. The molecular beam source is a 100% CHF@sub 3@ plasma, and we have investigated the surface rea ctivity of CF and CF@sub 2@ with silicon. silicon dioxide, silicon nitride, 304 stainless steel, and system 8 photoresist. Surface reactivity measurements were determined under a range of plasma powers, with ambient and heated surfaces, as well as under low and high ion bombardment conditions. On all surfaces we see generation of CF@sub 2@ radicals whereas CF radicals are consumed at the surface under similar plasma conditions. Mechanisms for film formation and for the surface production of CF@sub 2@ will be discussed

5:00pm **PS-WeA10 Optical Monitoring of Surface Adlayers by Laser-induced Thermal Desorption during Plasma Etching of Si and Ge***, J.Y. Choe,* ***I.P. Herman,*** Columbia University*; V.M. Donnelly,* Bell Laboratories, Lucent Technologies

Laser-induced thermal desorption, with detection by laser-induced fluorescence (LD-LIF) and transient plasma-induced emission (LD-PIE), was used to analyze the surface during the chlorine plasma etching of Si and Ge in an inductively-coupled plasma (ICP) source. Quantitative information about the formation and ion-induced removal of this surface layer was obtained from the optical signals. A pulsed XeCl excimer laser (308 nm) was used to desorb the surface layer and (for LIF) to excite the desorbed species. LD-LIF was used to probe SiCl (292.4 nm) and GeCl (289.12 nm) to compare Si and Ge etching. The surface adlayer did not change with ion density for both Si and Ge, but the rate of adlayer chlorination for Ge was much faster (< 0.1 s) than that for Si (~ 5 s), as was indicated by the signal size when the laser repetition rate was varied. The chlorine content of the adlayer did not change with ion energy (16 - 116 eV) during Ge etching, as confirmed by XPS analysis; in contrast, for Si the adlayer became more chlorinated with increasing ion energy. The etch yield for ion sputtering from Ge increased from 1 to 3 atoms/ion from 16 to 116 eV ion energy. LD-PIE was also used to probe SiCl, SiCl@sub 2@, and Si atoms during Si etching. No LD-PIE signal from Cl or Cl@sub 2@ was detected, suggesting that steady-state chlorine desorption is negligible during the plasma etching of Si. LD-LIF and LD-PIE signals during Si etching by Cl@sub 2@ have been compared for various processing conditions. The work at Columbia was supported by NSF grant DMR-94-11504.

Selected Energy Epitaxy Topical Conference
Room 327 - Session SE-WeA

Novel Sources for Selected Energy Growth

Moderator: R.B. Doak, Arizona State University

2:00pm **SE-WeA1 UHV Arcjet Atomic Nitrogen Source: Beam Characterization and GaN Epitaxial Growth***, **F.J. Grunthaner,*** Jet Propulsion Laboratory*; R. Bicknell-Tassiuis,* Jet Propulsion Laboratory, US*; P. Deelman, P.J. Grunthaner,* Jet Propulsion Laboratory*; J. Guilani,* Naval Research Laboratory*; C.E. Bryson,* Surface/Interface, Inc. **INVITED**

2:40pm **SE-WeA3 Flow Characteristics of a UHV Nitrogen Arcjet***, **C.H. Chang,*** Thermosciences Institute, US*; F.J. Grunthaner,* Jet Propulsion Laboratory*; R. Bicknell-Tassiuis,* Jet Propulsion Laboratory, US*; P. Deelman, P.J. Grunthaner,* Jet Propulsion Laboratory*; J.L. Giuliani, J.P. Apruzese, P. Kepple,* Naval Research Laboratory, US

Flow characteristics in the nozzle of a nitrogen arcjet have been simulated by a model. Electrons, ions, and neutral atoms and molecules are represented as separate species. Dissociation, ionization, and recombination are treated as separate reactions. Thermal non-equilibrium is represented by a two-temperature model. Energy input to plasma from the arc is modeled as a source determined by local current and electrical conductivity. Momentum and energy losses and recombinations at the nozzle wall are included as source/sink determined by fluxes to the wall. The results show essentially frozen gas-phase reactions and thermal nonequilibrium due to Joule heating of electrons and in the expansion part of the nozzle. Wall interactions have strong effects on the results, indicating that they play important roles in the flow due to very high surface area relative to the volume of the plasma. For example, plasma velocity decreases from 6000 m/s without wall interactions to 3000 m/s with modest amount of wall interactions. These results also show reasonable agreement with optical emission measurements, which confirms that the arcjet plasma is far from LTE. The spectra suggest nitrogen dissociation levels of 0.3% - 9%, depending on nitrogen flow rate and arc plasma current, which also determine the relative amounts of excited atomic and molecular nitrogen. Langmuir probe studies of the source show that electron and ion fluxes increase with increasing power, and that the ion energy distribution shifts to lower energies. Typical ion fluxes were on the order of 4E-9 A/cm@super 2@ with a maximum ion kinetic energy of 3.5eV. The median electron energy was 1eV, with a maximum of less than 4eV.

3:00pm **SE-WeA4 Gas-Phase Diagnostics for Wide Bandgap Semiconductor Development**, ***D.G. Fletcher***, *G.A. Raiche,* NASA Ames Research Center

Efforts to develop commercially viable wide bandgap semiconductors can be aided considerably by a characterization of the atomic beam. For arcjet devices used for nitride epitaxy, this involves determining the thermochemical state of a partially dissociated nitrogen flow. Since arcjet flows of nitrogen are also used in the development of thermal protection systems for aerospace applications, laser-spectroscopic techniques have been developed for flow characterization, and this has been driven by the need to relate test results to the flight environment. Recently, two-photon laser-induced fluorescence of ground-state atomic nitrogen has been used to determine the degree of dissociation and the enthalpy distribution in a large scale arcjet facility.@footnote 1@ Based on observations from these experiments and the similarities between the arcjet devices used in nitride epitaxy and aerospace materials testing, diagnostic strategies are proposed to establish the link between electronic state populations and nitride material growth. The paper will include a discussion of recent, relevant experimental results for ground state atomic nitrogen, and will report on progress made in developing laser-diagnostic strategies for determining the populations of the two low-lying, metastable doublet states of atomic nitrogen. @FootnoteText@ @footnote 1@D.G. Fletcher "Arcjet Flow Properties Determined from Laser-Induced Fluorescence of Atomic Nitrogen", AIAA Paper No. 98-0205, Reno, NV, January, 1998.

3:20pm **SE-WeA5 Fast Deposition of Amorphous Hydrogenated Silicon and Carbon**, ***D.C. Schram***, *M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands **INVITED**

For solar cell and other developments faster and more efficient deposition of thin layers amorphous hydrogenated materials are necessary. With plasma beam expanding from very efficient thermal plasma sources rates of 10-100 nm/s over a large area has been studied. For a-C:H it proves that the faster the deposition the more dense the material and 100 nm/s has been reached. For a-Si:H good electronic material can be grown with rate of 10 nm/s and elevated substrate temperature (T~350 oC). A picture based on plasma fragmentation processes and surface kinetics will be discussed and illustrated with measurements on mass spectrometry, FTIR and other diagnostics.

4:00pm **SE-WeA7 Inexpensive Corona Discharge Source for the Growth of III-N Semiconductors**, ***D.C. Jordan***, *C.T. Burns, R.B. Doak,* Arizona State University

The III-N nitrides AlN, GaN and InN are under intense study due to their wide bandgap properties. It is thought that the ideal nitrogen species for GaN growth may be the metastable A@super 3@@SIGMA@@super +@@sub u@ state of molecular nitrogen@footnote 1@. We have developed a low cost supersonic free-jet corona discharge source that produces exclusively this nitrogen species. The source consists of a quartz tube drawn to an orifice diameter in the range of 100-250 µm enclosing a tungsten or rhenium wire. A high voltage ranging between 2-2.5 kV at 5-9 mA is applied to that wire, resulting in a readily discernible bright plume at the tip of the nozzle. A custom-made refractory graphite skimmer then extracts a beam of activated species as the free-jet expands into vacuum. The beam transits a differentially pumped section then enters the deposition chamber where controlled growth can take place under molecular beam epitaxy (MBE) conditions. We have performed optical spectroscopy at several different locations downstream of the nozzle for different tip polarity and different argon/nitrogen gas mixtures, characterizing the expansion as it unfolds. Overall nitrogen intensities range from the 5x10@super 17@-2x10@super 18@ molecules/sr/s. Our calculations indicate that an appreciable percentage (ca.10%) of the nitrogen molecules is in the desired metastable A@super 3@@SIGMA@@super +@@sub u@ state. Growth studies of AlN on Si(100) are currently under way. The low cost, the ease of operation and the ability to produce only a single excited species are in stark contrast to the broad spectrum of different species of any other commercially available plasma source, making the corona discharge source attractive for a broad range of future applications. Supported by ONR grant # N00014-95-1-0122 & N00014-96-1-0962 @FootnoteText@ @footnote 1@ R.P.Muller, B.L.Tsai and W.A.Goddard III, SEE-3 Workshop, Tempe 1998

4:20pm **SE-WeA8 Development of Atomic Nitrogen Sources and Atomic Nitridation Processes**, ***O. Gluschenkov***, *K. Kim,* University of Illinois, Urbana-Champaign

With the goal of developing an efficient source of atomic nitrogen suitable for electronic materials processing, we have fabricated novel atomic nitrogen sources and with them conducted an investigation of nitrogen dissociation in a low-pressure nitrogen plasma. Plasma electric field, electron density, and vibrational temperature of nitrogen molecules have been estimated from experimental data obtained with the prototype sources. A simple model has been developed to predict the efficiency of atomic nitrogen production as a function of the source parameters: pressure, geometry, deposited power, and nitrogen throughput. An atomic nitrogen source with 60% of nitrogen atoms at the output has been constructed to study the atomic nitridation processes, the processes where nitridation is effected by atomic nitrogen only. The extremely high chemical potential of atomic nitrogen, small size of nitrogen atoms, and absence of other energetic particles and chemical contaminants lead to a dramatically different chemical kinetics and allow for high-rate, low-temperature, low-pressure, and low-damage processing. The processes investigated include the nitridation of thin SiO@sub 2@ gate dielectric and the growth of Group-III-Nitride crystals.

4:40pm **SE-WeA9 Energetic Oxygen Atom Surface Passivation of Cd@sub 1-x@Zn@sub x@Te Radiation Detectors**, ***M.A. Hoffbauer***, *S. Cook, T. Prettyman, J. Rennie,* Los Alamos National Laboratory*; J.C. Gregory, M.A. George,* University of Alabama, Huntsville

Recent investigations show considerable progress in developing large-volume Cd@sub 1-x@Zn@sub x@Te radiation detectors for room-temperature x-ray and gamma-ray spectroscopy and imaging where bulk material with high resistivity and uniform electrical properties is required.@footnote 1@ Surface effects can also play an important role in the performance of CdZnTe spectrometers, since dark current may be dominated by surface leakage in gridded or pixellated devices.@footnote 2@ A novel surface oxidation process has been developed for the treatment of CdZnTe using a source of energetic oxygen atoms to treat the surface held near ambient temperatures.@footnote 3@ Following the oxidation process the chemical composition and morphology of the surface were investigated using X-ray photoelectron spectroscopy and atomic force microscopy. No detectable unreacted Te substrate XPS feature is observed. The Te-oxide peak indicates that the oxidation process is complete, and that the suspected Te precipitates left on the surface following polishing and etching have been totally reacted to form a uniform Te-oxide layer >10 nm thick. AFM studies show a relatively uniform and smooth surface oxide layer. A significant reduction in surface leakage current and detector noise results in a 25% improvement in detector resolution measured at a gamma-ray energy of 662 keV. This new surface passivation method for high-quality, spectrometer-grade material increases the accuracy and sensitivity of measurements of radionuclides with complex gamma-ray spectra, including special nuclear material. When CdZnTe detectors with small spacing between electrodes become available, surface passivation will be even more critical in determining performance and energy resolution. @FootnoteText@ @footnote 1@K. B. Parnham, "Recent Progress in Cd@sub 1-x@Zn@sub x@Te Radiation Detectors," Nucl. Instr. Meth. Phys. Res., A377, 487(1996). @footnote 2@K.T.Chen, D.T. Shi, B. Granderson, M.A. George, W.E. Collins, A. Burger, and R.B. James, "Study of Oxidized Cadmium Zinc Telluride Surfaces," J. Vac. Sci. & Technol. A15, 850(1997). @footnote 3@M.A. Hoffbauer, J.C. Cross, and V.M. Bermudez, "Growth of Oxide Layers on Gallium Arsenide with a High Kinetic Energy Atomic Oxygen Beam", Appl. Phys. Lett., 2193(1990).

5:00pm **SE-WeA10 The Atmospheric-Pressure Plasma Jet: Properties and Materials Applications**, ***A. Schütze***, University of California, Los Angeles*; J. Park,* Los Alamos National Laboratory*; S.E. Babayan, J.Y. Jeong, V.J. Tu,* University of California, Los Angeles*; G.S. Selwyn,* Los Alamos National Laboratory*; R.F. Hicks,* University of California, Los Angeles

Atmospheric-pressure plasma jets can be used in a wide range of materials applications, including surface cleaning, selective etching and thin-film deposition. The plasma source consists of two closely spaced electrodes through which helium and other gases flow (O@sub 2@, CF@sub 4@, etc.). A variety of electrode configurations can be used, and the source is suitable for large-area processing of materials. Measurements with an impedance probe have shown that this source exhibits a low breakdown voltage at atmospheric pressure, between 50 and 300 V, depending on the gap spacing and gas mixture. The current-voltage characteristics are analogous to a low-pressure DC discharge, in which normal and abnormal glow regions occur. Normal glow is observed between 0.01 and 1.0 A with a corresponding voltage of about 150 V. As an example application, we will discuss the plasma-assisted chemical vapor deposition of silicon dioxide. Film growth rates of 0.3 to 1.0 µm/min are achieved using tetraethoxysilane or silane sources. The growth rate increases linearly with RF power and Si source pressure, but decrease with increasing pressure.

The properties of the SiO@sub 2@ films deposited at 350 °C, as determined by infrared spectroscopy, photoemission spectroscopy and capacitance measurements, are comparable to those of thermally grown SiO@sub 2@ films at 900 °C.

Surface Science Division
Room 308 - Session SS1-WeA
Electromigration and Surface Transport

Moderator: T.L. Einstein, University of Maryland

2:00pm **SS1-WeA1 Quantifying Surface Electromigration: Si(111) as a Model System@footnote 1@***, **E.D. Williams**,* University of Maryland, College Park **INVITED**

Electromigration induced changes in structure result from a diffusion bias caused by an imposed external electric field. The mechanisms by which the diffusion bias is induced (wind force or direct force) are similar in the surface and the bulk. Thus in temperature regimes where surface diffusion is more readily activated than bulk diffusion, surface electromigration should play an important role in changes in morphology of a current-carrying structure. Surface electromigration occurs on Si(111) surfaces at elevated temperatures. The signature is the spontaneous evolution of non-equilibrium configurations of the steps with one direction of the current, and the return to equilibrium with the opposite direction of current with respect to the "down-hill" step direction. Quantification of the nature of the surface electromigration force has been performed by STM-measurement of the shapes and rates of the evolving non-equilibrium morphologies, and by comparison of the rates of decay in the presence and absence of the stabilizing direct current. The basic mechanism of both formation and decay is the motion of individual steps, which occurs with a rate governed by the rate of equilibrium fluctuations of the steps. During formation of non-equilibrium structures, individual fluctuations couple to the external field, yielding single-point step collisions which then "zip" up to form step bunches. The curvature at the "zip" point has been quantified in terms of the competing effects of energetic costs of step bending and the electromigration force. During decay, steps move in a nearly one-dimensional mode which has been quantified in terms of the step-step repulsions and the electromigration force. The results are consistent with an effective charge less than 0.01 electron units. The applications of this approach to studying broader problems in electromigration will be discussed. @FootnoteText@ @footnote 1@Supported by the U. of MD NSF-MRSEC

2:40pm **SS1-WeA3 Electromigration and Cluster Motion@footnote 1@***, **O. Pierre-Louis**, T.L. Einstein,* University of Maryland, College Park

We describe the fluctuations, dynamics, and instabilities of adatom and of vacancy single-layer islands during electromigration, generalizing earlier work on straight steps without driving forces.@footnote 2@ We emphasize the dependence on the mass-transport mechanism: periphery diffusion (PD), terrace diffusion (TD), or evaporation-condensation (EC).@footnote 3@ In particular, we find non-circular steady states and derive the cluster diffusion constant D@sub c@. Analytical calculations using Langevin formalism are corroborated by both Monte Carlo simulations and numerical integration. We determine the cluster drift velocity, which in the 3 limiting cases has the size dependence of cluster-area x D@sub c@. In EC, clusters elongate perpendicular to the drift axis. Differences exist in this novel behavior for atom and vacancy clusters. In PD a morphological instability leads to cluster splitting.@footnote 4@ We show that adatom diffusion across the terrace induces a new morphological instability for vacancy clusters and discuss the threshold. Shape fluctuations and D@sub c@ are studied in our Langevin framework. For weak electromigration the cluster responds isotropically for TD or PD but not EC. Fluctuation behavior close to the instability threshold is characterized analytically and numerically. An electric current can also alter attachment/detachment probabilities; novel consequences on cluster dynamics (drift velocity, shape, etc.) are investigated. We discuss experimental relevance of our results. New phenomena should be observed on metal surfaces, and implications for voids in electric lines are discussed. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@O. Pierre-Louis and C. Misbah, Phys. Rev. Lett. 76, 4761 (1996); Phys. Rev. B 58, xxx (1998). @footnote 3@S. V. Khare and T. L. Einstein, Phys. Rev. B 57, 4782 (1998); 54, 11752 (1996). @footnote 4@W. Wang and Z. Suo, J. Appl. Phys.79, 2394 (1996); M. Schimschak and J. Krug, Phys. Rev. Lett. 80, 1674 (1998).

3:00pm **SS1-WeA4 Theory of Surface Electromigration on Metals***, **P.J. Rous**, D.N. Bly,* University of Maryland, Baltimore County, US

We describe the application of layer-KKR theory to the calculation of the driving force for adatom electromigration on metallic surfaces. We find that the dominant component of the force arises from momentum transfer to the adatom from the charge carriers; the so-called wind force. We have computed the direction and magnitude of the driving force for electromigration along typical migration pathways on low Miller index surfaces. Averaging the force felt by an adatom traversing these paths permits the calculation of the effective wind valence Z@sub w@. By comparing Z@sub w@ for impurity and self-electromigration on various substrates we have correlated the magnitude of the driving force with the local carrier density and the adatom transport cross-section. For migration of isolated adatoms, we find that the ballistic model, appropriately modified for the effect of the substrate provides a reasonable qualitative description of the calculated effective valence. @FootnoteText@ This work is supported by the National Science Foundation under Grant No. DMR-9632521

3:20pm **SS1-WeA5 Theory of Surface Electromigration on Stepped and Islanded Surfaces.***, **J. Cheng**, P.J. Rous,* University of Maryland, Baltimore County, US

We have applied multiple scattering theory to explore the variation of the electromigration wind force experienced by an adatom in the vicinity of steps and islands on a metal surface. We find that the electromigration wind force felt by a migrating adatom is strongly perturbed as it approaches a step or island edge. This is a result of multiple scattering of the carriers between the adatom and step/island which alters the local current density. The implications of this inhomogeneity in the electromigration driving force for current-induced changes in surface morphology are discussed. Since the calculated wind valence may be directly related to the surfaceinduced resistivity of an adatom we discuss the how the scattering interactions between steps and adatoms may be manifest in the resistivity of a metallic surface. @FootnoteText@ This work is supported by the National Science Foundation under Grant No. DMR-9632521

3:40pm **SS1-WeA6 Surface Electromigration Processes on Gold and Copper Films***, **N. Shimoni**, O. Biham, O. Millo,* The Hebrew University, Israel

Electromigration processes on the surfaces of gold and copper films are studied using scanning tunneling microscopy (STM). We perform time-lapse STM scans under controlled sample temperature conditions, both with and without current stressing. We shall present results regarding the following issues: 1. The evolution of monolayer islands, voids and terraces on the surface of polycrystalline gold films. 2. The appearance and evolution of surface dislocations on flame-annealed gold films. 3. Grain boundary migration, and elongation of surface grains in the direction of the applied current in copper films. Our results will be discussed in context of the various possible surface dynamic processes, including the affect of the sub-surface layer on these dynamics. We will also address differences between thermally activated and electromigration induced processes.

4:00pm **SS1-WeA7 Molecular Dynamics Studies of Interlayer Mass Transport and Dendritic-to-Compact Morphological Transitions during Submonolayer Growth on Pt(111) Surfaces***, **V. Chirita**, E.P. Münger, J.-E. Sundgren,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Urbana

We use embedded-atom method molecular dynamics simulations to investigate the kinetics of two processes which are critical in achieving the layer-by-layer growth mode: interlayer mass transport and dendritic-to-compact morphological transitions. The former investigation is carried out by following the dynamics of adatoms, vacancies and adatom-vacancy pairs within hexagonal Pt@sub 19@ clusters on Pt(111) at 1000 K, for simulation times totalling ~ 135 ns. The latter study concentrates on the dynamics of Pt dendrites containing up to 25 atoms on the same surface at the same temperature. The mapping of adatoms motion on top of the clusters shows that prior to incorporation, adatoms are trapped near the cluster edge for ~ 80% of the total simulation time. Cluster configurations with central vacancies are found to be quite stable. Adatom incorporation is observed to occur mainly via the two well known mechanisms of hopping and push-out/exchange with edge atoms. However, our simulations for adatom-vacancy pairs within clusters, bring the first direct evidence that both mechanisms can be active in the central region of the cluster, i.e. monovacancies are filled by adatom hopping or via exchanges with one of the atoms adjacent to the vacancy. We carry out minimum energy path calculations to examine the energetics of the two mechanisms. The results show that activation barriers are comparable to the corresponding interlayer mass transport mechanisms observed at the outer edge of the cluster. We have also followed the dynamics of Y-shaped Pt dendrites for simulations times in excess of 100 ns. The results show that, in agreement with previously proposed models, the dendritic-to-compact morphological transition proceeds via diffusion around branch corners,as well as edge diffusion. Our simulations reveal however, the presence of a new diffusion mechanism, in which the entire corner of a dendritic branch translates to adjacent terrace sites via a concerted motion of the atoms forming the corner. The process has an activation barrier similar to that of two-fold coordinated atoms diffusing around the corner.

4:20pm **SS1-WeA8 Edge Barriers and Mass Transport on Metal (100) Surfaces@footnote 1@**, ***W.W. Pai,*** The University of Tennessee; *J.F. Wendelken,* Oak Ridge National Laboratory

Since epitaxial growth is subject to kinetic limitations, epitaxial growth morphology is usually thermodynamically unstable. These kinetic limitations, in particular the Schwoebel barrier in homoepitaxial systems, often result in a rough, multilevel morphology which begins during deposition of the first monolayer. Post-deposition equilibration of the resultant morphology occurs through several avenues of mass transport. When the starting condition consists of monolayer height islands following a submonolayer deposition at room temperature, coarsening is observed to result from island diffusion and coalescence on Cu(100) and Ag(100) surfaces, where the island diffusion occurs via rapid edge diffusion.@footnote 2@ When a multilevel system results from higher depositions, islands may still diffuse, but this diffusion is inhibited at downhill step edges due to an edge barrier just as the Schwoebel barrier inhibits downhill transport of adatoms. On the (100) surface, this barrier is found to be very high when the step edge is in the close-packed [110] direction, but very low, or even non-existent, when the edge is oriented in a non-close-packed direction. If a diffusing island encounters an edge with such a low barrier, the island may very quickly descend to the lower level with its atoms being incorporated into the step edge in a manner similar to that which has been reported for Cu(111).@footnote 3@ These low barrier sites, in combination with island diffusion and edge diffusion are found to provide the main pathway for smoothening at room temperature on Cu(100) and Ag(100). This is in contrast to the evaporation-condensation mechanism implied by the line tension driven smoothening at higher temperatures on Cu(100).@footnote 4@ @FootnoteText@ @footnote 1@Research performed at ORNL, which is managed by Lockheed Martin Energy Research Corporation for the U.S. DOE under Contract No. DE-AC05-96OR22464 @footnote 2@Woei Wu Pai, Anna K. Swan, Zhenyu Zhang and J. F. Wendelken, Phys. Rev. Lett.79, 3210 (1997).@footnote 3@M. Giesen, G. Schulze Icking-Konert, and H. Ibach, Phys. Rev. Lett. 80, 552 (1998).@footnote 4@J.-K. Zuo and J.F. Wendelken, Phys. Rev. Lett. 70, 1662 (1993).

4:40pm **SS1-WeA9 Metal Row Growth on a High-Index Silicon Surface**, ***H.H. Song***, *K.M. Jones, S.R. Blankenship, J.A. Carlisle, A.A. Baski,* Virginia Commonwealth University

Recent STM studies of high-index silicon surfaces have revealed unique morphologies not found on their low-index counterparts.@footnote 1@ For example, Si(5 5 12) forms a single-domain reconstruction composed of row-like structures, primarily pi-bonded chains. This highly anisotropic surface is expected to provide a unique template for the growth of metal overlayers, particularly in the formation of one-dimensional nanometer-scale structures. Our STM studies show that Ag deposited onto Si(5 5 12) and annealed to moderate temperatures does form row-like overlayer features. At coverages as low as 0.05 ML, rows appear on top of the most prominent pi-bonded chains, resulting in a 5.4 nm inter-row spacing. These rows have high aspect ratios (up to 40:1) and a mean length of 20 nm. As the Ag coverage is increased, the overlayer rows grow in length and number until the surface forms a periodic array of such rows at ~0.25 ML. Above this coverage, Ag appears to be incorporated into other structures on the surface and the long-range ordering becomes disrupted. A statistical analysis of the row lengths reveals the expected increase in mean row length as a function of coverage (0.05 to 0.2 ML) and annealing temperature (400 to 550°C). At annealing temperatures above 550°C, however, the deposited Ag causes local faceting of the Si surface, disrupting the ordered arrays of Ag rows. The metal rows must therefore be a metastable arrangement of the surface. @FootnoteText@ @footnote 1@A.A. Baski, S.C. Erwin, L.J. Whitman, Surf. Sci. 392, 69 (1997).

5:00pm **SS1-WeA10 One Dimensional Growth Behavior of Xe Atoms on Step Edges of Cu(111)**, ***J.-Y. Park,*** *Y. Kuk,* Seoul National University, Korea; *K. Miyake, H. Shigekawa,* University of Tsukuba, Japan

A rare gas atom adsorbed on graphite or various metal surfaces has been extensively studied as a model two dimensional system because of its weak interaction with the substrate. In this study, we used a low temperature scanning tunneling microscope to understand the interaction of Xe atom with Cu(111) surface in the temperature range of 10K ~ 30K. Quite different one dimensional wetting behavior was observed at the lower and upper side of Cu surface steps. Xe atoms first adsorb at lower side of steps, but they reveal repulsive interaction among themselves. The Xe adsorbates then modify the Ehrlich-Schwoebel barrier, resulting in the wetting at upper side of steps. A model is proposed to explain the 1D growth behavior. As observed earlier,@footnote 1@ standing waves, caused by reflection of surface state electrons at step edges and impurities, were observed. It was also observed that the surface state energy is shifted in the presence of the Xe overlayer. @FootnoteText@ @footnote 1@M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature 363, 524 (1993).

Surface Science Division
Room 309 - Session SS2-WeA
Photochemistry and Deposition

Moderator: C.M. Greenlief, University of Missouri, Columbia

2:00pm **SS2-WeA1 Photochemical Routes to Group IV Deposition**, ***G.J. Batinica***, *J.L. Stepnowski, J.E. Crowell,* University of California, San Diego

The fabrication of high-speed electronic devices requires the controlled epitaxial deposition of Si and SiGe thin films. We have explored both thermal and photochemical routes to Si and Ge deposition using disilane (Si@sub 2@H@sub 6@) and digermane (Ge@sub 2@H@sub 6@) as model hydride deposition sources. We have also compared the thermal and photochemical reactivity of Si(100) versus that of Si(111). The deposition reactions have been studied using multiple internal reflection infrared spectroscopy (MIRIRS), temperature programmed desorption (TPD), and Auger electron spectroscopy (AES). Hydrogen and silane (SiH@sub 4@) desorption yields were used to determine the reactivity of disilane on the Si surfaces with and without UV irradiation. Hydrogen and germane desorption yields and relative Ge/Si AES signals were used to determine the reactivity of digermane. UV irradiation during or after dosing of the Si crystal surfaces at 110K greatly enhanced the reactivity of disilane and digermane compared to similar exposures without UV irradiation. Comparison of the reactivity of disilane with Si(100) versus Si(111) show that Si(111) is thermally less reactive than the Si(100) surface. However, both surfaces show similar photo-reactivity to disilane. The photo-induced mechanism of disilane and digermane reactions has been studied using clean, partially deuterated and fully deuterated Si(111) and Si(100) surfaces. Thermally, the reactivity is controlled by the surface dangling bonds; whereas the photo-induced deposition chemistry appears to primarily involve insertion by the photo-generated diradicals, silylene and germylene. The implication of our results on deposition methodologies will be discussed.

2:20pm **SS2-WeA2 Electron Induced Deposition of Germanium on Si(100): TPD, XPS, and HREELS Study**, ***J. Lozano***, University of Texas, El Paso, U.S.; *J.H. Craig, J.H. Campbell,* University of Texas, El Paso

Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) were used to investigate the effects of an electron beam on Si(100) dosed with digermane at 110 K. At high digermane coverages (>1 ML), three peaks appear on hydrogen TPD traces at 140 K, 575 K, and 740 K. The peak at 140 K corresponds to desorption of hydrogen from molecular overlayers of digermane, as confirmed by the desorption of digermane fragments at 140 K. The TPD features at 575 K and 740 K correspond to hydrogen desorption from surface germanium and from silicon, respectively. The vibrational losses at 820 and 2040 cm@super -1@ in the HREELS data obtained from digermane-covered Si(100) indicate the presence of germanium hydride species on the surface. The formation of the silicon monohydride state is evident by the high-energy broadening of the loss feature at 2040 cm@super -1@. Upon exposure of the highly dosed surface to an electron beam (maximum current density of 9µA/cm@super 2@), the intensity of the low temperature TPD peak at 140 K decreases, while the intensity of the peak at 575 K increases. XPS data show an increase on the relative surface concentration of germanium following electron irradiation of the digermane overlayers. Annealing the surface to 200 K does not decrease the relative concentration of germanium on the electron-irradiated surface. Electron irradiation of digermane/Si(100) at low digermane exposures does not have any detectable effects. These results indicate that the electron beam dissociates the digermane molecular overlayers and deposits germanium on the surface.

2:40pm **SS2-WeA3 Photodesorption of Condensed Gases by Lyman-@alpha@**, ***D.A. Bahr***, *R.A. Baragiola,* University of Virginia

We measured the absolute desorption yield of water and carbon dioxide films condensed at low temperatires under irradiation with Lyman-@alpha@ (121.6 nm) photons as a function of sample temperature and irradiation fluence using a double quartz-crystal resonator. We also determined the species desorbed using mass spectrometry. We will discuss the results in terms of basic processes and discuss astrophysical implications.

3:00pm **SS2-WeA4 Photodesorption of Positive Ions from Oxyanion-Containing Inorganic Crystals**, ***C. Bandis***, *M.L. Dawes, S.C. Langford, J.T. Dickinson,* Washington State University

Surfaces of inorganic, ionic crystals with complex oxyanions can be dramatically altered by UV and electron irradiation. Previous work has shown that such irradiation desorbs XO@sub n@ and O@sub 2@, where X = N, P, C, and possibly S. This electronic decomposition produces cation defect complexes from which intense positive ion emission can be photo-induced. We describe two-beam experiments where either two laser beams or a laser and an electron beam are cofocused. One beam (UV laser or electron) is used to generate defects, and the second beam (laser) is used to photodesorb ions. We report metal and metal-containing ion emission accompanying nanosecond laser pulses at 248 and 1064 nm from alkali nitrates and calcium phosphates. The resulting ion kinetic energies can exceed the photon energy by factors of ten. The effect of time delay between two pulsed beams will also be presented. The critical role of radiation induced chemistry and the ion emission mechanism will be discussed. This work is supported by the Department of Energy under Contract DE-FG06-92ER14252.

3:20pm **SS2-WeA5 Direct Observation of Synchrotron-Radiation-Stimulated Decomposition of SiO@sub 2@ Thin Films on Si(111) Surfaces using Scanning Tunneling Microscopy**, *T. Miyamae,* ***T. Urisu***, *S. Hirano,* Institute for Molecular Science, Japan*; H. Uchida, T. Yagi,* Toyohashi University of Technology, Japan*; I. Munro,* Institute for Molecular Science, Japan

Synchrotron radiation (SR) stimulated decomposition of silicon dioxide thin films on Si(111) surfaces were observed by using a ultrahigh vacuum scanning tunneling microscopy (UHV-STM) and Low energy electron diffraction (LEED). SiO@sub 2@ films were shown to be almost removable by SR irradiation. Si(111)-(7 by 7) reconstructed structure were observed by LEED after two hours SR irradiation at surface temperatures as low as 650 C°. In spite of the observation of clear 7 by 7 LEED pattern, the STM images did not show clean and flat surface at this temperature. The clean (7 by 7) reconstructed surface was generated after two hours irradiation at a surface temperature of 700 C°. Analysis of the evolution in the clean region suggests that the desorption mechanism may be different between thermal and SR stimulated desorption processes. The results show that the feasibility of this technique for low-temperature cleaning of silicone surface is demonstrated.

3:40pm **SS2-WeA6 Surface Decomposition Reaction of Trisdimethylaminoantimony on GaSb(100)-(3x1)**, ***K. Yong***, *P.D. Kirsch, J.G. Ekerdt,* University of Texas, Austin

Trisdimethylaminoantimony (TDMASb) is a novel Sb-precursor for the deposition of Sb-containing alloys by organometallic vapor phase epitaxy. Deposition using TDMASb can lower the growth temperature and also minimize carbon incorporation in the layers. The decomposition of TDMASb on GaSb(100)-(3x1) was studied using temperature programmed desorption, temperature programmed static secondary ion mass spectroscopy, low energy electron diffraction, and X-ray photoelectron spectroscopy. TDMASb decomposes on the surface at temperatures below 200 K and dimethylamine was desorbed through two reaction pathways. Homolysis of the antimony-nitrogen bond resulted in desorption of the dimethylamine radical at 380 K. Methylmethyleneimine was formed and desorbed from the surface through hydrogen elimination at 480 K. Deposition of Sb from 5 monolayers of TDMASb on GaSb(100) induced the change of surface structure from (3x1) to (1x1). We propose that surface Sb atoms are the reactive sites for the decomposition of TDMASb.

4:00pm **SS2-WeA7 Interaction of Ethylene with the Ge(100)-2x1 Surface: Coverage and Time-Dependent Behavior**, ***A.V. Teplyakov***, Stanford University*; P. Lal, Y. Noah, M.J. Kong,* New York University*; S.F. Bent,* Stanford University

Chemical modification of semiconductor surfaces has been a subject of thorough investigations for decades because of its relevance to the fabrication of electrical and optical devices. Despite these efforts, very little is known about the chemical properties of germanium surfaces. Here we present studies of the adsorption and thermal chemistry of ethylene on Ge(100)-2x1. Ethylene has been studied in detail on Si(100)-2x1, and provides a good reference system for comparing silicon and germanium reactivity. The results of multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and temperature programmed desorption (TPD) studies suggest that ethylene chemisorbs on the Ge(100)-(2x1) surface at room temperature. IR spectroscopy gives evidence for only one adsorbate structure on this surface at room temperature. However, TPD measurements show two molecular desorption features, indicating that at least two adsorption configuration can exist. Complex temperature-, time-, and coverage dependent behavior of ethylene adsorption on Ge(100)-2x1 will be presented and analyzed.

4:20pm **SS2-WeA8 Interaction of Amines with Hydrogen on Al(111)**, ***J.N. Russell, Jr.***, *C.S. Kim,* Naval Research Laboratory

High quality AlN films, for optoelectronic devices, high power electronics and sensors, are generally produced via MOCVD of NR@sub 3@ and R@sub 3@Al (R = H, CH@sub 3@, or C@sub 2@H@sub 5@). We explored the chemical interaction of ammonia, methylamine, and ethylamine with clean and hydrogenated Al(111) in an UHV environment using temperature programmed desorption and/or infrared reflection absorption spectroscopy. On clean Al(111), the compounds adsorb molecularly and desorb by 200 K. In contrast, on the H-covered surface, a new desorption state (ß) is seen at about 250 K for each reactant. The ß-state coverage of each compound tracks that of H. Infrared spectroscopy shows that NH@sub 3@ preferentially adsorbs via a Lewis acid-base interaction at monohydride sites with the Al-N bond inclined away from the surface normal. While NH@sub 3@ does not dissociate nor exchange H atoms with the H-precovered surface, the alkylamines dissociate. New HD desorption features, at 240 and 270 K, are observed for perdeutero-alkylamines on H/Al(111). In addition, hydrocarbon desorption is observed at about 600 K for the alkylamines when coadsorbed with hydrogen. We discuss the implications of this work on the MOCVD of AlN films.

4:40pm **SS2-WeA9 Adsorption and Reaction of Chlorine on Low Index Diamond Single Crystal Surfaces**, ***S. Hadenfeldt***, *C. Benndorf,* University of Hamburg, Germany

The lowering of the substrate temperature achieved by the low pressure diamond deposition from halogenated precursors is believed to involve surface processes, including halogen adsorption, desorption and reaction with H(ad). In this work we studied the adsorption of chlorine on the low index diamond (100), (111) and (110) single crystal surfaces as well as on polycrystalline diamond CVD films in UHV using thermal desorption spectroscopy (TDS), Augerelectron spectroscopy (AES), low energy electron diffraction (LEED) and photoelectron spectroscopy (UPS / XPS). Elemental halogen was dosed by solid state electrolysis of silverchloride at elevated temperatures or direct dosing of chlorine gas through a heated oxide ceramics tube. The single crystals were regularely cleaned by pretreatment in a hydrogen plasma and showed clear reflexes in LEED. The CVD films were studied as received from the CVD process. In AES upon successive halogen dosing a linear increase of the intensity of the halogen Auger signal and a simultaneous decrease in intensity of the 272 eV carbon signal can be seen at first. No LEED overstructures could be observed upon adsorption on either surface. Depending on the sample preparation and history, in general two different desorption behaviours are observed in TDS. From the hydrogen rich, plasma prepared surface chlorine is desorbed continuously with a maximum around 600 K. Around 850 K chlorine is completely removed. On a hydrogen depleted surface, where less halogen adsorbs at a given exposure, two regions of chlorine desorption can be observed. Up to 730 K a steady decrease of chlorine is noted, which levels off, until finally all chlorine is desorbed around 950 K. Halogen uptake of the diamond surface can be increased either by thermally activating the surface or by dosing of atomic hydrogen prior to halogen adsorption.

5:00pm **SS2-WeA10 Desorption Kinetics of Hydrogen and Deuterium from Diamond (111)x(1x1) via Helium Atom Scattering**, ***S.A. Safron***, *J.G. Skofronick,* Florida State University*; A. Glebov, J.P. Toennies, S. Vollmer,* Max Planck Institut fuer Stroemungsforschung, Germany

The rate constants for the isothermal desorption of hydrogen and deuterium from diamond (111)-H(1x1) and -D(1x1) surfaces, respectively, have been measured over the temperature range 990 K to 1080 K by monitoring the helium atom Bragg diffraction beam intensities as a function of time. The rate behavior for both H and D followed first order reaction kinetics and a distinct isotope effect was observed in the desorption rates. The temperature dependence of the rate constants could be represented by an Arrhenius law. In fitting the data to determine the Arrhenius activation energies, the pre-exponential (or frequency) factors were taken to be the previously reported diamond (111)-(1x1) C-H or C-D stretching mode (S-mode) frequencies, 8.5x10@super13@ s@super-1@ for H and 6.4x10@super13@ s@super-1@ for D. The respective activation energies were then determined to be 2.69 eV (62.0 kcal/mol) and 2.74 eV (63.2 kcal/mol).@footnote1@ @FootnoteText@ @footnote1@ Work supported in part by US DOE grant no. DE-FG02-97ER45635 and NATO grant no. GRC.961145.

Thin Films Division
Room 310 - Session TF-WeA
Advances in Sputtering

Moderator: S. Zarrabian, Optical Coatings Laboratories, Inc.

2:00pm **TF-WeA1 Preferential Sputtering Effects in Thin Film Processing**, ***S. Berg***, *I.V. Katardjiev,* Uppsala University, Sweden **INVITED**

Predicting the partial sputtering yield (number of sputtered atoms of one element per one incident ion) for the different constituents during sputtering from a multielemental surface is a rather difficult task. For an alloy bulk target where no diffusion takes place, however, it can at least be assumed that the ratio of the outsputtered elemental fluxes is exactly equal to the corresponding composition ratio of the target bulk. During bias sputter deposition from an alloy target, however, the composition of the deposited film may deviate strongly from the target composition due to preferential re-sputtering of one (or more) elements from the growing compound film. We will present a systematic study that serves to clearify how and why some atomic elements are preferentially sputtered from a multielement matrix. By using a Monte Carlo based computer simulation program (T-DYN) it is possible to simulate the evolving collision cascades in the bombarded material and thus study the sputtering process in its dynamics. The results from such computer simulations indicate that the partial sputtering yield of one element in a multielement matrix depends in a systematic way on the atomic density of the material, the atomic number of the atomic elements and the projected range of the incoming energetic ion. Furthermore, from this study we have found out that it is possible to "tune" the partial sputtering yield of one element in a multielement matrix. The "tuning" effect can be quite dramatic. Adding a few percent of e.g. W to a pure Al target may increase the Al sputtering yield by as much as 100% as compared to the sputtering yield of pure Al. Other interesting effects caused by "controlled preferential sputtering" will also be demonstrated.

2:40pm **TF-WeA3 Measurements and Modeling of Ti and Ta Sputtering as a Function of Target Microstructure and Temperature**, ***J.P. Allain***, *D.A. Alman, 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 use of titanium and tantalum films are continually applied as effective underlayers for both barrier and enhanced metallization properties. This paper focuses on the influence of target microstructure and temperature on the sputtering and angular distribution yields. A Colutron ion gun is used to produce an ion beam which is decelerated near the target. The beam diameter near the target is modified so as to focus on a single grain. The beam diameter can also cover several grains including grain boundaries. Grain boundary density and orientation is studied on its effect on the distribution and yield. The diagnostics near the target can be rotated to intercept the sputtered flux. The diagnostics consist of a quartz crystal oscillator to measure total yield and a cylindrical pyrolytic graphite collector plate. The graphite plate is analyzed by an PHI Auger spectrometer to obtain areal densitites and thus the angular distributions. The target assembly is fixed and monitored by a thermocouple. A "cold finger" which can deliver liquid N2 is attached to the target. Modeling of the system is used by an enhanced version of VFTRIM3D, a code which includes fractal geometry and a non-binary collision model.@footnote 2@ @FootnoteText@ @footnote 1@W. Eckstein, C. Garcia-Rosales, J. Roth, W. Ottenberger, "Sputtering Data", pub. Max-Planck-Institut Fur Plasmaphysik, February 1993. @footnote 2@D.N. Ruzic, Nucl. Instrum. Methods B 47 (1990) 118.

3:00pm **TF-WeA4 Reactor-Scale Models for Rf-Diode Sputtering for GMR Thin-Film Growth**, ***S. Desa***, *S. Ghosal, R.L. Kosut, J.L. Ebert, A. Kozak, T.E. Abrahamson,* SC Solutions*; J.F. Groves, H.N.G. Wadley, D.W. Zou,* University of Virginia

This paper describes the development of a physical model for the Rf-diode sputtering of GMR thin-films. The model consists of: (1) a CFD finite element model for the velocity and pressure distribution of the Argon (Ar) gas flow in the chamber, (2) a steady-state plasma model for the flux and energy of Ar ions striking the target and the substrate, (3) a molecular dynamics (MD) sputtering model for the energy distribution, angle distribution, and yield of the Copper (Cu) atoms sputtered from the target by the Ar ions, and (4) a Direct Simulation Monte Carlo (DSMC) model for the transport of Cu atoms through the low-pressure argon gas to the deposition substrate. The individual models for gas flow, plasma discharge, Cu sputtering, and DSMC-based Cu atom transport are then integrated to create a detailed, steady-state, input-output model capable of predicting thin-film deposition-rate and uniformity as a function of the process input variables: power, pressure, gas temperature and electrode spacing. (Deposition and uniformity in turn define well-known device characteristics such as H@sub sat@ and GMR ratio.) The paper also describes the development of an approximate input-output model whose CPU time is several orders-of-magnitude faster than that of the detailed model. Both models were refined and validated against experimental data obtained from an actual GMR chamber.

3:20pm **TF-WeA5 Using Pulsed DC Power for Reactive Sputtering of Al@sub 2@O@sub 3@**, ***A. Belkind***, *A. Freilich,* Stevens Institute of Technology*; R. Scholl,* Advanced Energy Industries

Implementation of reactive sputtering of dielectrics such as Al@sub 2@O@sub 3@ by the use of steady DC power is obstructed by arcing. The arcing appears to be due to breakdown of the dielectric (oxide) films that grow on the metal target surface and which accumulate positive charges on their surfaces due to ion bombardment. The arcing can be greatly alleviated when pulsed DC power is applied. By pulsed DC power we mean that the power is applied for a short "on" period, and then removed for a short "off" period. During the "off" period the plasma can discharge the surfaces, provided certain conditions are met. The dependence of adequate discharging, and thus arc prevention, on the duration of the "on" and "off" periods is examined. In addition, the dynamics of plasma density loss in the "off" period and its re-establishment in the initial part of the "on" period are discussed. Reactive sputtering takes place only during the "on" period, and part of this period is lost for effective sputtering due to the necessity for full plasma re-establishment. This produces a dependence of the deposition rate on both the duty cycle and the frequency of pulsing, but not on the power. This dependence is examined and the power efficiencies of AC and pulsed power DC reactive sputtering are compared and speculation made as to the differences in results published between single and dual cathode systems.

3:40pm **TF-WeA6 Suppression of Hillocks and Whiskers on Al Films Deposited onto a Glass**, ***H. Saka***, *Y. Suzuki,* Nagoya University, Japan*; H. Takatsuji, K Tsujimoto,* IBM, Japan*; K. Kuroda,* Nagoya University, Japan*; S. Tsuji,* IBM, Japan

A new technique to suppress formation of hillocks and whiskers on an Al film deposited onto a glass substrate has been developed. First, an Al film was deposited on a LCD-grade glass substrate by industrially conventional dc magnetron sputtering. Heating this films above 573K resulted in formation of a number of hillocks and whiskers. Onto this Al film another layer of Al film was deposited by rf magnetron sputtering. When the thickness of the second Al layer is very thin, many hillocks and whiskers are formed on heating. However, when the thickness of the second Al layer is around 40nm, the formation of both hillocks and whiskers are completely suppressed. Cross-sectional TEM observation revealed that the second layer of Al deposited by rf sputtering is amorphous. The sheet resistance of the second layer was measured by van der Pauw method to be 3.5 x 10@super-6@ ohm cm.

4:00pm **TF-WeA7 Substrate Bombardment and Heating in Dual Magnetron Sputtering Using Mid-Frequency AC***, **J. Plaisted,*** Kinneo*; G.W. McDonough, G.A. Roche,* Advanced Energy

Dual magnetron sputtering (DMS) using mid-frequency AC has become a popular method for the reactive deposition of dielectrics. However, several studies have reported higher levels of substrate bombardment and heating with the use of this technique. In an effort to determine the cause, we separated the effects of plasma ignition from those of the anode arrangement. The anode arrangement employed in mid-frequency DMS was duplicated in DC operation using a pair of opposed magnetrons powered by a floating output generator. Values of the substrate self-bias, ion current, and temperature were compared to those obtained from running the sources with 40 kHz AC and standard DC techniques. Results indicate that a large fraction of the energetic species found in mid-frequency DMS can be explained by a restriction of the anode surfaces to the paired magnetrons.

4:20pm **TF-WeA8 A Novel Approach to Collimated Physical Vapor Deposition***, A.P. Paranjpe,* ***D. Heimanson****, J.C.S. Kools, P.V. Schwartz, K. Song, B. Bergner, S. McAllister,* CVC

In some applications of Physical Vapor Deposition (PVD), it is desirable to have the atoms arriving at the substrate at angles close to the normal (collimation). Applications of collimated PVD include filling of highaspect ratio vias, as used in multilevel IC metallization, or high resolution shadow masking as used in lift-off technology. Several approaches to collimation have been proposed in recent years: natural (or long throw) collimation, physical collimation, ion beam deposition ionized PVD and hollow cathode collimation. In this contribution, we introduce a novel approach to collimation. It is found experimentally that this approach leads to a strongly improved degree of collimation when compared to the conventional collimation methods. Contrary to ion beam deposition and ionized PVD, our approach allows to vary the kinetic energy of the sputtered atoms arriving at the substrate over a wide range. Simulations of the target-to-substrate atom transport using the Simbad package show that the improved collimation method leads to angular distributions with Full Widths at Half Maximum (FWHM) below 20 degrees.

4:40pm **TF-WeA9 Microcrystalline Silicon Thin Films Deposited By Low Temperature Reactive Magnetron Sputtering: The Effect Of Using Deuterium vs. Hydrogen***, **J.E. Gerbi**,* University of Illinois, Urbana-Champaign*; D.S. Kim,* SAIT, Korea*; G. Ben Amor,* Ecole Polytechnique, France*; J.R. Abelson,* University of Illinois, Urbana-Champaign

Microcrystalline silicon (uc-Si:H) thin films are of interest for macro-electronic technologies: they can serve as optical absorber or doped contact layers in solar cells, or as the nucleation layer in the direct deposition of polycrystalline silicon on glass for thin film transistors.@footnote 1@ The grain size, shape, and defect density significantly modify the electronic properties of uc-Si:H; therefore, it is highly desirable to control the film microstructure through the growth process. We previously showed that DC reactive magnetron sputtering (RMS) of a Si target produces uc-Si:H films when sufficient H@sub 2@ is added to the Ar working gas. In the sputtering plasma, H@sub 2+@ ions are accelerated towards the Si target and reflect as fast neutral H atoms, which impinge on the growing film and implant to a depth of ~ 50Å. This large flux of fast H atoms provides unique control over the nucleation and growth of the uc-Si:H phase.@footnote 2@ In this work, we explore the effects of using D@sub 2@ instead of H@sub 2@ to grow uc-Si:H films on glass at a substrate temperature of 230°C. The substitution of D@sub 2@ for H@sub 2@ lowers the partial pressure at which the microcrystalline regime is entered, and produces films with a higher degree of crystallinity throughout the entire pressure range investigated. Crystalline nucleation and the grain-size dependent electronic structure are observed in real time using spectroscopic ellipsometry. We report post-deposition TEM, Raman spectroscopy, and electrical characterizations. To explain the implantation-related isotope effect, we present binary collision (TRIM) simulations of the energy distribution, range, and recoil behaviors of the H vs. D neutral fluxes, and their resultant dynamic concentrations in the film. @FootnoteText@ @Footnote 1@Y. H. Yang and J. R. Abelson, Appl. Phys. Lett. 67, 3623 (1995). @Footnote 2@Y. H. Yang, M. Katiyar, N. Maley, and J. R. Abelson, Appl. Phys. Lett. 65(14), 1769 (1994).

5:00pm **TF-WeA10 Atomistic Simulations of the Sputter Deposition of Copper***, **W. Zou**, J.F. Groves, X.W. Zhou, H.N.G. Wadley,* University of Virginia

RF Diode sputter deposition is being explored for synthesizing metal and magnetic multilayer films. A discrete simulation Monte Carlo binary collision model has been developed to analyze the spatial uniformity and impact velocity of individual vapor atom with a substrate. The analysis began with the calculation of ion-impact with a metal target using Molecular Dynamics simulations. This provided both the initial energy distribution of vapor atom and its angular distribution immediately upon their sputter emission from the target. The model then used input conditions such as background pressure, temperature, gas type, and reactor geometry in combination with a discrete simulation Monte Carlo method to analyze vapor atom transport to the substrate. Results are shown of vapor atom deposition efficiency, the spatial distribution of the film thickness, the impacting atom energy and the impact angle distribution of the vapor atoms. These vapor transport model results provide a link between the microstructure of thin films and the deposition process conditions, and can be used for reactor design and control.

Vacuum Technology Division
Room 329 - Session VT-WeA

Vacuum Systems and Components

Moderator: J.L. Provo, Sandia National Laboratories

2:00pm **VT-WeA1 Design and Installation of a Low Particulate, Ultra-High Vacuum System for a High Power Free Electron Laser***, **H.F. Dylla**, G. Biallas, L.A. Dillon-Townes, E. Feldl, G.R. Myneni, J. Parkinson, J. Preble, S. Williams, M. Wiseman,* Jefferson Lab

A high-average power (kW) infrared free electron laser (FEL) is currently being commissioned for the Jefferson Lab FEL User Facility. The IR FEL is driven by a unique superconducting RF linac which is recirculated to recover electron beam power that is not radiated in the FEL. The design and installation of the vacuum system for the FEL involved particular attention to minimizing particulate contamination which could cause problems with the superconducting acceleration cavities and the high power FEL optics. Particulate contamination levels of all vacuum components were monitored during the cleaning process using laser scattering. Cleaning, transport and installation procedures were developed to minimize the contamination of the complete system. We will summarize a data base we compiled of particulate contamination levels of the various components installed in the FEL vacuum system. This work supported by the U.S. DOE Contract No. DE-AC05-84-40150, the Office of Naval Research, Commonwealth of Virginia and the Laser Processing Consortium.

2:20pm **VT-WeA2 Vacuum Instrumentation and Control System for the Relativistic Heavy Ion Collider***, **L.A. Smart,*** Brookhaven National Laboratory*; R.C. Lee, D. Weiss, D. Zigrosser,* Brookhaven National Laboratory, US

The Relativistic Heavy Ion Collider (RHIC) Project is a nuclear physics research accelerator entering its final year of construction, with beam circulation scheduled for March 1999. To achieve beam emittance growth and lifetime, the vacuum in the two concentric rings must be at specified levels, and the sector valves isolating the cryogenic beam lines from those at room temperature must be open. The RHIC vacuum instrumentation and control (I&C) system performs multiple functions, the first of which is operating the sector valves with input from over one thousand gauges and pumps distributed around the 3.8 km circumference of the accelerator rings. Other vacuum system control functions include operating all gauges, pumps and valves from remote locations, supplying data for beam permits, data logging, and display of vacuum system parameters. Vacuum gauging includes inverted magnetron and convection-Pirani total pressure gauges, and partial pressure analyzers with faraday cup and electron multiplier detectors. Pumps on the high and ultrahigh vacuum chambers include sputter-ion, turbo molecular, and titanium sublimation pumps. Multi-drop serial communication networks are used to transfer pressure readings from gauge and turbo molecular pump controllers 300 m distant to distributed programmable logic controllers, which form the heart of the vacuum system control. This paper describes the architecture and implementation of the RHIC vacuum I&C system from the pumps and gauges to the remote operator interfaces used to control them.

2:40pm **VT-WeA3 An Ultra-High Vacuum System for Hydriding Rare Earth Metal Films***, **S.J. Black**, F.J. Steinkruger, C.W. Walthers,* Los Alamos National Laboratory **INVITED**

Los Alamos National Laboratory has designed, fabricated, assembled and tested a state-of-the-art vacuum system for the hydriding of reactive rare earth metal films. The application of this system is dihydriding 5000Å erbium films on molybdenum substrates for neutron tubes. Neutron tubes are a major component of neutron generators, which are used in modern nuclear weapons. The system is capable of achieving pressures in the 10@super -10@ torr range. Such pressures are desirable in order to reduce contaminant gas species (which would otherwise compete with the hydriding reaction), to the parts per billion level. The vacuum is provided by oil-free turbomolecular/molecular drag pumps. Rough pumping is provided by a scroll pump backed by a metal bellows pump. In order to achieve these low pressures, measures were taken in the design and operation of the system. In order to reduce outgassing within the system, we eliminated all organic material within the system through the use of all-metal valves. All fittings are either welded or rely on metal O-rings. Passivation of the vacuum system interior surfaces was performed to reduce condensation of oxygen and water on the stainless steel surfaces. Other materials used within the vacuum system (film substrates, fixtures, and radiation shields) are made of molybdenum which is extensively cleaned prior to use. The loader system is capable of heating the films to 700°C while under vacuum, and continuing to maintain those temperatures after adding several hundred torr of hydrogen isotopes or inert purge gases to the system. Since the vacuum system is opened each time films are either loaded or removed from the vacuum chamber, the apparatus is installed within an inert (nitrogen) glovebox. Remote operation of the system is made possible through the use of pneumatically-actuated valves. The system is heavily instrumented in order to achieve tight process control. Two residual gas analyzers (RGA's) are used to determine the chemical composition of species within the system during evacuation. Details of the hardware design will be presented as well as performance data.

3:20pm **VT-WeA5 Thermal Stability and Sealing Performance of Perfluoroelastomer Seals as a Function of Crosslinking Chemistry***, **M.J. Heller**, J.M. Legare, S. Wang, S. Fukuhara,* DuPont Dow Elastomers

Perfluoroelastomer (e.g. Kalrez, Chemraz, etc.), fluoroelastomer (e.g. Viton, etc.) and silicone parts are widely used in sealing applications for semiconductor wafer processing equipment. More specifically, they are often used as O-ring seals in dry chemical process equipment (e.g., Plasma Etchers, Ashers, Diffusion Furnaces, CVD, LPCVD, RTP and Lamp Anneal, etc.). Many of these seals are required to function at process temperatures ranging from 200 - 300°C and in some cases higher. The ability of an elastomer to resist thermal degradation has a significant impact on its ability to function effectively as a seal over time. This paper evaluates and compares the relative long term sealing performance of perfluoroelastomers having different crosslinking chemistries and other typically specified high performance elastomers. Long term compression set and seal force retention data is presented, including a discussion of the different test methods and their relative value in predicting seal performance at elevated temperatures. In addition, air heat aging data for other typically measured physical properties (i.e., Shore A Hardness, 100% Modulus, Tensile Strength at Break, Elongation at Break, % Weight Loss) is also presented and discussed. Results indicate perfluoroelastomers seals have the best long-term compression set characteristics and retain the highest percentage of their original sealing force over time. In addition, data shows perfluoroelastomers having an organo-metallic cross-linking system are the most thermally stable and exhibit the best long term seal performance at elevated temperatures versus those having an organic-peroxide cross-linking system. Finally, because the test conditions best reflect static o-ring seal service conditions, analysis of seal force retention test results provide a more realistic comparison of thermal stability and its relative impact on sealing performance.

3:40pm **VT-WeA6 Vacuum Insulation, 100 years of Cryogenics, and Clean Ultra High Vacuum***, **G.R. Myneni,*** Thomas Jefferson National Accelerator Facility

Sir James Dewar invented vacuum insulation (~ 1872) for improving high temperature calorimetry. He improved the vacuum in his double walled containers with charcoal for cryogenics use. He further enhanced the effectiveness of his dewars by silvering the inner walls. Dewar liquefied hydrogen for the first time on May 10, 1898 and Kammerlingh Onnes won the race of liquefying helium by 1908. Onnes discovered superconductivity in the year 1911. The heat capacity of materials at cryogenic temperatures provided some of the earliest scientific validation of quantum theory. The American space program gave the impetus for developing the multi layer insulation (MLI) to reduce the weight of launch vehicles and spacecraft. Cryopumping is providing clean ultra high vacuum in many high tech systems including semiconductor fabs and accelerators. Jefferson Lab's accelerator (CEBAF) has three independent vacuum systems (vacuum insulation, wave guide vacuum and beam line vacuum) and all of them benefit from cryopumping. The beam line vacuum inside the CEBAF cryomodules is extremely low. Diamond field emitter based extreme high vacuum instrumentation is being developed presently to measure such low pressures. High efficiency dewars are also being used in high tech medical diagnostic systems such as magnetic source imaging (MSI). These historic and present developments will be reviewed in this paper on the occasion of the centenary of the liquefaction of hydrogen by Sir James Dewar. This work supported by the U.S. DOE under contract No. DE-AC05-84ER40510.

4:00pm **VT-WeA7 Method for Measuring Deuterium in Erbium Deuteride Films***, **J.R. Brangan**, S.M. Thornberg, M.R. Keenan,* Sandia National Laboratories **INVITED**

Determining the quantity of deuterium in an erbium deuteride (ErD@sub 2@) film is essential for assessing the quality of the hydriding process but is a challenging measurement to make. First, the ideal gas law cannot be applied directly due to high temperature (950@super o@ C) and low temperature (25@super o@ C) regions in the same manifold. Additionally, the metal hydride does not release all of the deuterium rapidly upon heating and metal evaporation occurs during extended heating periods. Therefore, the method developed must provide a means to compensate for temperature inhomogeneities and the amount of deuterium retained in the metal film while heating for a minimal duration. This paper presents two thermal desorption methods used to evaluate the kinetics and equilibria of the deuterium desorption process at high temperatures (950@super o@ C). Of primary concern is the evaluation of the quantity of deuterium remaining in these films at the high temperature. A multiple volume expansion technique provided insight into the kinetics of the deuterium evolution and metal evaporation from the film. Finally a repeated pump-down approach yielded data that indicated approximately 10% of the deuterium is retained in the metal film at 950@super o@ C and approximately 1 Torr pressure. When the total moles of deuterium determined by this method were divided by the moles of erbium determined by ICP/AES, nearly stochiometric values of 2:1 were obtained for several erbium dideuteride films. Although this work presents data for erbium and deuterium, these methods are applicable to other metal hydrides as well. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DEAC04-94AL85000.

4:40pm **VT-WeA9 Characterization of Aluminum Materials Focusing Electron Stimulated Gas Desorption and Its Surface Analysis in Surface Treatment Techniques***, **M. Nishiwaki**, S. Kato,* KEK, Japan

In a hot vacuum environment such as a particle accelerator, gas desorption from a vacuum surface during the operation seriously affects the stability, the quality and the lifetime of the electron or ion beam. In order to adopt vacuum materials and surface treatment techniques to hot vacuum, reported data of thermal outgassing from vacuum surface do not always give established indication for outgassing due to particle irradiation. Therefore it is very important to evaluate gas desorption of the materials and the treatment techniques using energetic particle bombardment. We focused on measurement of electron stimulated gas desorption from aluminum materials mainly and its surface analysis in this study. Four different surface treatment techniques for aluminum materials were carried out to make comparison, that is, machining with oil lubricant and subsequent degreasing (OL), machining with a liquid jet of ethyl alcohol (EL), machining in a gas mixture of argon and oxygen (EX) and machining with corona discharges in the same gas mixture (EXP). In order to measure electron stimulated desorption rates from those surfaces quantitatively, a throughput method was used with a pressure calibrated RGA. The base pressure of the sample chamber was in an order of 10@super -7@ Pa. Electrons from an e-gun were irradiated against the samples at a typical condition of a kinetic energy of 1.5 keV, a current density of 10@super -3@ A/cm@super 2@ at a normal incident and a sample temperature of 27 ° C. Surface characterization of those samples was also done by use of Auger electron spectroscopy with sputter etching. This gives information about depth profiles of atomic compositions in an altered surface layer due to the treatment discussing the relation between the electron stimulated desorption rates and the surface atomic compositions.

Applied Surface Science Division
Room 307 - Session AS-ThM
Gaede-Langmuir Award Address and Quantitative Surface Analysis

Moderator: P.M.A. Sherwood, Kansas State University

9:00am **AS-ThM3 Resolution Enhancement of XPS Spectra by Maximum Entropy Deconvolution**, *S.J. Splinter,* B.C. Research Inc., Canada*;* ***N.S. McIntyre,*** The University of Western Ontario, Canada **INVITED**

Detailed Analysis of XPS spectra is often limited by the resolution available in the measurements. Energy resolution improvement can be achieved in practice by monochromatization of the exciting x-rays and/or by very high energy resolution analysis of the emitted photoelectrons through improved instrumentation. Both of these approaches, however, require expensive high-intensity photon sources. This added cost therefore provides an acute motivation for the development of a reliable computational means for resolution enhancement. In this talk, I will describe a method for enhancing the energy resolution of photoelectron spectra by deconvolution based on the maximum entropy method (MEM). I will first review the theory of deconvolution as applied to XPS and briefly discuss previous work in this area. I will then present the mathematical description of MEM, explaining why this represents a better approach to take, and describe the algorithmic and computational details used to solve the large-scale non-linear constrained optimization problem. Several representative examples of simulated and experimental spectra will be presented.

9:40am **AS-ThM5 Evaluation of Calculated and Measured Electron Inelastic Mean Free Paths**, *A. Jablonski,* Polish Academy of Sciences, Poland*;* ***C.J. Powell,*** National Institute of Standards and Technology

NIST will release a database in 1998 that provides values of electron inelastic mean free paths (IMFPs) for use in surface analysis by AES and XPS. The database includes IMFPs calculated from optical data and measured by elastic-peak electron spectroscopy. IMFPs can also be obtained from the predictive formulae proposed by Seah and Dench, Tanuma et al., and Gries. We present here an evaluation of calculated and measured IMFPs for seven elemental solids (Al, Si, Ni, Cu, Ge, Ag, and Au); these solids were selected because, for each, there were two or more independent IMFP calculations and two or more independent IMFP measurements. For each element, calculated IMFPs have been compared, measured IMFPs have been compared, and calculated and measured IMFPs have been compared. Our preliminary results indicate that the best agreement among the calculated IMFPs (as determined from mean relative deviations with respect to a common fitted curve) is found for Al, Ni, and Ag. Similarly, the best agreement among the experimental values is found for Si, Cu, and Ge, and the best agreement between calculated and measured values is found for Cu, Ag, and Au. We will discuss reasons for the differences found in our comparisons.

10:00am **AS-ThM6 Development of Well Defined Reference Samples for ARXPS Depth Profiling Studies**, ***B.J. Tyler***, *S.J. Hunt,* Montana State University

Quantifying the changes in material composition in the near surface region is important for a wide range of research problems. With inorganic and metallic samples, this information can often be obtained by sputter depth profiling. However, for organic samples, ion sputtering typically destroys the chemical structures of interest before they can be measured. As a result, angle resolve XPS is the preferred method for studying concentration depth profiles (CDP) for polymeric materials and organic thin films. As the interest in organic surfaces has grown, demand for quantitative measures of CPDs for these surfaces has also grown. While qualitative interpretation of ARXPS results is routine, there are many barriers to quantitative calculation of concentration depth profiles (CDPs) from ARXPS results. Many algorithms have been developed for this purpose but determining accurate confidence limits for CDPs, which are calculated with these algorithms, is currently the most significant challenge for quantitative depth profiling with ADESCA. One barrier to assessing the accuracy of CDPs is lack of adequate reference samples. We have evaluated the use of self-assembling monolayers, spin cast polymers, and plasma deposited films for their potential as standards for ARXPS work. The thin films were made on ultra smooth gold and silca substrate. Surface roughness and film thickness have been measured with AFM. ARXPS data for the samples was measured on both a PHI 5600 XPS system and a SSI s-probe. Resulting depth profiles calculated with several algorithms will be presented.

10:20am **AS-ThM7 Trajectory Projection Factor Analysis**, ***D.J. Pocker***, *B.R. York,* IBM SSD

Linear least squares (LLS) analyses of arrays of Auger or ESCA spectra (as from depth profiles, line scans or maps) run into problems when the data does not contain regions with pure spectra for one or more of the compounds. In addition, target factor analysis (TFA) encounters problems when there is not prior knowledege of the profiles for each compound. We present here an eigenanalysis and coordinate transformation method which straightforwardly extracts spectra for the pure compounds along with their associated profiles from arrays with overlapping spectra of up to 4 compounds. In the method, the profiles for the mathematically distinct eigenspectra are plotted against each other, yielding a TRAJECTORY through the orthogonal eigenspace. PROJECTION of this trajectory onto/into a well chosen plane or volume then allows a simple transformation of coordinates to define a non-orthogonal, chemically interesting space. From this, the pure compound spectra and profiles are easily computed. (The limit of 4 is from the graphical nature of the analysis. The concept extends to an arbitrary number of compounds. Also, for favorable 4 compound cases, overlaps as bad as "never fewer than 3" can be treated.)

10:40am **AS-ThM8 Quantitative High-Resolution Imaging with Sputter-Initiated Resonance Ionization Spectroscopy**, ***K.F. Willey,*** Atom Sciences, Inc.*; H.F. Arlinghaus,* Westfälische Wilhelms-Universität Münster, Germany*; T.J. Whitaker,* Atom Sciences, Inc.

The demand for sub-micron lateral analysis, as a result of decreasing material size, has been met by the development of liquid metal ion gun (LMIG) sources capable of achieving spot sizes less than 50 nm. The trade-off however, is the reduction in ion beam current at the sample. Therefore, highly sensitive detection techniques are required. Our technique, Sputter-Initiated Resonance Ionization Spectroscopy (SIRIS), incorporates resonant ionization of sputtered neutral particles with time-of-flight mass detection. The two major advantages this approach has over conventional SIMS are that analysis of neutrals generally increases the detection efficiency by at least two orders of magnitude, and that resonance ionization nearly eliminates mass interferences. Additionally, analysis of neutrals substantially removes matrix effects, which is crucial for quantitative surface analysis. Sputtering is achieved with a gallium LMIG, a mass-filtered microbeam ion gun, and a mass-filtered low-energy sputtering ion gun. Sub-micron lateral resolution and few nanometer depth resolution have been obtained by eroding the sample with the low-energy ion gun while analyzing with the LMIG. In our presentation, we will describe the SIRIS technique and its dynamic range for quantitative analysis and imaging capabilities as they pertain to semiconductor research. In particular, Ge and B depth profiles on near one µm spot size and Cu trace element images obtained from Cd precipitates in CdZnTe films will be presented.

11:00am **AS-ThM9 Quantitative Detection of Metals in Organic Matrices by Laser-SNMS**, ***A. Schnieders,*** *H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany

TOF-SIMS and Laser-SNMS have been established as powerful tools for high sensitive trace analysis of elements in inorganic materials, like alloys and semiconductors. Detection limits for almost all elements are in the range of 10@super 8@ - 10@super 9@ particles/cm@super 2@ of a single monolayer. For many analytical applications comparable sensitivities for the detection of metals in organic matrices are required, e. g. in life sciences. Unfortunately, TOF-SIMS is limited by the low secondary ion yields for metals in these matrices. The sensitivity is several decades lower than for the same metals on semiconductor surfaces. Because of the decoupling of the desorption and ionization processes, the use of Laser-SNMS is a promising approach to get rid of this limitation. Laser-SNMS combines the advantages of ion beam induced desorption with the possibility to optimize the ionization efficiency. For our investigations we applied nonresonant multiphoton ionization allowing a nonselective and highly efficient postionization of sputtered neutrals. As a model system for metals in organic matrices we prepared submonolayer coverages of several metals (Be, Cr, Mn, Fe, Co, Ni, Mo, W) on different polymer foils (polycarbonate, polyimide, and polyvinylidenechloride) by sputter deposition. We used these standards for quantification. Relative sensitivity factors of the respective elements are found to be similar to those for material sputtered from alloys or semiconductors within a factor of 3. The detection limits are in the range of 10@super 8@ to 10@super 9@ particles/cm@super 2@. We also used Laser-SNMS for the identification of the active center of a purple acid phosphatase. Our results demonstrate the detection and identification of single metal atoms in organic macromolecules with an atom concentration down to < 100 ppm. The use of resonant photoionization lowers the detection limits for similar systems by further decades.

Electronic Materials and Processing Division
Room 314/315 - Session EM+PS-ThM

Processing of High K Dielectrics for DRAMs

Moderator: K.R. Milkove, IBM T.J. Watson Research Center

8:20am **EM+PS-ThM1 Growth and Characterization of Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ Thin Films on Si with Pt Electrodes***, **L. Kinder**, I.L. Grigorov, C. Kwon, Q.X. Jia,* Los Alamos National Laboratory*; L. Luo, J. Zhao,* Applied Materials, Inc.

The application of high dielectric constant materials like barium strontium titanate in dynamic random access memories requires the integration of these materials into the existing Si technology. In this study, pulsed laser deposition was used to grow Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ (BST) thin films on Si with Pt electrodes. Through scanning electron microscopy, x-ray diffraction, and electrical characterization, the Pt/BST/Pt capacitor processing on Si has been optimized. BST films on Pt sputtered at high power tends to show high leakage current. However, high leakage current is prevented if the Pt is sputtered at low powers. Low power deposition leads to not only smooth Pt film but also less hillocks. The smoother Pt electrodes allow the BST to grow with greater crystallinity. 150 nm BST on Pt shows a dielectric constant over 400 and dielectric loss of 0.01 at 10 kHz. The quality of the dielectric can be further improved by first depositing a thin seed layer of BST at lower temperatures. We have successfully used 20 nm BST deposited by metal-organic chemical vapor deposition as a seed layer to improve the over all device performance. The influence of interface and of initial nucleation of BST films on the structural and dielectric properties of the thin film capacitors will be also discussed.

8:40am **EM+PS-ThM2 Synthesized Single Crystalline Ba@sub (1-x)@Sr@sub x@TiO @sub 3@ Thin Films for DRAM Application***, **F.F. Feng**,* University of Houston*; C.L. Chen, Z.H. Zhang,* University of Houston, U. S. A.*; Y. Liou, P. Jin,* University of Houston*; W.K. Chu,* University of Houston, U. S. A.*; C.W. Chu,* University of Houston

Perovskite Ba@sub (1-x)@Sr@sub x@TiO@sub 3@ thin films have been synthesized on (001) LaAlO@sub 3@ and (001) SrTiO@sub 3@ substrates with SrRuO@sub 3@ or Pt bottom electrodes by pulsed laser ablation. Extensive X-ray diffraction, rocking curve, and pole-figure studies suggest that the as-grown films are (00l) oriented with single crystalline quality. RBS studies indicate that the epitaxial films have excellent crystalline quality with an ion beam minimum yield of only 2.6 % or less, suggesting that the crystallinity of the as-grown films can be compared with the single crystal silicon. Atomic force microscopy studies indicate that the as-epitaxial films are atomic smooth under the selected growth conditions. The dielectric property measurements show room temperature values of the relative dielectric constant and loss tangent of larger than 750 and 0.005, respectively.

9:00am **EM+PS-ThM3 Scanning Capacitance Imaging for Evaluation of High-k Dielectric Oxide Materials***, Y. Yamaguchi, K.P. Wiederhold, B.D. White, N.E. Wittry, **H.C. Galloway**,* Southwest Texas State University

We have used scanning capacitance imaging to measure the dielectric properties of oxide materials such as BST which have large dielectric constants (high-k). These materials are of interest as potential replacements for the dielectric in memory devices due to their increased capacitance per unit area. Several scanning capacitance methods have been developed using modified atomic force microscopes and they are actively used to measure quantities such as the thickness of SiO@sub 2@ layers or the doping levels across a p-n junction. We will discuss how this technique can be used as a diagnostic tool when applied to the high-k oxides. First, the measurement of the dielectric properties on a local scale may help to identify the causes of failure modes in materials. As an example, we will report on local variations of the dielectric constant observed in films of BST grown by RF planar magnetron sputtering. Second, we have used scanning capacitance to evaluate films of novel oxide materials grown by Dual Ion Beam Sputtering.@footnote 1@ The advantage of Scanning Capacitance Microscopy is that the relative merits of different growth conditions can be rapidly assessed and compared to each other or to a reference standard. This allows us to investigate new materials or deposition conditions without having to form complete devices for analysis. By identifying the most promising growth conditions that yield high dielectric constants, uniform films, and low leakage currents we can speed up the process of testing new growth methods and materials. @FootnoteText@ @footnote 1@P. Perera, R. Selestino, and C.J. Gutierrez, Department of Physics, Southwest Texas State University

9:20am **EM+PS-ThM4 Characterization of Thermal Annealing of Tantalum Pentoxide for High-k Dielectric Applications***, **R.L. Opila**, J.P. Chang, G.B. Alers,* Bell Laboratories, Lucent Technologies

Tantalum pentoxide is being studied as an alternative high dielectric constant material for storage capacitors or gate dielectrics. Since the oxide layers are thin, even for high dielectric constant materials, interfaces between the tantalum pentoxide and other thin film materials can greatly affect device electrical properties. This paper focuses on analyzing the bulk properties of the Ta@sub 2@O@sub 5@ film and the Ta@sub 2@O@sub 5@/TiN interface to assess a new TiN/Ta@sub 2@O@sub 5@/TiN storage capacitor structure that has lower contact resistance and higher specific capacitance than conventional poly-Si based capacitors. The effect of thermal annealing on the electrical performance of the capacitor will be presented. Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS) has been used to characterize the interfacial composition and stoichiometry of tantalum pentoxide deposited by CVD processes at low temperatures. The amount of carbon incorporated in the film during the CVD process decreases with increasing process temperature. Reduced leakage current has been observed as the concentration of carbon in the film increases. Formation of TiO@sub 2@ was observed at the Ta@sub 2@O@sub 5@/TiN interface at an RTA temperature of 450°C. Significant amounts of titanium suboxides are also observed at the Ta@sub 2@O@sub 5@/TiN interface. The imperfect interface is thought to reduce the specific capacitance and increase leakage currents, perhaps through partial reduction of the Ta@sub 2@O@sub 5@. Correlation between the interface chemical states and the electrical performance will be presented.

9:40am **EM+PS-ThM5 Structural Properties of Ultrathin Films of High Dielectric Constant Materials on Silicon***, E. Gusev,* IBM T.J. Watson Research Center*; H.C. Lu, T. Gustafsson, **E. Garfunkel**,* Rutgers University*; G.B. Alers,* Bell Laboratories, Lucent Technologies

The high tunneling rates in ultrathin gate oxides is driving the search for higher-K replacement dielectrics in silicon microelectronics. Ta@sub 2@O@sub 5@ and several other metal oxides are now attracting the attention of the device community. One problem that plagues the use of metal oxides on Si is the formation of an interfacial SiO@sub 2@ layer; such layers limit the capacitance and can degrade the electrical properties of the gate structures. We have examined the composition of interfacial layers of several high dielectric constant oxide systems using high resolution medium ion energy scattering. We find that the interfacial region is best described as neither Si/SiO@sub 2@/metal-oxide nor Si/metal-oxide, but can be viewed as a compositionally graded oxide with a dielectric constant significantly higher than that of pure SiO@sub 2@ (as inferred from electrical measurements). Annealing changes the near-interfacial composition substantially. When post anneal temperatures are kept low, stable composite oxide structures (with physical thickness greater than 7nm) can be obtained that demonstrate good electrical properties and an effective SiO@sub 2@ thickness of less than 2 nm.

10:00am **EM+PS-ThM6 Etching of High Dielectric Constant Materials for DRAMs and Ferroelectric Materials for FeRAMs***, **L.G. Jerde**, A. Cofer, K. Olson, P. Rajora, S.P. DeOrnellas,* Tegal Corporation **INVITED**

The introduction of ferroelectric and high dielectric constant films and their associated metals, barrier materials and adhesion layers for DRAM, embedded DRAM and FeRAM applications are driving some of the most challenging etch requirements in the IC fabrication industry. The specifications resulting from these requirements range from very aggressive profile and critical dimension control, to etch selectivities, contamination and damage, defects and chamber cleaning frequency. Some of the most difficult of these requirements are a result of the design rules that will be used in production for the DRAM applications (i.e., 0.15 m and below). The inherent involatility of the etch products of these materials is another key factor contributing to the difficulty in meeting the requirements. In this paper we will present and discuss the etch requirements for these materials, the reactor technology we use to etch them, selected process and manufacturability results for these materials and future directions for this work.

10:40am **EM+PS-ThM8 Patterning of Reactively Sputtered Tantalum Pentoxide, a High Epsilon Material, by Plasma Etching**, *L.B. Jonsson, F. Engelmark, J. Du, C. Hedlund,* Uppsala University, Sweden*; U. Smith,* Ericsson Components AB, Sweden*; **H.-O. Blom**,* Uppsala University, Sweden

The large size of integrated capacitors is a problem today. The capacitors can easily cover a major part of the total chip area. By using a high epsilon material as the dielectric material in the capacitor the size can be reduced significantly. One very promising candidate is Tantalum pentoxide (Ta@sub2@O@sub5@) which has an epsilon of 25 compared to Silicon dioxide which has 3.9. In order to make integrated capacitors the Tantalum pentoxide must be patterned. We have investigated and optimized dry etching processes for realizing a complete capacitor structure. One process for etching the Tantalum pentoxide on a back contact made of poly-silicon and one process for etching contact holes, in silicon dioxide, down to the Tantalum pentoxide. Data from Reactive Ion Etching (RIE) as well as for Inductively Coupled Plasma (ICP) processes will be presented.

11:00am **EM+PS-ThM9 The High Temperature Platinum Etching Using Titanium Layer**, ***H.-W. Kim**, B. Ju, B. Nam, W. Yoo, C.J. Kang, T.-H. Ahn, J. Moon, M.Y. Lee,* Samsung Electronics, Co., Korea

1. Introduction: It is necessary to use the platinum as a bottom electrode material of the BST capacitor in highly integrated deveces, however, the Pt etching of the fine patterns is difficult due to the inherent non-reactivity of platinum. It is revealed that the Pt etch slope of 80° was attained by O@sub 2@/Cl@sub 2@ chemistry by elevating the substrate temperature up to 160°C. This result is thought to be due to the reaction of O species with Ti layer and analyzed by TEM, XPS and AES. 2. Experimental & Results: As an experimental setup for high temperature etching, the modified chiller using Galden HS260 (B.P.=270°C) was chosen. The oxide 5000Å/ Ti600Å/ Pt 2000Å structure was used and the O@sub 2@/Cl@sub 2@ (O@sub 2@ = 80%) gas was chosen as an etchant combination in MERIE system. The change of the Pt etching profile at 100°C, 130°C, 160°C, respectively was investigated.The Pt etch slope does not depend on the substrate temperature up to the just etch time, the etch slope of the 160°C-sample was about 80° after 100% overetch and the Ti mask was not eroded significantly. It appeared that the titanium mask of 100°C, 130°C samples were eroded considerably, The Pt etching results of 160°C with Ti, TiN and TiO@sub 2@ layer were compared (not shown). TiN and TiO@sub 2@ layer does not help attaining high Pt etch slope even with the thermal heating. From the above result, it is surmised that the change or stabilization of Ti layer through the reaction/diffusion of O atoms during plasma etching plays a major role in attaining the higher Pt etching slope. From the XTEM investigation of the 160°C-etched one, the center of the Ti layer stays crystalline, however, the edge of the Ti layer became amorphous and the oxygen content increased up to more than 50%, by EDX analysis. The XPS analysis of 100-Ti layer showed that the considerable amount of Ti-Ti bond changed to the Ti-O bond during the O@sub 2@/Cl@sub 2@ plasma treatment. The AES analysis confirmed the above phenomena. 3. Conclusions: The etching slope of Pt was improved by the reaction of the mask material with the etching species, not by the reaction of Pt itself. The optimal overetching helps to attain the higher etch slope as long as the Ti mask stays. High temperature processing helped the duration of the titanium mask by activating the reaction of Ti with O-species.

11:20am **EM+PS-ThM10 Removal of Sidewall Re-depositions Formed by Reactive Ion Etching of Platinum for Embedded DRAM Applications**, *H.M. Ranpura, D.H. Butler, **S.P. Beaudoin**,* Arizona State University*; C.J. Tracy, L. Chang,* Motorola Semiconductor Products Sector

Removal of platinum sidewall re-depositions (SRDs) formed due to patterning of electrodes due to reactive ion etching (RIE) for an embedded dynamic random access memory (DRAM) project has been investigated. A serious problem in integrating these devices is the re-deposition of non-volatile etch products onto the pattern sidewall. Removal of these SRDs without damaging other exposed materials is a challenging process. A mixture of argon (Ar) and chlorine (Cl@sub 2@) plasma was used to etch the platinum electrodes. Following the etching step the wafers were processed in an oxygen plasma to remove the photoresist on the wafer. Results are presented for post-ashed wafers that were heated at different temperatures for varying times in different ambients. Following heating wafers were cleaned in aqueous hydrochloric acid (HCl). Results are also presented for ultrasonic cleaning of wafers in HCl.

11:40am **EM+PS-ThM11 Study on Surface Reaction of (Ba,Sr)TiO@sub 3@ Thin Films by High Density Plasma Etching**, ***S.B. Kim**, C.I. Kim, E.G. Chang,* Chung-ang University, Korea

Ferroelectric devices are attractive for dynamic random access memories (DRAMs) applications because of high dielectric constant. Using ferroelectric device structure, manufacturing cell capacitance of highly integrated memory device is possible. Small feature size requires anisotropic etching. Since research of (Ba,Sr)TiO@sub 3@ thin films etching is not widely, we studied on surface reaction of (Ba,Sr)TiO@sub 3@ thin films by high density plasma etching. (Ba,Sr)TiO@sub 3@ thin films were etched with an Inductively coupled plasma (ICP) by varying the etching parameter such as BCl@sub 3@/C@sub 2@F@sub 6@/Ar gas mixing ratio, RF power, and pressure. Etching effect were investigated in terms of etch rate, selectivity. In this study, (Ba,Sr)TiO@sub 3@ etching mechanism was investigated with XPS (X-ray photoelectron spectroscopy) and OES (Optical emission spectrometry) and QMS (Quadrupole mass spectrometry). Ion current density was measured by using single Langmuir probe. Surface of etched (Ba,Sr)TiO@sub 3@ investigated with SEM (Scanning electron microscopy).

Electronic Materials and Processing Division
Room 316 - Session EM-ThM

Compound Semiconductor Surface Chemistry

Moderator: R.S. Gold, University of Michigan

8:20am **EM-ThM1 Air-Stable Sulfur-Based Passivation of III-V Compound Semiconductor Surfaces**, ***C.I.H. Ashby**, K.R. Zavadil, A.G. Baca, P.-C. Chang, B.E. Hammons,* Sandia National Laboratories

Although the surface state density can be greatly reduced by sulfur bonding to III-V surfaces, this improvement is transient due to rapid oxidative loss of S from the surface. We have developed a method for stabilizing the improved properties of the semiconductor surface in the presence of S by stabilizing the S against air-oxidation. We employ a two-step process that forms an air-stable metal-S-semiconductor structure. A monolayer of S is applied by UV photodissociation of sulfur vapor. The sulfided surface is then reacted with a metal salt to form an insoluble metal-S overlayer on the semiconductor. XPS characterization of this overlayer shows the presence of the metal, S, and O in the overlayer. Photoluminescence (PL), and Raman spectroscopies have been employed to characterize the effect of the overlayer on surface-recombination-sensitive properties of the interface. For 7x10@super 16@/cm@super 3@ n-GaAs, a 15-fold increase in PL intensity results with the metal-S overlay, which is double the improvement obtained with S-treatment alone. Unlike photosulfidation or the more conventional sufidation with NH@sub 4@S@sub x@, PL intensity following metal-S overlayer deposition does not degrade rapidly in air at room temperature. Passivation of 1.8x10@super 18@/cm@super 3@ n-GaAs produces a 20-30% increase in PL intensity that is retained after more than 10 months in air. In addition, the PL improvements due to the metal-S overlayer are retained following low-temperature deposition of SiNx dielectric coatings. Application of the metal-S passivation layer to GaAs HBTs followed by SiNx encapsulation has produced an increase in dc current gain from 40 to nearly 100 for 2.5x5 µm devices and from 90 to over 100 for large-area (100x100 µm) devices, consistent with a large reduction in surface recombination in these devices. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

8:40am **EM-ThM2 Development of Surface Morphology During H@sub 2@ Plasma Processing of GaAs(001)**, ***S.W. Robey**,* National Institute of Standards and Technology, US

There is interest in hydrogen plasma etching as a route to low temperature, dry processing for oxide removal from semiconductors. The surface morphology that develops is a determining factor in the success of subsequent device fabrication, making it important to understand surface processes that can influence morphology development during plasma exposure. In situ Auger spectroscopy and RHEED were used in conjunction with ex situ AFM to investigate the development of surface morphology on H@sub 2@ plasma etched GaAs(001) surfaces. Etching of the GaAs, subsequent to the oxide removal, at temperatures above 600 K led to Ga-rich surfaces with a tendency for [11n]-type facet formation. Initial attack on the GaAs surface typically occurred in a localized manner leading to the formation of etch pits. Aligned rows of etch pits are often observed due to preferential etching at mis-cut steps. The preferential attack significantly influences subsequent morphology development. Height-difference correlation functions suggest scaling at small lengths with a roughness exponent in the range of 0.7 - 0.8. A crossover occurs for separations of ~ 30 nm to 60 nm, depending on substrate temperature. The crossover length appears to correlate with typical etch pit dimensions. For larger separations, the slope is much smaller, with some evidence of additional structure in the 100 nm to 200 nm range. Correlations between diffraction and AFM data, connections to continuum models for surface etching including processes such as diffusion, redeposition, etc., and comparison to other experimental work will be discussed.

9:00am **EM-ThM3 Thermal Chemistry and Photochemistry of Organothiols Chemisorbed on GaAs(110)***, **N. Camillone, III**, K.A. Khan, 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, atomic-layer-epitaxy precursor layers, and monolayer adhesives. We have recently begun fundamental studies of the surface chemistry and photophysics of small organothiols [CH@sub 3@SH, (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@] on GaAs. Temperature programmed desorption measurements indicate that each of these species interact strongly with the GaAs surface. The first monolayer of CH@sub 3@SH desorbs near 300 K, compared to approximately 100 K for the second layer, indicating a chemical interaction between the thiol and the surface, despite the fact that the molecule predominantly appears to desorb intact. The behavior of (CH@sub 3@S)@sub 2@ is quite different; the disulfide decomposes upon adsorption (or during the TPD temperature ramp) and desorbs predominantly as CH@sub 3@SCH@sub3@ at approximately 500 K, perhaps as the result of a concerted associative/dissociative desorption process which leaves sulfur at the surface. In addition, we will report on UV photoreaction cross section measurements and photoreaction products for these thiol, sulfide and disulfide compounds. For example, the measured cross section for photodissociation of an annealed (CH@sub 3@S)@sub 2@ monolayer at 193 nm is orders of magnitude smaller than that for CH@sub 3@SH.

9:20am **EM-ThM4 The Surface Structures of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ (001) Films Grown by Metalorganic Vapor-Phase Epitaxy***, **L. Li**,* University of California, Los Angeles*; B.-K. Han, M.J. Bergarney,* University of California, Los Angeles, US*; D. Law, Q. Fu, R.F. Hicks,* University of California, Los Angeles

Strained films of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ were grown on GaAs and InP (001) substrates by metalorganic vapor-phase epitaxy (MOVPE). The film thickness and composition, and the degree of strain were determined by analysis of high-resolution x-ray diffraction spectra. In addition, the large-scale morphology, the atomic structure and the composition of the film surfaces were characterized after growth by low-energy electron diffraction, x-ray photoelectron spectroscopy, infra spectroscopy of adsorbed hydrogen, and scanning tunneling microscopy. All the surfaces immediately following MOVPE are composed of atomically flat terraces that are separated by double height steps. The steps exhibit smooth, gradual undulations along the terrace edges. Close-up images of the terraces reveal a disordered (2x1) or c(4x4) structure, which arises from a random mixture of group V atoms and alkyl groups adsorbed on top of the surface. Annealing in vacuum desorbs the alkyl groups and then the group V atoms, generating a variety of reconstructions at progressively higher group III coverages. Many new reconstructions are observed on these films, including (2x3), (3x2) and other (nx2) unit cells, where n is an odd integer. Evidently, these surfaces do not obey the electron counting scheme that holds for unstrained GaAs (001), and therefore, they may be positively or negatively charged. The structure and properties of some of these new surfaces will be described at the meeting.

9:40am **EM-ThM5 Low Induced Damages Dry Etching of III-V Materials for HBT Applications using ICP in Chlorinated Plasma***, **J.J. Etrillard**, J.F. Bresse, C. Daguet, M. Riet, J. Mba,* CNET, France Telecom, France

Etching of InGaAs and InP in ICP using SiCl4 was studied for HBT application. Low sample temperature was used to minimize the etching isotropy and to reduce the element V desorption. The low ion energy etching process results in a damaged layer thickness of a few angströms. AES results on InP demonstrate a very thin layer of non-stoichiometric material. The nature of the etching mask impacts on the surface contamination: local contamination effects due to sputtering are observed. For such low ion energy processes, the sample preparation before ICP etching is shown to be very important for the surface roughness, as observed by AFM. Various preparation shemes have been investigated, before ICP etching, aiming at a reduction of the surface degradation resulting from ICP etching. It is shown that the best results in terms of roughness and etch-rate are obtained with a silicon nitride mask and a surface oxidation before a wet desoxidation immediatly preceding the ICP etching. An ICP process was used successfully for partly etching the base mesa of HBT structures. No significant difference was observed in terms of induced damages and HBT current gain.

10:00am **EM-ThM6 Variable Substrate Temperature for Precise Growth of II-VI Interfaces***, **Y. Luo**, M. Han, J.E. Moryl, R.M. Osgood, Jr.,* Columbia University

This paper describes the use of variable substrate temperature for the controlled growth of compound semiconductor hetero-interfaces. The investigation uses UHV surface probes to show that choice of surface temperature and temperature ramping during each half of bilayer growth, can lead to a precisely controlled interface composition. The emphasis on the investigation thus far is controlled interface abruptness, composition and crystallinity. The experiment uses sequential dosing of a ZnSe(100) substrate with dimethylcadmium and H@sub 2@S, respectively, in a UHV system. The substrate temperature is controlled by a temperature controller system and may be raised from 100K to 700K at 4K/sec. In situ surface analysis is accomplished with TPD, AES, LEIS and LEED. The experiments showed that, when DMCd was dosed onto a well ordered c(2x2) ZnSe substrate, the composition of surface growth varied dramatically with the substrate temperature. AES and TPD measurements show that this variation is directly dependent on the chemical interaction of the organic ligands at the surface at differing substrate temperatures. For example, within the temperature range from 250 K to 370 K, the Cd growth mode can change from a simple 0.5 monolayer Cd insertion, to a self-terminating one monolayer deposition or even a thick multilayer of Cd with significant Zn depletion near the interface. In the presence of a hydrogen sulfide flux the percentage of sulfur growth at the surface is directly dependent on the surface-coverage of existing methyl groups due to previous dosing of DMCd. Finally we have found that by selection of dosing temperature and the following temperature ramping one can accurately manipulate the interface compsition on a monolayer scale, e.g. a mixture of a half monolayer Zn and a half monolayer Cd, or an abrupt full monolayer of Cd or intermediate layers of Zn@sub 1-x@Cd@sub x@Se@sub 1-y@S@sub y@.

10:20am **EM-ThM7 Effect of Surface Interactions on Band Offsets at Buried Semiconductor-Insulator Interfaces***, **B.R. Schroeder**, S. Meng, M.A. Leskovar, M.A. Olmstead,* University of Washington

Once an interface between two materials is buried, it is generally assumed to be stable. However, when a CaF@sub 2@/Si film is exposed to atmosphere, the interface spacing increases by 1.7 Å and the band offset decreases by 0.5 eV. The mechanism for this modification of a buried interface is not understood. We have investigated the effect of surface exposure on the band offset at a buried CaF@sub 2@/Si(111) interface. Thin films (4-6 monolayers) of CaF@sub 2@, grown by molecular beam epitaxy on Si(111) substrates, were exposed to atmospheric pressure of various atmospheric constituents and the change in band offset was measured by core level photoemission spectroscopy. Exposure to nitrogen had a negligible effect, while exposure to water vapour (+ nitrogen) had the same result as atmosphere. Exposure to oxygen also reduced the band offset, but by a smaller amount. The decrease in band offset was partially reversible upon annealing at 450 °C. Besides the decrease in band offset, exposure to water or atmosphere also leads to the disappearance of the interface photoemission satellite. This may indicate a structural change in bonding at the interface, which in turn would alter the interface dipole. The magnitude of the band offset and decay of the interface satellite scale roughly with the amount of oxygen present in the film. To test this correlation, silicon was deposited at room temperature on (unexposed) CaF@sub 2@/Si(111). The band offset at the lower interface again decreased by about 0.5 eV, but in this case no additional oxygen was observed. This indicates that oxygen is sufficient to change the band offset but not necessary.

10:40am **EM-ThM8 Comparison of Morphology and Interfacial Composition of Pd Ultra-thin Films on 6H- and 4H-SiC at Different Annealing Temperatures***, **W.J. Lu**, D.T. Shi, E. Bryant, A. Burger, W.E. Collins,* Fisk University

Pd/SiC has been applied as a chemical sensor for hydrogen and hydrocarbon gases at high temperatures. The diffusion and interfacial reaction between the thin film and SiC substrate alter the electrical properties of the device. In this work, the morphology and interfacial composition of Pd ultra-thin films on 6H- and 4H-SiC substrates are studied at different annealing temperatures using atomic force microscopy and X-ray photoelectron spectroscopy. The Pd ultra-thin films were deposited by RF sputtering with about 3 nm thickness. The SiC substrates are 3.5° titled, Si-face and n-type 6Hand 4H-SiC, and the Pd thin film deposition and annealing conditions are the same for both samples. The samples were annealed at 100 to 400°C for 30 minutes in air. The Pd ultra-thin films on both SiC substrates have a good uniformity. The morphology of the Pd ultra-thin films on 6H- and 4H-SiC are very similar for unannealed and annealed samples at 100 and 200°C, and the Pd diffusion on SiC has occurred at 200 °C. As the annealing temperature increases, the surface of the Pd film becomes rougher. At 300°C, the Pd islands, 40 to 70 nm in diameter, are found on 4H-SiC substrate by atomic force microscopy. The diameter of Pd islands on 6H-SiC are about 20-40 nm. At 400°C, the irregular shaped holes on the Pd ultra-thin film are formed on 4H-SiC substrate, while the morphology of the Pd thin film on 6H-SiC is unchanged. Using XPS measurements, at 300°C, more Pd on 4H-SiC has reacted with the SiC substrate to form Pd silicates than on 6H-SiC, thus 4H-SiC is more reactive with Pd than 6H-SiC. No significant changes in Schottky barrier height were found for both Pd/6H-SiC and Pd/4H-SiC samples. The relationships between the structural factor in SiC and the behavior of Pd diffusion and reaction on 6H- and 4H-SiC will be presented Keywords: Pd thin film, SiC, atomic force microscopy, X-ray photoelectron spectroscopy.

11:00am **EM-ThM9 Field Emission Studies of BN Overlayers on Various Substrates*, N. Badi*,** *A. Tempez, D. Starikov, A. Bensaoula,* University of Houston*; V.P. Ageev, S.V. Garnov, M.V. Ugarov, S.M. Klimentov, E. Loubnin, V.N. Tokarev,* General Physics Institute, Russia*; K.L. Waters, A. Shultz,* Ionwerks

We have studied electron field emission from BN films deposited on various substrates (flat and tip shaped) by End Hall ion source and electron cyclotron resonance plasma source-assisted physical vapor deposition. The chemical bonding states of B, C, N and the valence band structures were investigated by x-ray photoelectron spectroscopy XPS. Post-growth annealing, thermal processing and surface laser modification effects on the field emission properties were investigated. Thin carbon doped BN films exhibited a turn-on voltage as low as 30 V and a maximum current density of 1A/cm@super 2@. The ield emission nature was verified using Fowler-Nordheim plot studies. A significant difference between the initial I (E)-behavior and that measured during subsequent cycles, with a noticeable stepwise jump of the emission current by orders of magnitude, was observed. Similarly, features in the peak current variation with applied voltage were measured and are probably due to a resonance tunneling emission effect. To that end, the valence band distribution of both the acceptor and donor's energy levels in these BN thin films were investigated under a variety of excitations. In addition, the field emission and conductivity properties of the BN surfaces have been performed using scanning tunneling emission microscopy (STFEM). The total spatial resolution of this technique was as high as a few nm. The experiments were conducted in the emission mode under negative and positive bias. The 3-D surface topography mapping and its correlation to the field emission properties were investigated and the results will be presented and discussed. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061. This material is also based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. REI-247

11:20am **EM-ThM10 Influence of Ammonia Surface Reactions in GaN Chemical Vapor Deposition*, M.E. Bartram,*** Sandia National Laboratories

UHV thermal desorption mass spectroscopy measurements of N@super 15@H@sub 3@ chemisorbed on GaN(0001) have demonstrated that ammonia undergoes both reversible and irreversible decomposition on the surface. Overall, N@super 15@H@sub n@ fragments and surface hydrogen from ammonia dissociation either (I) recombined to liberate N@super 15@H@sub 3@ or (II) decomposed further to enrich the surface with nitrogen. This was accompanied by the desorption of N@super 15@@sub 3@, N@super 15@N@super 14@, N@super 14@@sub 2@, and H@sub 2@ at a temperature below that required for congruent GaN sublimation. These reactions are the "crossroads" for the other important reaction avenues on the surface. Considering case I, production of surface hydrogen from ammonia decomposition suggests that this rate may be sensitive to hydrogen coverage and hence be influenced by the H@sub 2@ carrier gas used commonly in GaN CVD. Case II suggests that in addition to supplying the nitrogen for GaN growth, ammonia decomposition can also lead to the extraction of nitrogen from the surface when the nitrogen coverages are sufficiently high. This catalytic removal of surface nitrogen in the form of N@super 15@N@super 14@ and not N@super 14@H@sub 3@ indicates further that N-H bond formation as an initial step in potential hydrogen etching reactions can be overwhelmed by the tremendous driving force of the NN bond energy (226 kcal/mol). Therefore, while the nitrogen feed to the surface in the form of ammonia is necessary to compensate for congruent GaN sublimation and also contribute to GaN growth, it can also provide a low energy reaction pathway for the removal of nitrogen from a nitrogen enriched surface. This suggests that the overall nitrogen incorporation rate must be well-matched to the Ga deposition rate to maintain the proper stoichiometry and a reproducible overall growth rate. We have also observed that ammonia lowers the temperature for the desorption of TMG from surface defects. This decrease in the TMG-surface bond energy which can also lower the TMG residence time on the surface, suggests ammonia surface reactions have the potential to inhibit TMG reactions during GaN CVD. (Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the USDOE under DE-AC04-94AL85000.)

11:40am **EM-ThM11 Optimization of the Nitridation of Sapphire Substrates Using a Fractional Factorial Designed Experiment*, T.J. Kropewnicki*,** *P.A. Kohl,* Georgia Institute of Technology

Future advances in the performance of wide bandgap microelectronic devices depend on further improvements in the quality of the materials from which these devices are fabricated. Nitridation of the substrate is an important step that promotes the growth of high quality Group III nitride semiconductors; however, very few systematic studies of the nitridation process have been done. Herein, we report on a fractional factorial designed experiment to optimize the nitridation of sapphire substrates for the subsequent growth of GaN by plasma assisted molecular beam epitaxy (MBE). The sapphire substrates were nitridated with hydrazine using a process described elsewhere.@footnote 1,2@ Single replicates of a 2@super4-1@ fractional factorial design were performed. The investigated factors were the pretreatment of the sapphire substrate with a 3H@sub 2@SO@sub 4@ : H@sub 3@PO@sub 4@ etch prior to introduction into the reactor, an in situ H@sub 2@ cleaning step prior to nitridation, the substrate temperature, and the nitridation time. Four center points were included in the design to test for nonlinearity and to yield an estimate of the experimental error. The material properties used to assess the quality of the nitridated surfaces were the nitrogen content of the surface (as measured by x-ray photoelectron spectroscopy) and the surface roughness (as measured by atomic force microscopy). Bulk GaN films were then grown on each of the nitridated sapphire substrates by r.f. plasma assisted MBE. The bulk growth conditions were determined with a separate designed experiment,@footnote 3@ and these conditions were held constant for each of the growths. The influence of the nitridated surfaces on the quality of the bulk GaN films was studied by photoluminescence and x-ray diffraction. The results of this fractional factorial designed experiment as well as their impact on the growth of GaN on sapphire substrates will be discussed. @FootnoteText@ @footnote 1@T. Kropewnicki and P. Kohl, "Hydrazine Cyanurate as a Nitrogen Source for Thin Nitride Film Growth," Journal of Vacuum Science and Technology A, 16 (1), 139 (1998). @footnote 2@T. Kropewnicki and P. Kohl, "Nitridation of Substrates with Hydrazine Cyanurate for the Growth of GaN," Proceedings of the 1998 Spring MRS Meeting, San Francisco, CA, April 1998. @footnote 3@K. Lee and G. May, unpublished.

Magnetic Interfaces and Nanostructures Technical Group Room 324/325 - Session MI-ThM

Magnetic Spectroscopies

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

8:20am **MI-ThM1 Magnetic Characterization from Polarized Soft X-ray Scattering*, Y.U. Idzerda,*** Naval Research Laboratory **INVITED**

With the explosive growth in spin-polarized electron transport studies for spin-tunneling, spin-transistor, and magnetoresistive device applications, the importance of layer switching, interfacial magnetic roughness, and magnetic domain correlation is becoming increasingly apparent. Since the spin conductance of a magnetic heterostructure is controlled by the relative orientation of the magnetic moment directions of the component layers on a local scale (within a few spin mean-free-paths), quantifying these mechanisms on this length scale would be very advantageous. Combining magnetic circular dichroism and resonant x-ray scattering, soft x-ray resonant magnetic scattering (XRMS) has a demonstrated capability to determine the order of layer switching, extract parameters which independently characterize the magnetic and chemical roughness of an interface, and statistically quantify magnetic domain correlations. Recent results for CoFe/Cu/SiN3/Si thin films grown with different Cu buffer layer thicknesses show conclusively from both the perpendicular roughness parameters and the in-plane correlation lengths that the interfacial magnetic roughness is much smoother than the interfacial chemical roughness. In Co/Cr/Co trilayer structures, angle and magnetic field dependent XRMS scans used in conjunction with MCD element-specific magnetic hysteresis loops are used to statistically determine that magnetic domains are vertically anti-correlated (preferrentially anti-aligned), indicating the presence of interlayer anti-ferromagnetic exchange coupling.

9:00am **MI-ThM3 Magnetic Structure of Cr Layers in Fe/Cr(001)Superlattices from X-ray Magnetic Dichroism***, **F. Perjeru**, M.M. Schwickert, W.J. Antel, T. Lin, G.R. Harp, M.A. Tomaz,* Ohio University*; W.L. O`Brien,* SRC Madison, Wisconsin

Element-specific magnetometry is used to determine the magnetic moments of Fe and Cr in Fe/Cr(001) superlattices as a function of Cr thickness from 0-50Å, using x-ray magnetic circular dichroism (XMCD) and x-ray magnetic linear dichroism (XMLD). XMCD and XMLD are sensitive to the average magnetization, , and average of squared magnetization,, respectively. High quality Fe/Cr(001) multilayers are prepared by sputter epitaxy and several AF coupling peaks between Fe layers are observed in these films. If antiferromagnetism is present in the Cr layer, it is expected that will be enhanced relative to , that is @sr@ (this assumes layer antiferromagnetism in the Cr with 180° alignment of atom-thick Cr layers). Comparatively, roughness at the experimental Fe/Cr interface might cause frustration which could suppress the antiferromagnetism in the Cr. From measurements of XMCD and XMLD from sputter deposited films, it was found that the Cr atoms have net spin polarization only near the Fe/Cr interface and @sr@ = . This leads to the conclusion that the Cr layers are mainly paramagnetic in the present multilayers, at room temperature. Further experiments are underway to repeat these measurements at 100K, where the tendency to antiferromagnetism within the Cr layer may be enhanced. Both room temperature and low temperature results will be presented.

9:20am **MI-ThM4 On the Nature of Resonant Photoemission in Gd***, **J.G. Tobin**, K.W. Goodman,* Lawrence Livermore National Laboratory*; S.R. Mishra, W.J. Gammon,* Virginia Commonwealth University*; T.R. Cummins, G.D. Waddill,* University of Missouri, Rolla*; G. van der Laan,* Daresbury Laboratory, England, UK

The phenomenon of "resonant photoemission" occurs when, in addition to a direct photoemission channel, a second indirect channel opens up as the absorption threshold of a core level is crossed. A massive increase in emission cross section can occur, but the nature of the process remains clouded. Is it truly "resonant photoemission" or merely the incoherent addition of a second emission channel? Using novel magnetic linear dichroism in photoelectron spectroscopy experiments and computational simulations, we can now clearly demonstrate that temporal matching of the processes as well as energy matching is a requirement for true "resonant photoemission." The photoemission of 4f and 5p electrons from rare-earth metals and their compounds is strongly enhanced when the photon has just enough energy to excite a 4d electron to an unoccupied 4f level, leading to a process called "resonant photoemission". In a generic picture, the indirect channel of the resonant photoemission is interpreted as due to a process where a 4d electron in the initial state is first excited to the unoccupied 4f level, forming a tightly coupled, bound intermediate state, 4d core hole plus 4f electrons. Then a decay via autoionization occurs into the final state, thus producing a final state indentical to that obtained by a direct photoemission process for the ejected electron. The transition rate is greatly enhanced if the excited state decay is by a Coster-Kronig or a super-Coster-Kronig process. The key question is whether these processes are coherent or incoherent: should the overall intensity be treated as a squaring of the sum of the amplitudes (coherent) or summing of the squares of the amplitudes (incoherent)? A true "resonant photoemission" process should be coherent, involving interference terms between the direct photoemission and indirect photoemission channels. Possibly, incoherence would give rise to the loss of photoemission characteristics in the process, with a domination of auger-like properties. To this problem we have applied the new photoelectron spectroscopy technique of magnetic linear dichroism in angular distributions (MLDAD). This technique is related to but distinct from the techniques of magnetic xray circular dichroism (MXCD) in photoelectron spectroscopy and xray absorption. The key is that while large dichroic effects in ferromagnets can be observed with MXCD-photoemission and MXCD-absorption, the large MLDAD effects in ferromagnets is solely a photoemission, not an absorption-driven, process. This is because the chirality which gives rise to magnetic sensitivity is due to the vectorial configuration in MLDAD as opposed to the intrinsic chirality of circularly polarized xrays in the MXCD techniques. In absorption, where there is an essential averaging over all emission angles, the vectorial chirality is lost. Thus, MLDAD is the perfect measurement to distinguish between photoemission and absorption processes. Angle-resolved photoemission in a magnetic system should show an MLDAD effect: xray absorption and thus auger emission will show no MLDAD effect. It is this test which we have applied to the "resonant photoemission" of the Gd5p and Gd4f emissions.

10:00am **MI-ThM6 Combined Spin Polarized Photoemission and Inverse Photoemission of Rare Earth Surface States***, **T. Komesu**, C. Waldfried, P.A. Dowben,* University of Nebraska, Lincoln

The surface of gadolinium has been a subject of much controversy over past years, as to what extent spin mixing and/or Stoner-like exchange coupling are the predominant ingredients of magnetic ordering. The contention is stimulated by the complication that the Gd(0001) surface state is located in the direct vicinity of the Fermi level. For strained Gd(0001) grown of Mo(112), the situation is far worse.@footnote 1@ The surface state is composed of partially occupied spin majority and minority states that extend across the Fermi level into the unoccupied region. Consequently, the magnetic and electronic structure of the Gd(0001) surface cannot be studied by a single experimental technique. Rather the two complementary techniques of photoelectron spectroscopy (PES) and inverse photoemission spectroscopy (IPES) are necessary for a comprehensive investigation of the Gd(0001) surface electronic structure. In this work, we study the surface magnetic structure of strained Gd(0001) through a combination of spin-polarized PES, and spin-polarized IPES. We also find that oxygen antiferromagnetically aligns the surface for strained Gd(0001) which is distinctly different from the case of unstrained Gd(0001).@footnote 2@ @FootnoteText@ @footnote 1@C. Waldfried, T. McAvoy, D. Welipitiya, E. Vescovo and P. A. Dowben, submitted; C. Waldfried, T. McAvoy, D. Welipitiya, P. A. Dowben and E. Vescovo, Europhys. Lett. (1998) in press @footnote 2@D. N. McIlroy, C. Waldfried, D. Li, J. Pearson, S. D. Bader, D. -J, Huang, P. D. Johnson, R. F. Sabirianov, S. S. Jaswal and P. A. Dowben, Phys. Rev. Lett. 76, 2802 (1996)

10:20am **MI-ThM7 X-ray Dichroism Studies of Induced Magnetism in Magnetic Multilayers***, **G.R. Harp**, M.A. Tomaz, W.J. Antel, M.M. Schwickert, T. Lin, F. Perjeru,* Ohio University **INVITED**

X-ray magnetic circular dichroism (XMCD) and linear dichroism (XMLD) are applied to study the element-specific magnetization in Fe/TM(001) superlattices (here TM = V, Cr, Co, Ni, Nb, Mo, Ru, Rh, Pd, Ta, W, Pt). Within the Fe layers (5-20 Å thickness) we observe a wide variety of behaviors, from strong enhancement to complete suppression of the magnetic moment. The details depend on the spacer material and the crystal structure of the superlattice (bcc, fcc, or hcp). The real power of x-ray dichroism, however, is seen in studies of the spacer layer moments, which are often quite small. Various behaviors are observed depending on the spacer material. For ferromagnetic elements (Ni, Co) a strong moment enhancement is sometimes observed (Ni) or sometimes not (Co). For nonmagnetic elements, the induced magnetization may be parallel or antiparallel to that of the Fe. This induced magnetic moment may be confined to the interface region (e.g. Cr), may decay slowly toward the layer interior (e.g. V), or may be almost ferromagnetic, in the sense that the average moment per atom is constant over a range of thicknesses (e.g. Pt). Additionally, x-ray magnetic LINEAR dichroism can probe antiferromagnetic arrangements within spacer layers. As an example, XMLD is applied to the Fe/Cr system to search for commensurate antiferromagnetism within the Cr layers.

11:00am **MI-ThM9 A Controversy Over the Magnetic Structure of Mn Overlayers on Fe and the Role of Oxygen Impurities@footnote 1@***, **S. Banerjee**,* University of Wisconsin, Milwaukee*; W.L. O'Brien,* University of Wisconsin, Madison*; B.P. Tonner,* University of Wisconsin, Milwaukee

The magnetic coupling across the Fe-Mn interface for ultrathin films of Mn grown on Fe has recently been the focus of both experimental and theoretical research efforts, but without substantial agreement. For example, experimental results claim both parallel@footnote 2@ and antiparallel@footnote 3,4@ magnetic coupling between a submonolayer Mn film and the Fe substrate. This disagreement is made even more interesting by a theoretical analysis which shows that the interlayer magnetic coupling between Mn and Fe is very sensitive to both lattice spacing and valence band structure.@footnote 5@ In an effort to better understand the interface magnetic coupling of this model system we have made a series of x-ray magnetic circular dichroism (XMCD) measurements on the Mn-Fe interface for different Mn coverages, on Fe substrates with both the fct and bcc crystal structures. In addition we investigated the effects of small exposures to oxygen on the magnetic order and coupling for coverages up to one monolayer. The Mn/Fe system is extremely reactive, and shows changes in magnetic state with exposures times as low as 10 minutes at 2 X 10@super -10@ Torr. Our findings show that the chemical state of Mn has a tremendous effect on the magnetization at the Fe-Mn interface while the in plane lattice constant and crystal structure do not. The effect of oxygen exposure is to ferromagnetically align the Mn atoms with an orientation antiparallel to the Fe. The intrinsic magnetic state of Mn on Fe, found by extrapolation to zero exposure to contaminating gases, is that of zero magnetic moment at room temperature. @FootnoteText@ @footnote 1@Work supported by the National Science Foundation DMR and performed at the Wisconsin Synchrotron Radiation Center. @footnote 2@S. Andrieu et. al., Phys. Rev. B 57, 1985 (1998). @footnote 3@O. Rader, W. Gudat, D. Schmitz, C. Carbone, and W. Eberhardt, Phys. Rev. B 56, 5461 (1997). @footnote 4@J. Dresselhaus et. al., Phys. Rev. B 56, 5461 (1997). @footnote 5@ R. Wu and A.J. Freeman, Phys. Rev. B 51, 17131 (1995).

11:20am **MI-ThM10 Morphology of Mn Films on Fe(001)@footnote 1@*,* *A.D. Davies,*** *D.T. Pierce, J.A. Stroscio, R.J. Celotta,* National Institute of Standards and Technology

Manganese and iron thin film structures have shown promise for studying indirect exchange coupling and for investigating novel magnetic thin film systems. As a function of temperature and stress, Mn has a large variety of structural and magnetic states, so it is particularly important to fully characterize the structure in these films to understand the magnetic behavior. Here we report on scanning tunneling microscopy (STM) measurements of epitaxial Mn films up to ~10 atomic layers grown on Fe(001) at 155 ± 10 °C. The film growth and structure varies dramatically with film thickness and exhibits a range of unusual spatial inhomogeneities. At this growth temperature, the growth is nearly layer-by-layer and shows a decrease with thickness in the island density of ~25 times. Concurrent with this length scale change, the island shape changes from facets along directions to oriented facets. While the atomic-layer height for submonolayer films is difficult to define due to electronic differences, the atomic step height of the second Mn layer is 1.44 ± 0.07 Å and surface step heights of all subsequently thicker films are 1.61 ± 0.03 Å. For films beyond ~2 atomic layers, curious small regions are observed that are a fraction of an atomic step high. The height, shape, frequency, and location of these regions vary with film thickness. The film structure is markedly different in the vicinity of steps on the Fe substrate at almost every coverage. This difference and other observed aspects of the growth suggest that the growth is very sensitive to local stress. @FootnoteText@ @footnote 1@ Supported in part by the Office of Naval Research.

11:40am **MI-ThM11 Light Scattering Cross Section for Mode Crossing of Spin Waves in Magnetic Films*, F. Nizzoli,*** University of Ferrara and INFM, Italy*; J.M.V. Ngaboyisonga,* Makerere University, Uganda*; L. Giovannini,* University of Ferrara and INFM, Italy

The dispersion curves of spin waves in magnetic films show a typical behavior as a function of the surface wave vector, film thickness and in-plane propagation angle, i.e. mode repulsion between the surface mode and bulk modes. The purpose of this work is to study theoretically the Brillouin light scattering (BLS) intensity from spin waves versus the surface wave vector Q in case of mode repulsion in a magnetic film of thickness d, under the condition Qd nearly equal to 1. In such a case both dipole and exchange interactions are equally important and must be included. The calculations, for a 85 nm thick iron film, are performed within the macroscopic partial waves approach of Rado-Hicken and Cochran-Dutcher, based on the solution of the Landau-Lifshitz equation of motion of the magnetization with the proper boundary conditions. It is found that the BLS cross section shows an antiresonant behavior close to the gap between the modes. We have investigated the physical meaning of this behavior by analyzing the different contribution of the partial waves to the cross section . For Q below the gap three relevant partial waves interfere destructively, while the opposite occurs for a wave vector above the gap. The interference effects, responsible for the Fano-type antiresonant behavior of the total scattering intensity, are explained in terms of a sudden change of the dynamic magnetization across the film, when mode repulsion occurs. The effect of the magnetic anisotropy on the antiresonant behavior of the BLS cross section is also investigated.

Manufacturing Science and Technology Group
Room 317 - Session MS-ThM

Sensors and Support Technology

Moderator: B. Van Eck, SEMATECH

9:00am **MS-ThM3 RF Monitoring of PECVD Tools in a Manufacturing Environment*, M.B. Freiler,*** IBM

The use of RF monitoring systems for plasma enhanced chemical vapor deposition (PECVD) tools in an advanced microelectronics production environment is discussed. Data obtained from the measurement of RF current and voltage at the input to the process chamber provides valuable process information that is unavailable from data recorded using traditional process control techniques, such as RF forward and reflected power. RF current and voltage data is presented for silicon oxide and nitride films deposited in commercial PECVD reactors. The application of this data to improvement of the periodic chamber cleaning process with the goal of reducing gas emissions and chamber contamination will be shown. In - film wafer contamination measurements showed an improvement of 10 X in number of particles when the improved clean was implemented. RF measurements have also been used to improve the effectiveness of post - clean chamber seasoning, by giving an indication of the completion of the seasoning. Inadequate seasoning will result in increased variability of film thickness and stress. Changes in RF current and voltage during the deposition process give an indication of this increase in variability. Finally, the application of RF measurements to reactor matching will be discussed; RF signal strength of different reactors running the same process can be compared in order to understand and control performance differences between the reactors.

9:20am **MS-ThM4 Advances in Broadband RF Sensing for Real-time Control of Plasma-Based Semiconductor Processing*, C. Garvin,*** *D.S. Grimard, J.W. Grizzle,* The University of Michigan

Ever shrinking geometries are putting heavy pressure on sensor systems to provide adequate process knowledge for control and diagnostics. Plasma processing specialists in industry and academia have recognized that a substantial amount of information about the plasma state should be contained in the RF signal (13.56 MHz) and its harmonics. On the surface, making measurements for control purposes should be straightforward, and the real work should lie in making the connections (mathematical models) between measurements and key plasma quantities. Unfortunately, this is not the case. Work reported in this area from major University and Government research facilities, as well both US and Japanese chip manufacturers, has shown disappointing results and revealed that the RF sensing problem itself is non-trivial. An approach which has shown promise is `broadband sensing', a novel sening method based on the Resonance Probe used in ionospheric physics. The goal of the broad band RF work is to create a diagnostic with much greater signal to noise ratio, and much higher sensitivity to the plasma state and its environment than standard RF sensing. The idea is to scan the plasma with a very low wattage, broad band RF signal from 100 MHz to 1 GHz, measuring the reflected signal. In a typical scan, the large amount of data taken over a wide range of frequencies provides redundancy and enhances the signal to noise ratio of the sensor. Preliminary work has shown this sensor to have favorable performance when compared to standard RF sensing. We will present novel results of a non-intrusive implementation of the sensor.

9:40am **MS-ThM5 NOVA In-Line CMP Metrology and Its Use for Lot-to-Lot Process Control*, T.H. Smith,*** Massachusetts Institute of Technology*; S.J. Fang, J.A. Stefani, G.B. Shinn,* Texas Instruments*; D. Boning,* Massachusetts Institute of Technology*; S.W. Butler,* Texas Instruments

The use of in-line metrology with run by run (RbR) process control is becoming a means to meet the future demands on improved processing quality without sacrificing throughput. This control will become critical for large variation processes such as chemicalmechanical polishing (CMP). In response to this, other works have described the use of the NOVA in-line CMP metrology system for use in RbR process control. This work describes a similar system, but focuses on quantifying 1) the quality of measurements obtained from the NOVA system, 2) improvements gained by simple RbR control of post-polish patterned wafer thickness over fixed-time polishing and pilot wafer control, and 3) the increases in throughput using an in-line measurement and control system. The results of a gauge study of the NOVA system and a 600 wafer RbR control experiment performed at Texas Instruments, Inc. are discussed. The variability of the system is shown to be well within standard requirements. The reliability of the system over the 600 wafer experiment was very good. The NOVA measurements are shown to correlate well with ex-situ measurements. The 600 wafer RbR control experiment indicates that even a simple control approach provides a 25% improvement over the fixed-time approach. The results demonstrate that controlling directly on patterned wafers provides a 23% improvement over control using pilot wafers. The experiment shows a 25-40% improvement in throughput using the system. The number of cleans were reduced by 0-66% (depending the number of look-aheads and amount of re-work) and ex-situ measurements were eliminated, indicating significant cost of ownership reductions.

10:00am **MS-ThM6 In Situ CD Measurement during Post Exposure Bake***,* ***R.H. Krukar,*** Bio-Rad Semiconductor*; N.T. Sullivan,* Digital Semiconductor*; S.L. Prins, J.R. McNeil,* Bio-Rad Semiconductor

As critical dimensions are reduced below 0.18 micron, post exposure bake is emerging as a critical and controllable process. Direct correlations between bake times and line width have been reported. We built an in-situ post exposure bake sensor and monitored the critical dimensions of a SRAM pattern as it baked. The data indicates that production of an accurate in-situ PEB monitor is possible.

10:20am **MS-ThM7 Process Environment Monitoring of Plasma Etching for Advanced Process Control***,* ***H. Enami****, A. Kagoshima,* Hitachi, Ltd., Japan **INVITED**

The development of 0.18um process is our current target. Some equipment, at present, cannot meet the requirements from the process (e.g. Selectivity, uniformity, aspect ratio, etc., in dry etching). Considering the facts: (1) Physical limitation against the countermeasures in equipment (2) Decrease of Overall Equipment Effectiveness due to increasing QC time, we suggest quick installation of advanced process control (APC) system such as In-Situ control. To make the best use of In-Situ Control, following 3 steps are necessary. (1) To find useful methods and instruments for process condition analysis. (2) To make digital network among instruments for analysis and to reduce sampling period (less than 1 sec./time) and the prices of those instruments. (3) To find a correlation between monitoring data and process condition or results. Firstly, In-Situ data comparison between Plasma Probe Data and RF Impedance (RFIM) Data shows that RFIM is more useful monitoring method than Plasma Probe for unstable plasma discharge and fluctuating process condition. Secondly, Plasma diagnostics by Plasma Optical Emission Spectroscopy (OES) per sub-micro-sec shows that Pulsed-Plasma-Discharge contributes to improve etching uniformity and control the quantity of etchant. Quadrupole Mass Spectrometry (QMS) is also useful for the same purpose. Comparing OES and QMS, OES is useful for short life species in plasma, on the other hand OMS is for reacted species or products. Both are necessary as In-Situ-Monitoring. In dry etching (SiO@sub 2@ film) process, for example, the combination of OES and RFIM for Gas flow rate and RF Power control contributes to reduce the dispersion of Selectivity among wafer to wafer in a batch to 25% of it without control. This data shows the advantage of In-Situ Control by simple, convenient and high-speed sensor. Then we have began the development of process control system using RFIM, OMS, OES allowing more than one time feedback per second.

11:00am **MS-ThM9 Improvement of Process and Equipment Performance Using Online and Real Time Optical Emission Spectroscopy***,* ***D. Knobloch,*** Siemens Microelectronics Center GmbH & Co. OHG, Germany*; F.H. Bell,* Siemens AG, Germany*; J. Zimpel,* Fraunhofer Institute, Germany*; A. Steinbach,* Siemens Microelectronics Center GmbH & Co. OHG, Germany

The semiconductor industry is continually driven towards the use of larger wafers (200 mm and larger) and smaller device dimensions (0.18 mm). More and more sophisticated technologies are necessary to improve overall production performance and reduce manufacturing costs. Intelligent process and equipment control applied to plasma processing is an excellent candidate to improve productivity, and thus profitability. We use optical emission spectroscopy to characterise etching processes for 64Mbit DRAM fabrication by in-situ analysis of plasma conditions. Parameters to be optimised include: increased wafer throughput and wafer yield, reliable processes, reduction of monitor wafers, optimisation of cleaning procedures. Four MxP@super +@ oxide etch chambers mounted on a Centura platform are equipped with optical multichannel analysers (200 - 950nm). The dynamic evolution of the spectra can be recorded every 20msec during wafer processing. The spectrometers are coupled to the etch chambers via the fab host computer allowing in-situ and real time process and equipment control. Intelligent data reduction techniques, such as principal component analysis (PCA), are used to extract process and equipment related wavelength ranges. Every process parameter, such as pressure, power and gas flows, shows a typical optical signature. Therefore, the cause of process variations can be determined. Furthermore, even without variation in the external parameters, the plasma processes are plagued by process drift phenomena: the process performance (e.g. etch rate, uniformity, selectivity) varies continually as a function of time. These phenomena are linked to the chemistry occuring at the reactor walls and the influence of thin films deposited by the plasma. These drifts can be correlated to changes of certain wavelength ranges in the optical emission spectra. Major benefits of this technique are early process fault detection and optimisation of chamber cleaning cycles. @FootnoteText@ The presented work was part of a project funded by the saxonian department of economy (SMWA), project number: PT2648.

11:20am **MS-ThM10 Multivariate Spectral Analysis of Optical Emission Spectroscopy for use in Low-Open Area Endpoint Detection***, D. White,* ***B. Goodlin****, A. Gower, D. Boning, H. Sawin,* Massachusetts Institute of Technology*; T. Dalton,* Digital Equipment Corporation

As device dimensions continue to shrink, the need for tighter control of semiconductor processes is increasing. In particular, 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. Many sensors have been utilized for the purposes of determining endpoint including optical emission spectroscopy(OES), laser interferometry, optical emission interferometry, mass spectrometry, and rf impedance monitoring, but OES is the most widely used sensor. Traditional endpoint algorithms using OES observe only a few selected wavelengths corresponding to major product and reactant species, thus utilizing only a small fraction of the data provided by OES. For instance in an oxide etch process, using C@sub 2@F@sub 6@, we might follow the emission lines corresponding to a reactant species C@sub 2@ (e.g. 516 nm) and a product species SiF (e.g. 440 nm) during an etch process. Endpoint would be indicated by an increase in the ratio of the C@sub 2@ line intensity to the SiF line intensity. Since both lines are changing in intensity at endpoint we say that these lines are correlated or covarying. The OES spectrum, however, consists of a number of other emission lines which also correspond to reactant and product species, including many more lines corresponding to the many different excitations of C@sub 2@ and SiF. All of these lines have correlated changes that occur at endpoint, so by throwing away all of the spectra except a few spectral lines, the traditional endpointing algorithms do not take full advantage of all of the information available, resulting in a lower signal to noise ratio than that resulting if all of the lines were kept. In this paper, we examine the use of a multivariate technique called principal component analysis (PCA) which utilizes the entire OES spectrum and thus demonstrates superior signal to noise over the traditional univariate methods. We then demonstrate the technique for real-time endpoint detection in an industrial oxide contact etching process with low open areas (~1%). Lastly, implementation issues such as adjusting for process drift due to window fogging and PCA model validation are discussed.

11:40am **MS-ThM11 Simulations of the Performance of Novel Ion Current Sensors***,* ***M.A. Sobolewski,*** National Institute of Standards and Technology

To obtain optimal results from plasma processing, the properties of ions and neutrals incident on the substrate must be carefully controlled. If sensors for the relevant properties of the ions and neutrals were available, they could be used to detect process drift and equipment malfunctions, diagnose their origin, and take correction action, if needed. One particularly important parameter to monitor is the total ion current at the substrate. Recently, a method has been demonstrated for using external, radio-frequency (rf) electrical measurements to monitor the ion current at an electrically insulating or conducting wafer during processing by a high-density plasma.@footnote 1@ The rf signals are generated by the rf bias power which is normally applied to wafers. There is no need for any probe to be inserted into the reactor or for any additional power supplies which might perturb the plasma. At low rf bias frequencies (0.1-1 MHz) ion currents measured by this technique agree well with dc measurements of the ion current, but they agree less well at higher frequencies.@footnote 1@ In this work, this disagreement was investigated using a fluid model of the sheath region of high-density plasmas. Simulations show that, as the rf frequency approaches the ion plasma frequency at the edge of the sheath, the ion current at the electrode varies strongly with time during each rf period. Under these conditions, the rf measurement of ion current differs from the time-averaged value of the ion current. The simulations are used to characterize the error in the rf measurement technique and to suggest new rf methods which more accurately determine the time-averaged ion current. @FootnoteText@ @footnote 1@M. A. Sobolewski, Appl. Phys. Lett. 72, 1146 (1998).

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS-ThM

Nanoscale Patterning and Modification

Moderator: J.F. Wendelken, Oak Ridge National Laboratory

8:20am **NS-ThM1 Fabrication of Nanometer Size Photoresist Wire Patterns with a Silver Nanocrystal Shadowmask*, S. Choi*,** *K.L. Wang,* University of California, Los Angeles*; M. Leung, G. Stupian, N. Presser,* The Aerospace Corporation*; S. Chung, G. Markovich, S. Kim, J.R. Heath,* University of California, Los Angeles

We propose a new method of fabricating precisely defined nanometer size photoresist wire patterns by exposing electron beams onto silver(Ag) nanocrystal wires which have already been deposited on photoresist film. Ag nanocrystals linked with organic ligands were fabricated first using an organically functionalized Ag nanocrystal technique. Arrays of high aspect ratio wires formed spontaneously at the air/water interface when these Ag nanocrystals were dropped onto water. Ag nanocrystal wire structures were then transferred onto the polymethyl methacrylate(PMMA) coated substrates by the Langmuir-Blodgett lift-off process. To prepare a thick Ag nanocrystal shadowmask, a second monolayer of Ag nanocrystal wires was added to the previously deposited monolayer. The occupied areas by organic ligands between the nanocrystals in the wire decreased through a metallization process in air. Monte Carlo simulation was done to estimate the electron stopping effectiveness for the Ag nanocrystal shadowmask at low voltages. Low energy electron beam exposure resulted in numerous 50nm wide wire patterns on photoresist film. The wire patterns were defined in the photoresist material by spatially selective electron beam exposure on the Ag nanocrystal wire shadowmask. The wire patterns on photoresist film can be used for pattern transfer to many different substrates by subsequent selective etching for use in device fabrication. Our new method therefore enables rapid and low cost fabrication of quantum wire structures.

8:40am **NS-ThM2 Fabrication and Structuring of Ordered Two-Dimensional Nanopore Arrays in Anodic Alumina*, A.P. Li,*** *F. Mueller, A. Birner, K. Nielsch, U.M. Goesele,* Max-Planck-Institute of Microstructure Physics, Germany

We will describe the fabrication of nonlithographic nanopore arrays in anodic alumina with areal pore densities in the 6*10@super 8@ - 5*10 @super 10@ cm @super -2@ range, and the lithographic structuring of the arrays for potential applications in photonic crystal. A two-step anodization process was used to oxidize aluminum in oxalic, sulfuric, and phosphoric acid solutions. Self-organized hexagonal pore arrangements were formed in the end of the first anodization process. After removing the irregular upper part, the densely ordered pits in the bottom of anodic layer act as natural masks, and the nanopore arrays were fabricated by the second anodization process. Perfect ordered pore arrays were obtained within domains of a few micrometers, which are separated from neighboring domains with different orientation of the pore lattice by grain boundaries, i.e., the nanopore arrays show polycrystalline structure. The pore distance can be controlled by changing the anodic electrolyte and voltage. The ratio of pore diameter and wall thickness can be adjusted by chemical etching after anodization. The structural characteristics make the ordered porous alumina a potential two-dimensional photonic crystal material for the visible to ultra-violet light range. Although they are polycrystalline, these structures are expected to exhibit interesting photonic crystal properties analogous to electronic properties of polycrystalline semiconductors. For optical transmission measurements, light has to be coupled in perpendicular to the pore arrays and to traverse a well defined number of pore layers. For this purpose we have developed a lateral structuring technique that allows to remove the porous alumina precisely yielding vertical walls. Bars of porous alumina which are 100-400 µm wide, 100-300 µm high and several mm long have been prepared. The achieved samples are well suited to investigate the optical properties of these structures with light traveling perpendicular to the pore arrays.

9:00am **NS-ThM3 Chemically Assisted Ion-Beam Etching of Submicrometer Features in GaSb-based Quantum Wells*, G. Nagy,*** *R.U. Ahmad, M. Levy, R.M. Osgood, Jr.,* Columbia University*; M.J. Manfra, G.W. Turner,* Massachusetts Institute of Technology

GaSb-based semiconductor systems are of interest because of their potential applications in advanced microelectronic and optical devices. For example, GaSb-based materials have been used for the fabrication of resonant interband tunneling devices, as well as high performance laser diodes, and midinfrared photodetectors. Anisotropic, high-resolution dry etching is a desirable processing technology for device fabrication in this semiconductor system. Here, we have used electron beam patterning and chemically assisted ion beam etching to fabricate structures down to 200 nm in diameter in GaSb and in GaInAsSb/AlGaAsSb multiple quantum well material. The chemically assisted ion beam etching was performed with chlorine as the reactive gas and Ar@super +@ ions of 400-900 eV energy. With the GaSb substrate, the Cr masks used to fabricate the features exhibited good etch selectivity and smooth, highly anisotropic structures were realized. The measured etch rates of GaSb were successfully fitted to a model of chlorine-based chemically assisted ion beam etching that assumes the formation and desorption of trichloride etch product species. With the GaInAsSb/AlGaAsSb multiple quantum well material, the chemically assisted ion beam etching provided highly anisotropic pattern transfer using Cr as the mask material. Efforts are underway to examine the dependence of etch damage on incident ion energy for 200-1000 nm diameter features in the multiple quantum well material using photoluminescence spectroscopy at 4K.

9:20am **NS-ThM4 Nanometer-scale Sputter-Induced Rippling of the SiO@sub2@ Surface Characterized with Real-Time X-ray Scattering*, C.C. Umbach,*** Cornell University*; R.L. Headrick,* Cornell High Energy Synchrotron Source*; B.H. Cooper, J.M. Blakely,* Cornell University*; E. Chason,* Sandia National Laboratories

Certain advanced technologies (quantum wires, dots, etc.) may require surfaces with periodic topographic modifications to produce desirable length scales during fabrication. The formation of ripples on the surfaces of materials during ion sputtering has been known for decades and represents a potentially useful type of periodically modified substrate. In this paper we report on forming ripples on thermally-grown SiO@sub 2@ while the structure of the ripples is monitored in real-time with x-ray scattering. Ripples were formed in UHV using argon ions with energies between 0.5 and 2 keV. Ripple wavelengths between ~150 and ~600 Å were formed, with the wavelength increasing linearly with the ion energy. During sputtering, both the specular and diffuse intensity of 11 keV x-rays scattered from the surface were measured. Well-defined peaks in the diffuse scattering allow the determination of the ripple morphology. The effects of annealing during or after sputtering can also be monitored. Real-time monitoring of the ripples may permit more precise control of aspects of the ripple structure. The mechanism of ripple formation will be discussed in the context of theories of surface instabilities associated with ion bombardment.

9:40am **NS-ThM5 Materials Considerations for Optical Lithography at the Nanometer Scale*, F.A. Houle,*** *W.D. Hinsberg, M.I. Sanchez, J. Hoffnagle, M. Morrison, C. Nguyen,* IBM Almaden Research Center

The extendability of polymeric photoresist systems to the fabrication of nanostructures is a critical issue for both conventional microelectronics and for new device concepts. We have developed techniques using deep-UV interferometric lithography to evaluate quantitatively the relationship between polymer properties and reactivity and structure formation, with a particular focus on chemically amplified resist systems. Extended grating structures ranging from 50 to 500 nm linewidth and millimeters of line length are readily produced using 257 nm light, enabling systematic studies of the scaling of both chemical and physical phenomena. The apparatus and experimental methods will be described. We will present data using real-time spectroscopy and AFM analyses that probe the role of acid diffusion and aerial image definition in determining dimensional control and line-edge roughness at the nanometer scale. Implications of the data for x-ray and electron-beam resists will be discussed.

10:00am **NS-ThM6 Nanofabrication of Organic Thin Film Materials Using Scanning Probe Lithography*, G. Liu,*** *S. Xu, K. Wadu-Mesthrige, Y. Qian,* Wayne State University

Scanning probe microscopy(SPM) allows the surface structure to be visualized with unprecedented spatial resolution. Under carefully chosen conditions, SPM tips or probes can be used as a manipulation tool to fabricate nanoscopic patterns on surfaces. Recent work in our laboratory focuses on using SPM tips to fabricate nanopatterns on the surfaces of organic thin films. The talk will describe two new techniques developed in our lab. First method is nanografting which utilizes atomic force microscopy (AFM) tips as a nanoshaver. Such a shaver is operated on a self-assembled monolayer matrix in a solution containing adsorbate molecules. New molecules adsorb onto the shaved area following the plowing track of the AFM tip. Second methods utilizes scanning tunneling microscopy (STM) tips which operates under a high tunneling current. Single layers of metals can be removed from desired locations. The advantage and potential applications of the two techniques will also be discussed.

10:20am **NS-ThM7 Proximity X-ray Lithography of Siloxane and Polymer Films Containing Benzyl Chloride Functional Groups***, **S.L. Brandow**, W.J. Dressick, C.S. Dulcey,* Naval Research Laboratory*; H. Witschi, P.F. Nealey,* University of Wisconsin

Siloxane and polymer films containing benzyl chloride functional groups were exposed to patterned proximity x-rays. Silicon wafers coated with films of (p-chloromethyl)phenyl-trichlorosilane (CMPTS) or spun coated poly-vinyl benzyl chloride (PVBC) were exposed at the University of Wisconsin synchrotron x-ray source using 0.9385 nm radiation (800 MeV) at doses ranging from 50-1500 mJ/cm@super2@. Exposure resulted in changes to the surface energy and chemical reactivity of the imaging layers. The loss of chlorine and formation of oxidized carbon photoproducts upon exposure was followed as a function of dose using x-ray photoelectron spectroscopy. A corresponding change in surface energy, as monitored by static water contact angle, was also observed. The successful chemical grafting of amine ligands to the portions of the siloxane and polymer films which have been exposed to proximity x-rays definitively establishes the formation of surface aldehyde or ketone groups as a major photochemical pathway. The resulting surface amine was used to covalently bind either a fluorescent tag or a colloidal Pd(II) nanoparticle capable of initiating the deposition of electroless Ni. Pattern formation is demonstrated and the mechanistic differences of photoproduct formation on siloxane and polymer films will be discussed.

10:40am **NS-ThM8 Nanofabrication of Apertures for Single Quantum Dot Spectroscopy***, D. Park, **C.R.K. Marrian**, D. Gammon, R. Bass, P. Isaacson, E. Snow,* Naval Research Laboratory

Optical spectroscopy of quantum dots can be performed by probing sub micron lateral regions of a quantum well through apertures in an opaque metallic film on the surface of a sample. The apertures must be small, smooth to avoid scattering the incident light and fabricated without inducing damage in the quantum well, i.e. without an etch process. We have developed a technique based on a metal lift-off using electron beam nanolithography in a negative resist. (The resist is patterned, developed, coated with metal film and then treated with a solvent to remove the remaining resist to lift-off the metal in areas where it covers the resist.) The use of a positive resist (the preferred choice for lift-off) would require prohibitively long write times as the entire sample except the apertures would have to be exposed. Obtaining the undercut (e.g. re-entrant) profile required to form a clean edged lift-off is difficult with negative beam resists. However, using 20 kV electrons, an undercut profile can be obtained by using a sufficiently thick (>1 µm) resist layer. To obtain sub 200 nm apertures, we have used our 50 kV e-beam tool. However, it is not possible to obtain an undercut profile directly with 50 kV electrons as even a thick resist film does not stop a sufficient number of the incident electrons as occurs at 20 kV. By changing to an area, as opposed to a point, exposure high aspect ratio (~10:1) resist features with vertical sidewalls can be obtained at 50 kV. An oxygen plasma treatment has been found to smooth the sidewalls of the resist features and to provide a slight undercut sufficient to give a clean aperture following metal lift-off. These lithographic results will be compared to, and shown to be in quantitative agreement with, the predictions of our simulations of electron elastic and inelastic scattering. Finally, an example of the spectroscopy will be presented along with a discussion of the relative advantages of this technique over spectroscopy with a near field probe.

11:00am **NS-ThM9 Nanolithography and Macromolecular PMMA***, **E.A. Dobisz**, S.L. Brandow, R. Bass, L.M. Shirey,* Naval Research Laboratory

Polymethylmethacrylate (PMMA) has been the standard high resolution resist for over 20 years. The limits to its resolution has been the subject of many controversies that center upon our understanding of e-beam interactions with materials over 10 nm length scales, resist development, and the utility of macromolecular resists for very high resolution lithography. In this work nanolithographic pattern development is examined from the latent image formation through the evolution of surface morphology as patterns develop. Two molecular weights of PMMA, 950K and 50K were spun onto Si wafers as 50 nm thick films. Lithographic patterns consisted of: (1) large (1-20 mm) pads with a 50 nm gap of exposure in the center and (2) grating patterns of 10 nm lines on periods from 40-100 nm to examine the limit of the resist material on pattern density. Exposures were made by 50 kV e-beam lithography system with a Gaussian probe standard deviation of 8 nm. The resist patterns were examined by AFM operated in tapping and contact modes. Examination of as-baked PMMA showed a nodular structure, with average particle diameters of 50 nm. Morphological changes during development will be discussed. AFM latent images of detected e-beam exposure show a 0.2-2.9 nm depression in the resist. Latent images are observed over a much larger dose latitude than observed in developed patterns. In developed grating patterns the 60 nm period is critical. The granular structure of 50K resist prevented the development of the 60 nm grating. In the 950K resist, the 60 nm grating developed readily, but the 40 nm period grating is problematic. AFM images show etching of the particle boundaries across the resist between the lines to prevent formation of the 40 nm grating. AFM images are compared and contrasted to SEM micrographs. The results are discussed in terms of electron scattering during exposure, resist contrast, stress, and resist structure.

11:20am **NS-ThM10 Indium Phosphide Nanocrystals formed by Sequential Ion Implantation into Fused Silica***, D.O. Henderson, R. Mu, A. Ueda, M.H. Wu, **D. Denmark**,* Fisk University*; C.W. White, A. Meldrum, R.A. Zuhr,* Oak Ridge National Laboratory

Indium followed by phosphorous were implanted into optical grade fused silica at energies of 320 and 120 keV, respectively and at doses ranging from 1x10@super 16@ ions/cm@super 2@ to 1x10@super 17@ ions/cm@super 2@. The implanted substrates were annealed at 800°C for 1 h in a reducing atmosphere (5% H@sub 2@ +95% Ar). Vibrational and electronic spectra were recorded before and after annealing the samples. The vibrational spectra revealed a peak at 320 cm@super -1@ after annealing at 800°C. The intensity of this peak increased with ion dose and is assigned to the surface phonon of InP nanocrystals. XRD measurements confirmed the presence of crystalline InP and TEM showed particles with radii ranging from 4.6 to 11.6 nm. Electronic spectra of the annealed samples indicated that the energy of the band edge absorption is well below the bulk value of 969 nm. The band gap energies increased with decreasing ion dose and is attributed to quantum confinement of the exciton. The quantum confinement of the exciton is supported by the TEM measurements which demonstrated that the nanocrystals are nearly equal to or smaller than the InP exciton radius of 10.7 nm.

Plasma Science and Technology Division
Room 318/319/320 - Session PS-ThM

Plasma Applications in Copper Metallization

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

8:20am **PS-ThM1 Plasma Processes for Copper Dual Damascene Interconnect in Advanced CMOS Technologies***, **J.E. Heidenreich**, D. Edelstein, R. Goldblatt, W. Cote, C. Uzoh,* IBM - Semiconductor R & D Center*; T. McDevitt, A. Stamper,* IBM Microelectronics*; A.H. Simon,* IBM - Semiconductor R & D Center*; J. Dukovic,* IBM T.J. Watson Research Center*; R. Wachnik, H. Rathore,* IBM - Semiconductor R & D Center*; S. Luce, J. Slattery,* IBM Microelectronics*; J. Ryan,* IBM - Semiconductor Research and Development Center **INVITED**

IBM has announced the implementation of Copper interconnect for a sub-0.25µm CMOS technology.@footnote 1@ This technology uses up to 6 levels of Copper wiring with a minimum metal contacted pitch of 0.63µm. Copper metalization offers the advantages of upto 40% reduction in wire resistance, increased allowable current density, and increase scalability, relative to Ti/Al(Cu) wiring which is commonly used in semiconductor applications. This technology was produced using a Dual Damascene integration scheme that dramatically reduces the number of steps necessary to build wiring levels. The industry, as a whole is moving toward both Copper metalization and Dual Damascene integration for reduced cost and increased performance. This talk will review the characteristics of this technology, and the results of our reliability evaluation. It will also focus on some of the special plasma processing challenges and opportunities that arise with the use of Dual damascene and Copper. @FootnoteText@ @footnote 1@D. Edelstein et al., Proc. IEEE IEDM, 773 (1997).

9:00am **PS-ThM3 Low k Dielectric Etching in High Density Plasmas*, O. Joubert*,** France Telecom CNET/DTM/TFM, France*; L. Vallier, P. Czuprynski,* France Telecom CNET, France

Dielectric etching remains one of the most challenging etching process for ultra large scale integration (ULSI) technology. The need to move to the so-called low k dielectric materials open a all new area of investigation. Among different options, one is to use polymers as low k dielectric. Opening high aspect ratio contact holes in polymer type materials can be as challenging as opening high aspect ratio contact holes in SiO@sub 2@. In this paper we have been studying the etching of high aspect ratio contact holes (higher than 5) in polymers. Studies were performed in a high density helicon source using various chemistries and plasma operating conditions. The etching was controlled using real time ellipsometry and optical emission techniques. First, oxygen plasmas were tentatively used to open high aspect ration contact holes. In all the plasma operating conditions used (low density and high density regimes and always at very high chuck bias power), undercut due to spontaneous etching reactions between the polymer and oxygen atoms present in the discharge or profile deformation such as bowing were observed. Other chemistries such as H@sub 2@/N@sub 2@ gas mixtures where spontaneous etching reactions between the polymer and reactive species are less important were also investigated. Oxygen based chemistries such as O@sub 2@/CO, O@sub 2@/CH@sub 4@, O@sub 2@/SO@sub 2@ allowing passivation layers to be formed on the polymer sidewalls of the contact were investigated. The best contact hole profiles were obtained using O@sub 2@/SO@sub 2@ gas mixtures where sulfur deposition on the polymer sidewalls strongly minimizes spontaneous etching reactions. On the other hand, some sulfur-based species are left behind which can react with air moisture possibly inducing metal corrosion during the subsequent interconnect formation. In situ anticorrosion treatments were performed to remove sulfur based species. The anticorrosion efficiency was evaluated by measuring the sulfur concentration on all the contact hole surfaces before and after anticorrosion treatment using chemical topography analyses by x ray photoelectron spectroscopy (XPS). @FootnoteText@ This work has been carried out within the GRESSI consortium between CEA-LETI and France Telecom-CNET.

9:20am **PS-ThM4 High Density Plasma Patterning of Organic Low Dielectric Constant Materials*, T.E.F.M. Standaert*,** *P.J. Matsuo, S.D. Allen,* State University of New York, Albany*; K.H.J.M. Robben,* Eindhoven University of Technology, The Netherlands*; G.S. Oehrlein,* State University of New York, Albany*; J.G. Langan, W.R. Entley,* Air Products and Chemicals, Inc.*; R. Gutmann, T.M. Lu,* Rensselaer Polytechnic Institute

We have studied the etching of several organic low dielectric constant materials in a Transformer Coupled Plasma (TCP) source employing in-situ diagnostics, such as ellipsometry, x-ray photoelectron spectroscopy (XPS), and optical emission spectroscopy (OES). Dielectrics of particular interest are Polyarylene ether (PAE-2) and Parylene-N. Etched microstructures were examined by scanning electron microscopy (SEM). Successful pattern transfer into these organic dielectrics has been demonstrated using an Ar/O@sub 2@ chemistry and a SiO@sub 2@ hard mask. A systematic study has revealed how the erosion of the sidewall can be controlled as a function of the oxygen radical and ion flux. Following the dielectric etch, characterization of the surface residues and modifications were performed. The efficiency with which the original underlayer surface can be recovered was also investigated.

9:40am **PS-ThM5 Plasma Deposition of Low-Dielectric-Constant Fluorinated Amorphous Carbon Interlayer Dielectrics*, K. Endo*,** NEC Corporation, Japan **INVITED**

As LSI circuits continue to shrink, delay time of wiring caused by parasitic capacitance of interconnects becomes more important and further reduction becomes more difficult. Low-dielectric-constant (low-k) interlayer dielectrics (ILD) and low resistively wiring metals are now promising for reducing the RC delay of interconnects. Polymers are promising low-k materials. However, poor adhesion with Si substrates, poor thermal stability, and production difficulties have hindered their use in microelectronics. On the other hand, plasma-enhanced chemical vapor deposition (PE-CVD) of polymer films has many advantages that overcome these problems. Recently, a use of low-k fluorinated amorphous carbon (a-C:F) films, that have both crosslinked and PTFE (polytetrafluoroethylene)-like structures, has proposed.@footnote 1@ Now, a class of materials is widely investigated using PE-CVD. Around 400°C thermal stability and the dielectric constant of 2.3-2.7 are realized by controlling the fluorine concentration in the films. For an easier integration, a-C:F film is covered with SiO@sub 2@ that protect the a-C:F film during processing. Si-rich SiO@sub 2@ glue layer is used to maintain adhesion strength between them. Also, excellent gap filling was realized by using a biasing PE-CVD technique. The fabrication of globally planarized 3-lebel Al interconnect using a-C:F ILD achieved 50% reduction in capacitance. Now, a combination of Cu and low-k materials is most promising for the further reduction in RC delay. Also, lower deposition temperature of Cu is appropriate for the low-k materials that are typically less thermally stable than SiO@sub 2@ films. The a-C:F deposition technology can also be applied to Cu wiring system. A damascene structure with Cu wiring and a-C:F ILD was successfully fabricated and no reaction between Cu and fluorine was observed. @FootnoteText@ @footnote 1@K. Endo, MRS Bulletin 22, 55 (1997).

10:20am **PS-ThM7 Sources of Asymmetry in Ionized Metal PVD Reactors@footnote 1@*, J. Lu*,** *M.J. Kushner,* University of Illinois, Urbana-Champaign

Ionized metal physical vapor deposition (IMPVD) can produce highly ionized metal fluxes for use in filling high-aspect-ratio vias and trenches in microelectronic devices. A typical IMPVD reactor uses inductively coupled plasma (ICP) excitation in conjunction with a dc or rf magnetron. Directionality, uniformity, and high deposition rate are the most desired properties in the deposition process. One factor that significantly affects the cited properties is the symmetry of excitation and sputtering in the IMPVD reactor. Asymmetries may be caused by nonuniform erosion of the target, asymmetric gas injection and/or pumping, or non-uniformities in the inductively coupled field due, for example, to transmission line effects. These asymmetric processes couple nonlinearly with each other. In this paper, sources of asymmetry in metal deposition will be numerically investigated. The computational tool used in this study is the three-dimensional Hybrid Plasma Equipment Model (HPEM), in which a Monte Carlo sputter model is coupled self-consistently to the plasma simulation. The reactor being modeled uses an external coil (made possible by a Faraday shield). Typical operating conditions are 10 mTorr gas pressure, 1kW ICP power, and 13.6MHz frequency. The uniformity of the ion flux and ionization fraction for Cu and Al IMPVD systems will be discussed as a function of aspect ratio, target geometry and antenna design. @FootnoteText@ @footnote 1@Work supported by SRC, Materials Research Corporation, and NSF.

10:40am **PS-ThM8 Simulations for Process Optimization Issues in Ionized Metal PVD*, P.L.G. Ventzek*,** *M. Hartig, V. Arunachalam, D.G. Coronell, D. Denning,* Motorola Inc.

Magnetron plasma sources for ionized metal plasma physical vapor deposition (IMP-PVD) are being exploited for metal deposition in semiconductor device manufacturing applications because of their ability to lay down films with the required step coverage at high rates and reasonable uniformity. Challenges exist to extend the technology to ever more aggressive features with tighter tolerances on process parameters (e.g. uniformity). Despite their importance, multidimensional numerical models that treat the plasma dynamics in IMP chambers are relatively rare. This is possibly due to the difficulty in considering the complex magnet arrangements that characterize these systems. In this paper, we will present results obtained using the Hybrid Plasma Equipment Model (HPEM)@footnote 1@ and MAXWELL3D@footnote 2@ to simulate the behavior of a generic IMP source for metal deposition. This generic source employs internal coils to ionize metal sputtered from a target in a dc magnetron. As is typical, the dc magnetron structure is azimuthally asymmetric and will consist of concentric spirals of oppositely oriented permanent magnets. A special feature of the model is that energy and angle dependencies in the sputter yield are considered and that we have developed a methodology for looking at 3- dimensional effects.@footnote 3@ First we will present design-of-experiment studies of various process parameters and magnet configurations. In general, reasonable agreement has been found between ion fluxes to the target and experimentally determined erosion profiles. Second we will illustrate how various process parameters affect across wafer thickness uniformity, compositional uniformity and step coverage. @FootnoteText@ @Footnote 1@M. Grapperhaus et al., J. Appl. Phys., 83, 39 (1998) @Footnote 2@Ansoft Corp. @Footnote 3@see AVS paper by J. Kress et al.

11:00am **PS-ThM9 Modeling of IMP Copper for Electroplating Seed Layer Application*, H.M. Zhang*,** *I. Hashim, P.J. Ding, B. Chin, J.C. Forster,* Applied Materials

Copper is being considered for semiconductor metallization because of its better conductivity, and higher electromigration resistance compared to aluminum. Current trends suggest that electroplating will be the primary choice for copper deposition in sub-0.25 µm generations because of its relatively low cost, high deposition rates, and ease of filling high aspect ratio features. However a conducting seed layer is required prior to electroplating. Ion-metal-plasma (IMP) deposition of copper has been demonstrated to provide a good seed layer for aspect ratios up to 4.5 :1.@footnote 1@ To meet the challenges of filling even higher aspect ratio features, a better understanding of both the electroplating and IMP process is required. In this paper, we will focus on extending the limits of the IMP copper deposition process by using simulations. A 2-dimensional hybrid plasma equipment model (HPEM),@footnote 2@ developed at the University of Illinois, is used to model the IMP Cu system. Simulation results of the deposition rate show good agreement with experimental data. The ionization ratio of copper can be increased by increasing the RF power or the process pressure. TEM analysis of IMP copper deposition into high aspect ratio features show a significant improvement of the step coverage at higher pressures. A good correlation was obtained between ionization fraction predicted by simulation and experimentally obtained bottom coverage measurements. This study will show that with proper optimization, the application of IMP Cu to the deposition of seed layers for electroplating can be extended to future generation and geometries. @FootnoteText@ @footnote 1@I. Hashim et al, Abstract submitted for VLSI Multilevel Interconnection Conference, 1998. @footnote 2@M. Grapperhaus and M.J. Kushner, J. Applied Physics., 81, 569 (1997)

11:20am **PS-ThM10 Metal Flux Ionization Fraction in Copper Ionized Physical Vapor Deposition@footnote 1@***, T.G. Snodgrass, J.E. Foster, S. Lu,* ***A.E. Wendt****, J.H. Booske, J.L. Shohet,* University of Wisconsin, Madison

A characterization and modeling effort is directed at a more complete understanding of the potential and limitations of copper ionized physical vapor deposition (IPVD) for damascene processes. An rf inductively-coupled IPVD tool operating in argon includes a dc magnetron sputter source mounted in the top of an 18" D chamber. A 14'' D internal single-turn rf induction antenna is positioned between the magnetron and a 12" D substrate holder. Improved filling of high aspect-ratio features depends on the degree to which metal atoms are ionized as they pass through the rf plasma. To identify factors governing the "ionized flux fraction," measurements of metal properties have been made in the gas phase and at the substrate. Optical spectroscopy and Langmuir probes measure gas phase concentrations of neutral and ionized copper, and an improved quartz crystal microbalance@footnote 2@ is used to determine both neutral and ion fluxes at the substrate. The sputter rate from the target as well as the deposition rate radial profile at the substrate location have been characterized in detail. Results with and without the rf plasma show that the rf induction plasma has the primary effect of increasing the ionized metal flux and has only a minor effect on the flux of neutral copper. Selfsputtering of the internal rf antenna has also been examined, and methods to control it will be presented. A model has been constructed that, along with the measurements described, provides a physical explanation of the IPVD operating characteristics. @FootnoteText@ @footnote 1@This work supported by NSF grant #EEC8721545 @footnote 2@T. G. Snodgrass, W. Wang, J. H. Booske, A. E. Wendt, J. L. Shohet, submitted to Rev. Sci. Instr.

11:40am **PS-ThM11 Scattering and Sputtering Processes of Energetic Ar@super +@ and Cu@super +@ Ions on Cu Surfaces: Molecular Dynamics Simulations***,* ***C.F. Abrams****, D.B. Graves,* University of California, Berkeley

Two competing technologies, electroplating and ionized PVD, show promise in filling narrow, high aspect ratio trenches and vias with copper. While energetic metal and inert gas ions play central roles in IPVD, they are potentially no less important in plating due to the need to deposit a high-quality seed layer of metal on top of a thin barrier layer before plating from solution can proceed. Therefore, a better understanding of how energetic Ar@super +@ and Cu@super +@ ions interact with copper surfaces is crucial for further development of both technologies. We present results of molecular dynamics (MD) simulations of Ar@super +@ and Cu@super +@ ions impacting model Cu surfaces with a variety of impact energies (50 - 200 eV) and angles. We modeled Cu-Cu interactions using the EAM potential energy function (PEF) and Ar-Cu interactions using the ZBL PEF.@footnote 1@ We report the distributions in reflected angles and energies for these ions. We report both total and differential sputter yields with respect to angle of ejection, and compare our MD results to recent experimental findings.@footnote 2@ The effect of changing ion energy and angle on these quantities is discussed. For example, we observe that the sputter yield for Ar@super +@ on Cu decreases as the Ar@super +@ ion's incident angle is increased from 30@super o@ to 60@super o@ from normal. These results shed light on the dynamics of low energy ion/metal surface interactions and provide a useful database of events for profile evolution simulations of Cu seed layer deposition and trench/via fill. @FootnoteText@ @footnote 1@ K. Gartner et al., Nucl. Instr. Meth. Phys. Res. B 102, p183 (1995). @footnote 2@ C. Doughty, S. M. Gorbatkin, and L. A. Berry, J. Appl. Phys. 82, p1868 (1997)

Selected Energy Epitaxy Topical Conference
Room 327 - Session SE-ThM

In Situ Characterization and Real-Time Diagnostics of Surface Growth Processes

Moderator: R.D. Tromp, IBM T.J. Watson Research Center

8:20am **SE-ThM1 Low Energy Electron Microscopy of SEED Growth of GaN Layers***, A. Pavlovska,* ***E. Bauer****, I.S.T. Tsong, V.M. Torres, R.B. Doak,* Arizona State University **INVITED**

The early stages of growth of GaN layers on GaN(0001), 6H-SiC(0001) and on Si(111) surfaces are studied in a low enery electron microscope equipped with a NH@sub 3@ seeded He supersonic jet source, a RF discharge nitrogen source and a thermal NH@sub 3@ beam source. This allows a comparison of the influence of the different substrates and deposition modes on the growth and structure of the layers. Results will be reported on the effects of relative arrival rate of Ga and N containing species, of the substrate temperature and surface condition.

9:00am **SE-ThM3 Observation and Nucleation Control of Ge Growth on Si Surfaces using Scanning Reflection Electron Microscopy***,* ***M. Ichikawa****,* Joint Research Center for Atom Technology, Japan **INVITED**

Scanning reflection electron microscopy (SREM) is one of the useful techniques for studying surface phenomena and also for modifying surfaces through the use of a focused beam. We have developed high-resolution SREMs (2 nm beam diameter) combined with other surface analysis techniques, such as STM, scanning Auger electron microscopy and X-ray photoelectron spectroscopy (XPS), and applied these to study and control surface reaction phenomena. In this study, we mainly show that focused electron beam (EB)-stimulated reactions in ultra-thin SiO@sub 2@ films on Si substrates, are useful for controlling Ge growth on Si surfaces. Ultra-thin Si oxide films less than 1 nm thickness are formed by heating clean Si substrates in oxygen gas at about 700 °C. The thermal oxidation occurs layer-by-layer. The interface between the oxide film and Si substrate becomes atomically abrupt. The oxide film is mainly composed of silicon dioxide (SiO@sub 2@), which is confirmed by XPS. When the samples are annealed at about 750 °C after focused EB irradiation on the SiO@sub 2@ films at room temperature, Si clean surfaces (open windows) are exposed in the oxide films on the substrates due to the EB-stimulated oxygen desorption and selective thermal decomposition of SiO@sub 2@ at the EB irradiated areas. The typical size of these open windows is about 10 nm. After the deposition of Ge on the sample with Si open windows and subsequent annealing, Ge island growth occurs only in the window areas by Ge diffusion from the surrounding areas during the thermal decomposition of SiO@sub 2@ where Ge reacts with SiO@sub 2@ producing volatile SiO and GeO gases. Ge islands with 10-20 nm size can be formed at given areas on the Ge wetting layer by this method. Other Si nanostructures can be also formed by the selective thermal reactions on the patterned ultra-thin SiO@sub 2@. This work is supported by NEDO.

9:40am **SE-ThM5 Wurtzite GaN Surface Structure Studied by Scanning Tunneling Microscopy and Total Energy Calculations***,* ***A.R. Smith****, R.M. Feenstra, D.W. Greve, M.-S. Shin, M. Skowronski,* Carnegie Mellon University*; J. Neugebauer,* Fritz-Haber-Institut der MPG, Germany*; J.E. Northrup,* Xerox Palo Alto Research Center **INVITED**

Using scanning tunneling microscopy (STM) and electron diffraction, two new families of reconstructions have been identified on wurtzite GaN surfaces. First-principles theoretical calculations have yielded a number of novel structural models - many consisting of metallic Ga surface layers - for these reconstructions. The two families of reconstructions are those associated with the inequivalent (0001) and (000-1) surfaces, denoted as Ga-face and N-face respectively. Films are grown using molecular beam epitaxy with an RF plasma source to activate the N@sub 2@ molecules. The N-face results from nucleating the growth directly on sapphire, while the Ga face is prepared through homoepitaxial growth on an MOCVD-grown GaN/sapphire template. For either polarity, smooth growth occurs under Ga-rich growth conditions whereas N-rich growth leads to surface roughening. On the N-face, the least Ga-rich structure is the 1x1, composed of a single Ga monolayer (or adlayer) bonded to the ideal, N-terminated bilayer. Higher-order reconstructions on this face, 3x3, 6x6, and c(6x12), occur with increasing Ga coverage. On the Ga-face, the most Ga-rich structure is the pseudo-1x1, consisting of a double layer of Ga atoms in a fluid-like discommensurate structure on the surface. Removal of Ga atoms from the pseudo-1x1 results in the 6x4, 5x5, and 2x2, in order of decreasing Ga coverage. The 6x4 and 5x5 appear to be composed primarily of Ga adatoms. The 2x2, on the other hand, is formed through nitridation of the annealed surface or by growth under nearly N-rich conditions and therefore is consistent with a N adatom 2x2. @FootnoteText@ This work is supported by the Office of Naval Research under contract N00014-96-1-0214.

10:20am **SE-ThM7 Low-Energy Electron Microscopy of (0001) Surfaces of GaN Films@footnote 1,2@*, M.G. Lagally*,** University of Wisconsin, Madison **INVITED**

The ability to observe growth in real space and in real time at growth temperatures and manipulate growth conditions dynamically is essential to determine fundamental mechanisms of epitaxial growth, especially in complex systems. Only low-energy electron microscopy (LEEM) provides this capability. We have begun a program of LEEM investigations of the surfaces of GaN films prepared in several ways as a springboard to subsequent in-situ exploration of homoepitaxial growth. Surfaces of films grown by metal-organic vapor phase epitaxy (MOVPE), by halide vapor phase epitaxy (HVPE), and by lateral epitaxial overgrowth (LEO) using MOVPE are compared. Although a number of surface reconstructions have been observed, clean stoichiometric GaN(0001) surfaces are unreconstructed, and hence conventional dark-field imaging cannot provide information on terrace sizes and step heights, although steps themselves can be viewed with step-contrast imaging. We demonstrate that through use of multiple scattering we can view terraces and step heights and determine terrace size distributions. We compare surface morphologies of the above films. We have also demonstrated (so far only on SiGe/Si) that LEEM has potential for imaging 3D features. We have identified 3D epitaxial islands and have followed in real time their shape and size evolution during embedding by matrix material. We will describe initial LEEM measurements of Ga deposition on the above GaN surfaces as a start to homoepitaxial growth. Although none of this work as yet reflects selected-energy epitaxy, it will help to establish the baseline for understanding growth mechanisms that might be modified by selecting the energies of the depositing species. @FootnoteText@ @footnote 1@Research supported by ONR. @footnote 2@Work done in conjunction with J. Maxson, L. Zhang, T. Kuech, and P. Sutter.

11:00am **SE-ThM9 Defect-Driven Nucleation Kinetics of GaN Growth on Sapphire(0001)*, A.R. Woll,*** *J.D. Brock, R.L. Headrick, S. Kycia,* Cornell University

Real-time, x-ray scattering techniques using the Cornell High Energy Synchrotron Source have been used to study the kinetics of GaN nucleation and growth on sapphire (0001) by RF plasma-assisted MOMBE. The initial growth rate of GaN, measured by gallium fluorescence, is observed to be highly nonlinear. The time to form the first bilayer was the same for substrates from the same wafer, but increased from 10 to 30 seconds on substrates with decreasing surface defect density, as indicated by x-ray measurements of surface quality. This suggests that the initial nucleation of GaN is defect-driven, perhaps occurring at steps on the surface. This work is supported by NSF Grant Nos DMR--9632275 (MSC) and DMR--9311772 (CHESS).

11:20am **SE-ThM10 Site-Selective Reaction of Br@sub 2@ with the Second Layer Ga Atoms on the As-rich GaAs(001)-2x4 Surface***, Y. Liu, A.J. Komrowski,* ***A.C. Kummel,*** University of California, San Diego **INVITED**

The top layer of the GaAs(001)-2x4 surface consists of rows of As-As dimers while the second layer has exposed Ga atoms between the arsenic rows. Using scanning tunneling microscopy (STM), we have observed that in the initial adsorption stage monoenergetic Br@sub 2@ molecules (0.89 eV) react exclusively with the second layer Ga atoms exposed in trenches or at defects on the As-rich GaAs(001)-2x4 surface. This gallium-selective chemisorption indicates that bromine molecules preferentially react with exposed atoms which have the least filled dangling bonds regardless of their layer. Both abstractive and dissociative chemisorption of Br@sub 2@ molecules are observed to be surface-site selective. The abstractive chemisorption of Br@sub 2@ molecules formed isolated gallium monobromides at As atomic vacancies, As-As dimer vacancies, and in trenches. However, the dissociative adsorption of Br@sub 2@ molecules forms paired gallium monobromdies at As-As dimer vacancies and in trenches. Dissociative adsorption of a Br@sub 2@ molecules in a trench is orientation-specific and results in two GaBr species on the opposites sides of the trench.

Surface Science Division
Room 308 - Session SS1+NS-ThM
Growth and Thin Films

Moderator: J.B. Hannon, Sandia National Laboratories

8:20am **SS1+NS-ThM1 Peter Mark Memorial Award Address - Morphology of Epitaxial Films during Low Temperature Growth*, D.G. Cahill*[1]**, University of Illinois, Urbana-Champaign **INVITED**

9:00am **SS1+NS-ThM3 The Influence of Dislocations on the Intermixing Kinetics of Pd-Au Monolayer Films*, O. Schaff,*** *A.K. Schmid, M.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

The kinetics of surface alloying differ dramatically from the bulk counterparts. This is due to the fact that the dominant diffusion mechanisms are fundamentally different on surfaces. In this work, we used classical bulk studies as a guide to construct an effective experimental approach to directly determine such atomic mechanisms controlling intermixing kinetics in two-dimensional samples. On a clean Ru(0001) substrate, we prepared prototypical two-dimensional diffusion couples, consisting of monolayer regions of Au adjacent to monolayer regions of Pd. Between carefully controlled annealing steps, atomic resolution scanning-tunneling microscopy was used to image changes in the adlayer structure, and thereby identify and characterize the phenomena leading to the formation of a Pd-Au surface alloy. We report several striking observations: (I) The Pd-Au surface alloy forms only on the Au-rich side of the diffusion couple, reflecting strong asymmetry in the diffusion constants of the two metals across the Pd-Au seam. (II) Diffusion constants, and thus alloying, in this system are strongly anisotropic. Specifically, the rate of interdiffusion at a given Pd-Au boundary, measured from changes in the average position of the alloy interface, depends strongly on the orientation of the boundary with respect to the underlying Ru lattice. We relate these observations to the energetics of exchange of surface atoms with the "gas" of Au and Pd adatoms, as well as to the dynamical properties of the dislocation network present in the Au side of the diffusion couple.

9:20am **SS1+NS-ThM4 The Kinetic Nature of Slope Selection during Unstable Growth*, S. van Dijken,*** *L.C. Jorritsma, B. Poelsema,* University of Twente, The Netherlands

At temperatures below 320 K, the Cu(001) transforms into an arrangement of facets upon epitaxial growth, resulting in a pyramidlike surface morphology. The sides of the pyramids all have the same facet orientation, selected by the growth temperature. With increasing growth temperature, [113], [115] and [117] facet faces are obtained.@footnote 1,2@ Up to now, it is not clear whether this slope selection is determined by local equilibrium or by the kinetics of the growth process. We present evidence for the kinetic origin of this phenomenon. At the same temperature various facet orientations can be obtained, depending on the angle of incidence of the impinging adatoms. We will show that the observed slope selection can be explained by the refraction of atoms above the surface. @FootnoteText@ @footnote 1@H.J. Ernst, F.Fabre, R. Folkerts and J. Lapujoulade, Phys. Rev. Lett. 72, 112 (1994) @footnote 2@L.C. Jorritsma, M. Bijnagte, G. Rosenfeld and B. Poelsema, Phys. Rev. Lett. 78, 911 (1997)

9:40am **SS1+NS-ThM5 Growth on Cu(100) Using Improved Simulation Algorithm@footnote 1@*, J.G. Amar,*** University of Toledo*; M.R. D'Orsogna, T.L. Einstein,* University of Maryland, College Park*; I. Beichl,* National Institute of Standards and Technology*; F. Sullivan,* Center for Computing Sciences

We have developed a novel Monte Carlo scheme to simulate homoepitaxial growth on (100) surfaces of sc and fcc crystals, using tree and list structures. We have applied it to the specific case of Cu, in both the submonolayer and multilayer growth regimes. Energy barriers were calculated using Effective Medium Theory, and diffusive processes were grouped into 4 classes. The effect of an Ehrlich-Schwoebel barrier was also considered. For the submonolayer regime at 213 K, we find reasonable agreement with experimental results@footnote 2@ for the scaling of the island density as a function of the ratio of diffusion and deposition rates. For multilayer growth at 160 K we find good quantitative and qualitative

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

agreement with experimental results@footnote 3@ for the width as a function of coverage. In particular, the width exponent ß agrees with the experimentally reported value. At higher temperatures (T=200 K), our simulations underestimate the exponent ß. Presumably a new diffusion channel becomes important. We have tried several single-atom processes, e.g. up-stairs climbing and biased upward and downward funneling, but none improve agreement significantly. The initial surface morphology may also exert an important influence on ß at high coverages. We are currently investigating the effects of different initial growth conditions such as a slightly rough or stepped substrate. @FootnoteText@ @footnote 1@Work partly supported by DoD; MRD and TLE primarily supported by NSF MRSEC grant DMR 96-32521. @footnote 2@A. Swan, Z.P. Shi, J.F. Wendelken, and Z. Zhang, Surface Sci. 391, L1205 (1997). @footnote 3@H.J. Ernst, F. Fabre, R. Folkerts, and J. Lapujoulade, Phys. Rev. Lett. 72, (1994); JVSTA 12, 1809 (1994).

10:00am **SS1+NS-ThM6 The Atomistics of Homoepitaxial Growth on bcc(110)-Surfaces***,* ***U.K. Koehler****, C. Jensen, A. v. Stockhausen,* Ruhr-Universitaet Bochum, Germany

Time lapsed STM-movies, which allow a direct observation of the kinetics of growth processes on an atomic level up to 500°C, SPA-LEED and Monte-Carlo simulations are used to study the nucleation and growth behavior of homoepitaxy on the bcc(110)-surface. For Fe on Fe(110) and W on W(110) a strongly anisotropic growth with islands elongated in [001]-direction is found. A very effective Schwoebel-barrier leads to a nearly perfect statistical growth at RT with increasing island anisotropy in upper layers. At higher coverage a complete facetting of the surface is found and analyzed with SPA-LEED. A quantitative analysis of the STM-movies together with a kinetic Monte-Carlo simulation, which includes the full crystallographic symmetry of the bcc(110)surface, is used to extract information on the atomic diffusion behavior governing growth. A variety of growth features like the rugged appearance of the island edges and changes in the island shape with temperature are correctly reproduced in the simulation and can be assigned to the local diffusion energetics at step edges. Especially an anisotropic diffusion, which strongly suppresses diffusion along [001], is needed to reproduce the observed island anisotropies. A comparison of the layer distribution in the simulation with the one found with STM is used to determine the Schwoebel-barrier. Lateral island coarsening and an atom flux across the step edge following a temperature increase after growth is directly observed in STM.

10:20am **SS1+NS-ThM7 Probing the Forces Stabilizing Self-Assembled Structures: Dynamics of Vacancy Island Lattices in Ag films on Ru(0001)***, K. Pohl, M.C. Bartelt, J. de la Figuera, N.C. Bartelt,* Sandia National Laboratories*; J. Hrbek,* Brookhaven National Laboratory*;* ***R.Q. Hwang,*** Sandia National Laboratories **INVITED**

Nature exhibits processes that rival our most advanced patterning technologies used to create ordered lattices of nanoscale structures. Such self-organized phenomena have the potential to revolutionize materials performance, leading to higher density information storage and high-speed nanoscale electronics. Though many observations of self-organization have been reported, the fundamental mechanisms underlying such behavior remain unclear. The commonly accepted source of such mesoscopic-scale forces is the stress field mediated by the substrate which supports the grown structures. This, however, has not been confirmed, nor have such interactions been directly measured. In our work we have taken the approach of using observations of thermal fluctuations of an ordered array of surface defects to probe the interactions between the defects. In particular, we have used STM to study the array of vacancy lattice islands which forms upon exposure of a monolayer of Ag on Ru(0001) to sulfur. This is an extremely well-defined example of an ordered "mesoscopic" surface structure. At room temperature, each island is observed to vibrate around its equilibrium lattice postion. These vibrations appear to be harmonic and by performing a normal mode (phonon) analysis of the vibrations we can determine the elastic constants of the island array. The magnitude of the interactions is consistent with theories of elastic step-step interactions in strained films. This work was supported by the Office of Basic Energy Sciences of the U.S. DOE, Division of Materials Science (Contract No. DE-AC04-94AL85000).

11:00am **SS1+NS-ThM9 STM Study of Ultrathin NaCl(111) Layers on Aluminum***,* ***W. Hebenstreit****, J. Redinger,* TU Vienna, Austria*; R. Podloucky,* University Vienna, Austria*; M. Schmid, P. Varga,* TU Vienna, Austria

Polar surfaces like NaCl(111) are electrostatically unstable and cannot be found as terminating surfaces of crystals. But we can grow NaCl islands with (111) surface orientation on Al(111) and Al(100) single crystals. The (111) structure is revealed by atomically resolved Scanning Tunneling Microscopy (STM). The maxium coverage we could achive was 0.3 monolayer. The islands are triangular shaped, located at the lower side of substrate step edges and in the case of the Al(111) substrate alinged with the closed packed directions of the substrate. The islands consist of two Na layers with one Cl layer in between. We performed ab initio calculations with the FLAPW (full potential lineraized augumented plane waves) method of the electronic structure of a free standing Na-Cl-Na sandwich structure. These calculations reveal that the Na 3s level is filled with half an electron. The sandwich consists of two +0.5 charged Na metallic layers with a -1 charged ionic Cl layer in between, so the whole film ist neutral, free of dipoles, and electrostatically stable. The film is 4.6% laterally contracted and 5.3% expanded in vertical direction with respect to NaCl bulk distances.

11:20am **SS1+NS-ThM10 Three-Dimensional SiGe Island Density on Si(001) and Morphology After Si Overgrowth@footnote 1@***,* ***J.S. Sullivan****, E. Mateeva, H. Evans, D.E. Savage, M.G. Lagally,* University of Wisconsin, Madison

Thin films of SiGe deposited on Si(001) can form three-dimensional (3D), coherently strained islands via a modified Stranski-Krastanov growth mode. Single films as well as highly ordered 3D superlattices with specific island sizes and densities may exhibit unique electronic and optoelectronic properties. In order to investigate how common process variables in epitaxial multiple-layer film growth influence 3D island density and morphology, we deposited SiGe films on Si(001) using low-pressure chemical vapor deposition and varied alloy composition, substrate temperature, and deposition rate. Films containing {105} faceted SiGe islands were overgrown with and embedded in Si at various substrate temperatures. Film growth and morphological evolution were monitored with in-situ, real-time reflection high-energy electron diffraction. Atomic force microscopy was performed ex-situ to characterize film morphology, and buried-island morphology was determined with cross-sectional transmission electron microscopy. The 3D island number density exhibits an Arrhenius-type dependence on substrate temperature, a power law relationship with deposition rate, and an inverse proportionality to Ge mole fraction in the alloy. Islands broaden during overgrowth and embedding due to thermally activated mass transport and Si interdiffusion; such that the {105} facets grow outward producing a (001) mesa at the apex. We will discuss our results in the context of simple thermodynamic and kinetic models and describe possible methods of obtaining and maintaining a specific size and size distribution of 3D islands. @FootnoteText@ @footnote 1@Supported by the NSF.

11:40am **SS1+NS-ThM11 Effects of Ion Pretreatments on the Nucleation of Silicon on Silicon Dioxide***,* ***C Basa,*** University of North Carolina, Chapel Hill*; Y.Z. Hu,* AG Associates Inc.*; M.T. Tinani, E.A. Irene,* University of North Carolina, Chapel Hill

It is well known that the silicon (Si) surface condition is crucial for low temperature Si expitaxy.@footnote 1@ In particular, hydrogen has been implicated as an important factor inhibiting Si nucleation on Si,@footnote 2@ and SiO@sub 2@ surfaces.@footnote 3@ In addition, nuclei densities can change depending upon the preparation of the surface film.@footnote 3@ We previously studied the effects of pretreatments of various forms of hydrogen (molecular and ionic) on nucleation parameters (nuclei density, and incubation time (t@sub inc@)).@footnote 4@ We found that H@sub 2@ pretreatments passivated the surface causing longer t@sub inc@, lower nuclei density, larger nuclei, and rougher final films. H@super +@ pretreatments increased the number of nucleation sites resulting in shorter t@sub inc@, higher nuclei density, smaller nuclei, and smoother final films. However, the mechanism for H@super +@ effects on nucleation was not elucidated in that study. Therefore, the study was extended to include the effects of (1) ion dose and energy, (2) other ions (Ar@super +@, He@super +@, N@super +@) and (3) temperature of the pretreatment on the nucleation of poly-Si on SiO@sub 2@. There are three major results from the surface pretreatment experiments. First, in the range tested, ion dose has more influence on nucleation parameters than ion beam energy. Second, results with different ionic species indicate a physical, rather than chemical mechanism, for creating nucleation sites. Third, high temperature ionic pretreatments damage the surface less than room temperature treatments. @FootnoteText@ @footnote 1@T. Yamazaki, M. Miyata, T. Aoyama, and T. Ito, J. Electrochem. Soc., 139, p. 1175 (1992). @footnote 2@K. Tsubochi and K. Masu, Mat. Res. Soc. Symp. Proc., 315, p. 59 (1993). @footnote 3@J. T. Fitch, J. Electrochem. Soc., 141, p. 1046 (1994). @footnote 4@Y. Z. Hu, C. Y. Zhao, C. Basa, W. X. Gao, and E. A. Irene, Appl. Phys. Lett., 69, p. 485 (1996).

Surface Science Division
Room 309 - Session SS2-ThM
Oxide Surface Chemistry

Moderator: S. Joyce, Battelle Pacific Northwest for USDOE

8:20am **SS2-ThM1 Coadsorption Studies with Water: a Small Step Toward Understanding the Surface Chemical and Photochemical Properties of TiO@sub 2@**, ***M.A. Henderson,*** Pacific Northwest National Laboratory@footnote 1@*; W.S. Epling, C.H.F. Peden,* Pacific Northwest National Laboratory*; U. Diebold,* Tulane University **INVITED**

Perhaps the most prevalent surface species on an oxide surface in any environment or application is water. Depending on the conditions this molecule can be present on oxide surfaces as dissociation fragments (hydroxyls), as molecularly adsorbed species, as a thin physisorbed layer or as a bulk solid/liquid interface. The prevalence of water at oxide surfaces may lead one to think that its role in surface chemistry on oxides, such as TiO@sub 2@, is mostly that of a spectator. Although this appears to be the case in the UHV surface chemistry of more strongly bound species such as formate or methanol on TiO@sub 2@(110), water has a significant influence on more weakly bound species. This influence leads to interesting chemistry if defect sites are present. After a brief description of the properties of water on TiO@sub 2@(110), results will be presented for the formation of bicarbonate from coadsorption of water and carbon dioxide at oxygen vacancies, and for the reaction of molecular oxygen with bridging hydroxyl groups at oxygen vacancies. These results provide insights into photochemical oxidation and reduction processes occurring on titanium dioxide.@footnote 2@ @FootnoteText@ @footnote 1@PNNL is a multiprogram national laboratory operated for the U.S. DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.) 2. This work was funded by the DOE office of Basic Energy Sciences, Materials Sciences, and the DOE Environmental Management Science Program.

9:00am **SS2-ThM3 HCl Adsorption and Desorption on a Single-Crystal @alpha@-Al@sub 2@O@sub 3@(0001) Surface***, **C.E. Nelson**, J.W. Elam, S.M. George,* University of Colorado, Boulder

The adsorption and desorption of HCl on a single-crystal @alpha@-Al@sub 2@O@sub 3@(0001) surface were examined using laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) techniques. @alpha@Al@sub 2@O@sub 3@(0001) models Al@sub 2@O@sub 3@ particles generated by solid rocket motors and HCl interactions with these Al@sub 2@O@sub 3@ particles may affect the stratospheric ozone layer. The initial sticking coefficient for HCl on @alpha@Al@sub 2@O@sub 3@(0001) at 298 K was S~10@super -3@. The HCl sticking coefficient decreased nearly exponentially with HCl coverage and the HCl coverage saturated at @THETA@@sub HCl@=0.10x10@super 15@ molecules/cm@super 2@ after HCl exposures of >10@super 10@ Langmuir. HCl desorption from the @alpha@Al@sub 2@O@sub 3@(0001) surface occurred over a temperature range from 300 K to 650 K. This broad range suggests a distribution of surface sites with different binding energies. HCl desorption results versus HCl coverage prepared by progressively annealing a fully exposed @alpha@Al@sub 2@O@sub 3@(0001) surface confirmed a wide range of binding energies. Additional HCl desorption results versus HCl coverage prepared by varying the HCl exposure revealed that HCl dissociative adsorption randomly fills adsorption sites independent of their adsorption energy. These results also suggest that surface diffusion between the adsorption sites must be negligible. Modeling of the desorption results was consistent with surface site energies that range from 19 to 36 kcal/mole. These adsorption and desorption results predict that HCl will be stable on @alpha@Al@sub 2@O@sub 3@ rocket exhaust particles at stratospheric temperatures and pressures.

9:20am **SS2-ThM4 Dissociative Adsorption and Electron Stimulated Desorption of Cl on TiO@sub 2@(110) Studied by STM, AES and ISS***, **U. Diebold**,* Tulane University*; G. Leonardelli,* TU Vienna, Austria*; W. Hebenstreit,* Tulane University*; M. Schmid, P. Varga,* TU Vienna, Austria

The catalytic reactivity of a metal oxide can be significantly altered by adsorbed halogen species, but little is known about the adsorption of chlorine on well-characterized model oxide surfaces. We present a combined study of atomically-resolved Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES) and Ion Scattering Spectroscopy (ISS) of chlorine adsorption on TiO@sub 2@(110). Chlorine was dosed from a calibrated electrolytic AgCl cell at room temperature. STM reveals a dissociative adsorption process. For small doses (@<=@0.01 Cl atoms/unit cell), a large average separation (26 Å) between Cl-Cl pairs indicate that adsorption energy is transformed into kinetic energy of the Cl atoms. The saturation coverage for an annealed surfaces is 0.3 Cl/unit cell. STM does not show any prefered adsorption at step edges, kink sites or oxygen defect sites. Chlorine atoms can be desorbed from the surface with STM by scanning at sample bias voltages @>=@+4 V. AES measurements are complicated by electron stimulated desorption of the Cl atoms. The desorption cross section is 3 10@super -20@cm@super 2@ for a sputtered surface and >2 10@super -17@ cm@super 2@ for a annealed surface. ISS (He@super +@ ions 1keV, scattering angle 90°) detects Cl only after adsorption on a sputtered surface, while the ISS signal of an annealed surface remains unchanged during adsorption of chlorine.

9:40am **SS2-ThM5 Photocatalytic Dehydrogenation of 2-Propanol on TiO@sub 2@(110)***, **D. Brinkley**, T. Engel,* University of Washington

The use of TiO@sub 2@ as a photocatalyst is not well understood at a fundamental level in environmental remediation. We have investigated the thermal and photocatalytic oxidation of small oxygen containing molecules on TiO@sub 2@ single crystal surfaces using modulated molecular beam techniques. The role of specific surface orientations, defect sites and densities, oxygen sources, surface temperature, and reaction mechanisms on the reaction probability of incident molecules are essential issues that must be understood in order to maximize the efficiency of TiO@sub 2@ as a photocatalyst. For the specific case of 2-propanol on TiO@sub 2@ (110), we found that the total probability for a thermal reaction is less than 0.03 for a single collision of an incident molecule with the surface. The major and minor products in the thermal reaction are propene and acetone respectively. The reaction probability can be increased to 0.15 in the presences of bandgap radiation and molecular oxygen on a sample which has been preannealed in vacuum to create oxygen vacancies. The increase in reactivity is due entirely to the dehydrogenation channel of the reaction. Even a fully oxidized TiO@sub 2@ (110) surface has a reaction probability of 0.08 under the same conditions. The steady state reaction yield for this system is maximized at a temperature of 350 K, with an appreciable reaction rate between 250 K and 600 K. The yield is limited by desorption of acetone below 300 K and by the decrease in the surface coverage of the reactants above 400 K. The low thermal reactivity and the significant photochemical reactivity is attributed to free radical reactions initiated through electron trapping by adsorbed molecular oxygen. Our results suggest that the reaction proceeds primarily through a mechanism in which holes are trapped by undissociated 2-propanol molecules. Studies on TiO@sub 2@ (100) are currently underway and a comparison of the reactivity of this orientation with that of the (110) surface will be presented.

10:00am **SS2-ThM6 Photo-stimulated NO Adsorption on Metal Oxides***, **E.R. Blomiley**, E.G. Seebauer,* University of Illinois, Urbana

Coal combustors generate large quantities of NO@sub x@ compounds that face increasingly stringent regulation. Current NO removal technologies depend in part on selective catalytic reduction (SCR) processes that react NO with reductants like CO or NH@sub 3@ at high temperature. The high costs of reheating the flue gas over the catalyst and problems with slip of the reductant past the reactor have stimulated searches for alternative technologies. Here we examine the surface photochemistry underlying one particularly novel alternative: injection of an inexpensive semiconducting metal oxide (like Fe@sub 2@O@sub 3@) in an illuminated flue geometry in order to stimulate photoadsorption. The NO-laden particulates are then removed in an electrostatic precipitator. We have shown in high and low-pressure experiments that while pure iron and titanium oxides are inactive for NO removal, iron oxides supporting adsorbed Cl display significant activity even at room temperature. The presence of such activity is surprising, and appears to result from a complex interaction between the underlying semiconductor, the adsorbed Cl, weakly adsorbed water, and the photogenerated charge carriers. The activity remains surprisingly robust even in the presence of active gaseous species like SO@sub 2@. Temperature-programmed desorption reveals that some of the NO desorbs essentially reversibly, some forms NO@sub 2@, and the remainder desorbs intact while the substrate decomposes by volatilization of iron chlorides. The potential for such reactions to influence tropospheric NO@sub x@ chemistry in urban areas will be discussed.

10:20am **SS2-ThM7 The Reaction of H@sub 2@S, S@sub 2@ and SO@sub 2@ with ZnO and Cu/ZnO Surfaces***, S. Chaturvedi, **J.A. Rodriguez**, T. Jirsak, J. Hrbek, M. Kuhn,* Brookhaven National Laboratory

The surface chemistry of H@sub 2@S, S@sub 2@ and SO@sub 2@ on polycrystalline ZnO and Cu/ZnO surfaces was investigated using synchrotron-based photoemission and ab initio SCF calculations. At 100 K, polycrystalline ZnO dissociates H@sub 2@S into HS, and the adsorbed HS species decompose at temperatures between 300 and 400 K leaving S atoms that are bonded to zinc sites of the oxide. By dosing S@sub 2@ to zinc oxide, one can generate a sulfur saturation coverage (0.7 ML) that is larger than that obtained after dosing H@sub 2@S (0.5 ML) and induce the formation of small amounts of SO@sub 3@ species on the surface. Possible reaction pathways for the dissociation of S@sub 2@ on ZnO(0001) and ZnO(1010) terraces were studied using ab initio SCF calculations. At low sulfur coverages, an adsorption complex in which S@sub 2@ is bridge bonded to two adjacent Zn atoms (Zn-S-S-Zn) is probably the precursor state for the dissociation of the molecule. H@sub 2@S and S@sub 2@ mainly react with the zinc sites of the oxide. In contrast, SO@sub 2@ preferentially bonds to oxygen forming a mixture of SO@sub 3@ and SO@sub 4@ at 100 K and pure SO@sub 4@ at 300 K. Results from ab initio SCF calculations indicate that SO@sub 2@ adsorbs on an oxygen site to form SO@sub 3@ which then extracts an oxygen from the ZnO lattice to form SO@sub 4@. The last step in this process has a substantial activation energy, and after dosing SO@sub 2@ to ZnO at 100 K a mixture of SO@sub 3@ and SO@sub 4@ is produced on the surface. Cu two-dimensional islands supported on ZnO show a band structure that is substantially different from that of pure metallic copper. The Cu/ZnO surfaces exhibit a reactivity towards H@sub 2@S and S@sub 2@ that is larger than that of ZnO but smaller than that of metallic copper.

10:40am **SS2-ThM8 Methanol Adsorption and Reactivity at U and UO@sub 2@ Surfaces***, **M.T. Paffett**, J.A. Lloyd,* Los Alamos National Laboratory

In specific actinide materials storage situations it has been often observed that deleterious hydrocarbon interactions at actinide oxide surfaces have lead to a buildup of potentially explosive gases (usually H@sub 2@) arising from predominately radiolytic effects. Much less emphasis however, has been given to the deleterious consequences of unforeseen catalytic or reactive chemical events, arising from the storage of actinides and actinide oxides in mixed waste (actinides with organic solvents). In this vein we are seeking to unravel some of the fundamental details of reactive surface chemistry at model actinide oxide surfaces. In this study, the interaction of methanol-d (CH@sub 3@OD) with U and UO@sub 2@ surfaces has been studied using x-ray photoelectron spectroscopy (XPS), thermal desorption-mass spectrometry (TDMS), and secondary ion mass spectrometry (SIMS) over the temperature range of 90-500K. Low temperature (90 K) adsorption on uranium resulted in formation of methoxy species along with condensed phase adsorbed methanol. Room temperature (300K) adsorption on uranium produces only methoxy species, uranium carbide and uranium oxide. Heating to 400K completely decomposes the adsorbed methoxy species: 25% desorbing as methane and the remaining methoxide irreversibly converting to uranium oxycarbide (UO@sub 0.7@C@sub 0.3@). Concomitant with these C fragment conversion processes, desorption of hydrogen and deuterium is also seen over a wide temperature regime. Methanol-d adsorption on UO@sub 2@ also produces a methoxy surface species at surfaces temperatures << 150K and submonolayer exposure. Adsorbate decomposition following thermal desorption releases gaseous CH@sub 4@, H@sub 2@, HD, and D@sub 2@. Oxygen derived from the methanol molecule was incorporated into the UO@sub 2@ layer. The reactive adsorption and thermal decomposition of methanol at U and UO@sub 2@ surfaces is compared with that observed at other metal and metal oxide surfaces.

11:00am **SS2-ThM9 The Chemistry of CeO@sub 2@(001) and Ce@sub 1-x@Zr@sub x@O@sub 2@(001) Studied by Mass-Spectroscopy of Recoiled Ions***, **G.S. Herman**, Y. Gao, C.H.F. Peden,* Pacific Northwest National Laboratory

Ceria has found considerable use in automotive catalytic converters due to its oxygen storage properties. Ceria can provide oxygen under fuel-rich conditions, to reduce CO and hydrocarbon emissions, and remove oxygen under fuel-lean conditions, to reduce NOx emissions. The addition of zirconium to ceria has been found to improve the oxygen storage properties and increase the stability of the ceria particles. We have used the technique of mass-spectroscopy of recoiled ions (MSRI) to investigate the interaction of O@sub 2@, D@sub 2@, and D@sub 2@O with CeO@sub 2@(001) and Ce@sub 1-x@Zr@sub x@O@sub 2@(001) (x<0.20) films grown by plasma-assisted molecular beam epitaxy. The MSRI technique is extremely surface sensitive, probing the composition in the very topmost atomic layers. By using the temperature programmed mode of MSRI we were able to measure the corresponding signals for @super 18@O@sub 2@, D@sub 2@, and D@sub 2@O to monitor the adsorption, desorption and dissolution of these species. In the temperature range from 300-1000 K, we have found that the O signal increases linearly with temperature for all three molecules. The Ce signal, however, varies considerably over this temperature range depending on the molecular species. The results for the pure ceria and mixed ceria/zirconia films will be compared.

11:20am **SS2-ThM10 Reduction of Trace Element Contaminants in Aqueous Solution by Iron and Iron Oxides***, **S.R. Qiu**, H.-F. Lai, J.A. Yarmoff, C. Amrhein, M.J. Roberson, M. Hunt,* University of California, Riverside

Irrigation drainage and wastewater often contain elevated levels of trace oxyanions and oxycations, such as selenate, chromate and uranyl, which can be detrimental to humans and wildlife. A potential remediation method is to reduce the contaminants to less mobile forms by reacting the water with zero-valent iron. In this reaction, the iron serves as both an electron source and a catalyst. Most previous studies of this system were limited to the simulation of field work on a macroscopic scale. Consequently, little is known about the basic chemical interactions of these toxic ions at the water-metal interface. Our objective is to determine the microscopic reaction mechanisms by combining surface science methods and bulk chemical studies. Our bulk studies have indicated that the reactions are first-order. For surface studies, iron foil is first prepared in a UHV chamber by sputtering, or iron oxides are prepared by exposure of a hot Fe foil to O2 in UHV. The sample is then transferred to an aqueous solution containing the relevant ions. The pH and amount of dissolved oxygen in the solution are carefully controlled. The reacted surfaces are then characterized in UHV by surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) or scanning tunneling microscopy (STM). We find that films of partially reduced Se, Cr and U are formed by the reaction. The reduction of U is very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. The details of the surface reduction reaction mechanisms will be presented, and the implications of our results on the practical deployment of this remediation method will be discussed.

11:40am **SS2-ThM11 Formation of Nitro-PAH on Flyash Particle Surfaces: The Significance of Particle Substrate on PAH Nitration***, **G.S. Strossman**, T.F. Fister, R.W. Odom,* Charles Evans & Associates*; R.W. Linton,* University of North Carolina, Chapel Hill

Polycyclic aromatic hydrocarbons (PAH) are present in the atmosphere in both the gas phase and condensed onto particle surfaces. Coal flyash particles are an important source of condensed PAH since both are byproducts of coal combustion. Many PAHs are hazardous in their own right due to their carcinogenic or mutagenic nature; however another factor to be considered is the transformation of PAH into potentially more harmful analogues during their exposure to the atmosphere. One example is the formation of nitro-PAH after exposure of the parent PAH to atmospheric NO@sub 2@. A full understanding of these reactions requires determining how the near surface composition of flyash particles can affect the rate of nitration of adsorbed PAH. The PAH studied in this work was benzo[a]pyrene (BaP). BaP was chosen for its reactivity and because its size (5 rings) makes it likely to exist in the atmosphere primarily in the condensed phase. Submonolayer coverages of BaP on four different flyashes were exposed to NO@sub 2@ in both dry air and with different levels of relative humidity. The samples were analyzed by TOF-SIMS, a technique that can both obtain surface elemental information and detect low levels of organic molecular species on single particles in the 3-10 @micron@ range. The results show a distinct relationship between the particle compositions and the formation of nitro-BaP, both macroscopically and among individual particles within a single flyash sample. Furthermore, for two Class C (calcium-rich) flyashes, the role played by the substrate is distinctly different between dry air and humid air exposures, while for a class F flyash (high Al, Si and Fe, low Ca) no such difference is observed.

Thin Films Division
Room 310 - Session TF-ThM

Thin Films for Flat Panel Applications

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

8:20am **TF-ThM1 New Dry Etch Applications for Amorphous TFTs in Flat Panel Displays(FPD)***, **W.W. Yao**,* dpiX; A Xerox New Enterprise Company **INVITED**

Key goals driving FPD process development are: 1. large panel size; 2. Low cost; 3. Low power consumption. Recent introduction of new process technologies especially in the dry etch area are key enablers for new display architecture. Increase in display size with longer gate and data lines is driving the switch to aluminum metal with its lower resistivity to reduce the RC time delay. Hillock free Aluminum gate metal is enabled by tapered Al dry etching and high rate PECVD process with short time-temepraturе cycle. Cost reduction has focused on productivity improvement but new 3rd generataion tools has renewed interest recently in reduced mask count display architecture. ITO pixel is etched using very strong acids and dictates its placement in the process architecture. New ITO dry etch removes process constraints and allows placement of the ITO on top of the passivation dielectric. Power consumption is dominated by backlight intensity and can be reduced by higher aperture ratio pixel design. The ITO pixel dimension is increased if the TFT size and its assoicated coupling capacitance is shrinked through the use of selective n+ etch in intrinsic silicon.

9:00am **TF-ThM3 Field Emission and Photo Emission from Si Micro Tip Arrays Coated with Bias-Grown Diamond Films***, **M.Q. Ding**, A.R. Krauss,* Argonne National Laboratory*; O. Auciello,* Argonne National Laboratory, U. S. A.*; D.M. Gruen, T.D. Corrigan,* Argonne National Laboratory*; M.E. Kordesch,* Ohio University*; D. Temple, D. Palmer, G.E. McGuire,* MCNC

A considerable improvement in the properties of field and photoelectron emission from ungated Si micro tip arrays coated with bias-grown diamond thin films is reported. Prior to loading into a MPCVD reactor (ASTeX PDS-17), the microtip arrays were ultrasonically treated in a 0.1 µmm diamond suspension. Diamond films were grown in a CH@sub 4@-H@sub 2@-N@sub 2@ plasma at a substrate temperature of 800 °C and a negative bias of -150 V. The film had a complete coverage over the tip arrays as observed from secondary electron microscopy (SEM). Electron emission characteristics were measured in two different systems: field emission current-field (IF) measuring apparatus and photoelectron emission microscopy (PEEM). IF measurements showed a very low turn-on electric field with a threshold fields of 1.5 V/µmm (vs 40 V/µmm for uncoated tip arrays), and a current density of 1 mA/cm2 at around 4 V/µmm. In the PEEM studies, UV light from a mercury arc lamp was used to excite photoelectrons. While the lamp was on, the PEEM revealed a uniform and bright photoelectron emission image of the coated tip arrays in contrast to that of the uncoated arrays. When the lamp was off, stable field electron emission images of the coated tip arrays were also seen with a reasonable brightness at an electric field 5.6 V/µmm, whereas images of uncoated arrays could hardly be discerned and emission was unstable. Such a remarkable improvement in both field emission and photoemission properties, as compared to those of the uncoated arrays, indicates that the microtip arrays coated with bias-grown diamond films are promising for applications such as flat panel displays. A possible mechanism for the improvement will be discussed. This work is supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-39.

9:20am **TF-ThM4 Hydrogen Concentration Distribution in Plasma Deposited Hydrogenated Amorphous Silicon and Silicon Nitride Films***, **B.F. Hanyaloglu**, D.C. Marra, E.S. Aydil,* University of California, Santa Barbara

Understanding H distribution in plasma deposited hydrogenated amorphous silicon and silicon nitride (a-SiN:H) films as well as at the interfaces of these films is important for manufacturing of thin film transistors (TFTs) for flat panel display applications. Hydrogen concentration distribution and bonding in plasma deposited a-Si:H and a-SiN:H thin films were studied using in situ multiple internal reflection Fourier transform infrared spectroscopy in conjunction with in situ spectroscopic ellipsometry. The infrared spectra as a function of time were recorded both during deposition of the film and during etching with CF@sub 4@ plasma. The hydrogen concentrations as a function of depth below the film surface were obtained from the spectra recorded during the deposition and the etching experiments. Analysis of the spectra shows that the H distribution in a-Si:H and a-SiN:H films is surprisingly complex and far from uniform. The a-Si:H film consists of a very thin H rich layer at the surface that is primarily composed of SiH@sub 2@ and SiH@sub 3@. This H-rich surface layer is followed by a few 100 Angstrom thick subsurface region that is depleted in H compared to the bulk film. The bulk a-Si:H film grows beneath these two layers, which move up and stay at the surface during deposition. In a-Si:H deposition, there is evidence that H penetrates into the film through a process other than simple diffusion. We have also investigated H distribution and bonding in a-SiN:H films deposited on a-Si:H and a-Si:H films on a-SiN:H in order to study how the deposition sequence alters the chemical composition and structure of the a-Si:H/a-SiN:H interfaces. Implications of these experimental results on the differences in the peformance of top-gate and bottom-gate configuration TFTs will be discussed.

9:40am **TF-ThM5 Poly-Si Thin Film Transistors Fabricated on Low Temperature Plastic Substrates***, **P.G. Carey**, P.M. Smith, P. Wickbolt, S.D. Theiss,* Lawrence Livermore National Laboratory **INVITED**

Flat panel displays made on plastic substrates are envisioned for use in certain commercial and military systems because they are more rugged and lightweight than displays made on glass substrates. High information content can be attained for such displays using active matrix arrays of thin film transistors (TFTs). In this talk the fabrication of poly-Si TFTs on flexible plastic substrates will by discussed. Plastic substrates pose severe temperature constraints on the fabrication process. To overcome these constraints, our group at LLNL has used low temperature (<150C) silicon, oxide, and aluminum thin film deposition steps and pulsed excimer laser processing to perform the TFT channel crystallization and the source/drain doping.

10:20am **TF-ThM7 Stability of Very Low Temperature Amorphous Silicon Thin Film Transistors on Flexible Plastic Substrates***, C.S. Yang, **L.L. Smith**, C.B. Arthur, G.N. Parsons,* North Carolina State University

Active matrix transistor arrays on transparent plastic substrates will enable new high resolution flexible and rugged large area electronic display systems, including liquid crystal displays (LCDs), and organic light emitting displays (OLEDs). Hydrogenated amorphous silicon thin film transistors (TFTs) for active matrix LCDs are currently formed on glass substrates using temperatures in excess of 250°C. Lower temperature processes are of interest for TFTs on plastics, but stability of low temperature TFTs has not been reported. In this presentation, we will describe low temperature (0.3 cm@super 2@/V-s and off currents

10:40am **TF-ThM8 Advanced Deposition Technique for Producing Thin Films of Polycrystalline Silicon***, **J.B.O. Caughman**, D.B. Beach, G.L. Bell,* Oak Ridge National Laboratory

An improved plasma enhanced chemical vapor deposition technique has been demonstrated for depositing poly-crystalline silicon thin films for flat panel display applications. The technique combines a high density radio frequency (rf) inductively coupled plasma source with downstream gas injection that has resulted in device quality films deposited at high rates. Unlike conventional rf reactors, inductively coupled sources have high plasma and atomic species density along with low ion energies hitting the film surface during growth. Our system uses a planar induction coil for the plasma coupling that creates a dense hydrogen plasma over a large area (30 cm diameter). The hydrogen plasma serves as a source of large quantities of atomic hydrogen that aid in the deposition process. For better control of the plasma chemistry, silane (100%) is injected downstream, where the precursors needed for film growth are separated from the ionization region. The films are deposited on quartz samples on a heated substrate (< 400 degrees C). The power coupling mechanism (inductive vs. capacitive coupling) has been analyzed by using an rf sensor (located after the matching network) to determine processing conditions favorable for polysilicon growth. Deposition rates increase substantially with the amount of inductive power coupling and reach values of 60-80 nm/min. Increasing the coupled power beyond 1 kW eventually leads to a decrease in the net deposition rate, possibly due to increased etching of the deposited film by the hydrogen. Deposition results show that the conductivity (10@super -7@ S/cm) and the crystallinity (>80% based on the Raman spectrum) of the films are good. Analysis of the X-ray diffraction spectrum shows a highly preferred grain orientation in the plane. Details of the deposition conditions and the power coupling mechanism will be discussed. @FootnoteText@ Research sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract no. DE-AC05-96OR22464.

11:00am **TF-ThM9 Polycrystalline Silicon Films Deposited Directly on Glass by Reactive Magnetron Sputtering Using a Microcrystalline Silicon Nucleation Layer***, **D.S. Kim**,* Samsung Advanced Institute of Technology, Korea*; J.E. Gerbi, J.R. Abelson,* University of Illinois, Urbana-Champaign

We investigate the microstructure of polycrystalline silicon (px-Si) thin films which are deposited directly onto glass substrates using reactive magnetron sputtering in a single-pumpdown, two step growth process. px-Si films are of technological interest as thin film transistors in flat panel displays and as absorber layers in solar cells. In the first step, we deposit a microcrystalline Si (µmc-Si:H) film 400 Å can easily be obtained. We will also report preliminary electrical characterizations in both the as-deposited and post-hydrogenated states.

Applied Surface Science Division
Room 307 - Session AS-ThA

SIMS - Depth Profiling and Molecular Surface Analysis

Moderator: D. Simons, National Institute of Standards and Technology

2:00pm **AS-ThA1 Sputtering Rate Change and Surface Roughening in SIMS Measurements Using Oblique and Normal Incidence Oxygen Bombardment, With and Without Oxygen Flooding***, **C.W. Magee,*** Evans East*; S.P. Smith, G.R. Mount,* Charles Evans and Associates*; H.-J. Gossmann, B. Herner,* Bell Laboratories, Lucent Technologies

Measuring depth profiles for ultra-low energy ion implants in Si requires accurate analyses within the top 1 to 10 nanometers of the sample surface where the "surface transient" affects secondary ion yields. Flooding the Si surface with oxygen during analysis is an accepted method for reducing the magnitude of the surface transient effect. However, a recent study by Wittmaack and Corcoran@footnote 1@ suggests that flooding with oxygen when using 2 keV oblique incidence O2 bombardment will result in an unavoidable change in the sputtering rate for the first 20-40 nanometers of the depth profile. Another recent study, this one by Jiang and Alkemade@footnote 2@, substantiated the claims of Wittmaack and Corcoran. Jiang and Alkemade used 1keV O2 bombardment instead of 2 keV, and they found that the depth of sputter rate change extended less than 11.7 nanometers. The study of Jiang and Alkemade used a Si sample in which contained internal Ge delta layers which were grown by MBE at intervals of 11.9 nanometers. This sample allowed them to compare unambiguously the apparent depth of the Ge layers to the known depths, thus exposing any changes in sputtering rate throughout the structure of 10 equally spaced Ge delta layers. The weakness of the Jiang and Alkemade experiment lay in the rather wide spacing of the delta layers (11.9 nanometers) as well as the fact that different energies and angles of primary ion incidence were not tried. This present study is an extension of the Jiang and Alkemade work. It involves using a similar MBE sample with internal marker layers to also determine, unambiguously, enhancements in initial sputter rates and the depths to which the enhanced initial sputter rates extend. Most importantly, we have investigated a large portion of the energy-angle of incidence parameter space and have found several sets of conditions of oblique incidence with oxygen bombardment which show virtually no enhanced sputter rate at the beginning of the analysis. Data will also be shown which duplicates the sputtering conditions of the experiments shown in reference 1. We will show that some of the conclusions drawn by the authors of reference 1 are not supported by our data. @FootnoteText@ @footnote 1@K. Wittmaack and S.F. Corcoran, J.V.S.T. B 16(1), 272 (1998). @footnote 2@ Z.X. Jiang and P.F.A. Alkemade, Proc. 11th Annn. Conf. On SIMS, edited by G. Gillen, R. Lareau, J. Bennett and F. Stevie, John Wiley & Sons, (1998).

2:20pm **AS-ThA2 Secondary Ion Mass Spectrometry of Deep Trench Capacitors in Dynamic Random Access Memory***, **C.C. Parks,*** IBM Analytical Services*; H. Glawischnig,* Siemens AG, Germany*; M. Levy,* IBM Burlington*; Chr. Dieseldorff,* Siemens at International Sematech

Secondary Ion Mass Spectrometry (SIMS) supported the development of deep trench capacitors in Dynamic Random Access Memory (DRAM). SIMS is done efficiently by analyzing thousands of cells in parallel and the approach described in this paper is scalable to the multi-Gbit generation. By projecting out fundamental values using geometrical formalisms, the behavior of contaminants and dopants in sub-micrometer geometries is understood without the need for small-area measurements. Contamination aspects are addressed: quantifying and partitioning of halogen, alkali, and transition-metal residues among deep trench and other processing sectors. The deposition of self-limiting layers of arsenic during polysilicon fill of the deep trench is explored in detail. The doping of the trench side-walls, either through angle ion implants or by drive-in of doped-glass deposition, is quantified.

2:40pm **AS-ThA3 TOF-SIMS Depth Profiling of Novel Si Devices***, **J.G.M. van Berkum,*** *P.C. Zalm,* Philips CFT - Materials Analysis, The Netherlands **INVITED**

Since about two years, concentration depth profiles of dopants in e.g. Si are not only measured with magnetic-sector SIMS or quadrupole SIMS, but also with time-of-flight (TOF) SIMS. In this technique, two ion sources are operated alternatingly: (i) a short-pulsed high-energy 'analysis' beam (typically 800 ps 11 keV Ar@super +@) produces secondary ion mass spectra and (ii) in between the pulses a low-energy 'sputter' beam (typically <1 keV O@sub 2@@super +@ or Cs@super +@) erodes the surface. The ion beam mixing is (almost) completely determined by the energy of the sputter beam. Therefore, a very good depth resolution can be obtained without concessions to the analysis beam. High mass resolution (up to M/@DELTA@M=10.000) can be maintained due to the short pulse length and imaging during the depth profile with a lateral resolution down to 100 nm is possible. Thanks to the simultaneous mass detection, TOF-SIMS is particularly useful for devices with ultra-steep dopant profiles in the presence of other dopants or in devices with oxide layers or SiGe hetero-epitaxial layers. For example, for understanding the electrical behaviour of Schottky diodes or tunnel diodes with a high concentration of one or two dopants in an ultra-thin SiGe layer, it is essential to measure the dopant and the Ge concentrations at exactly the same depth. The same holds for CMOS devices with SiGe channel (typically a few nm's of SiGe at a few nm's distance from the gate oxide) or bipolar transistors with hetero-epitaxial base. The optimum condition for such measurements may differ from the optimum conditions for the elements separately. For B, P, As and Ge in Si, we often use O@sub 2@@super +@ primary ions, positive secondary ions and oxygen flooding to enhance the ion yields and suppress the pre-equilibrium effects. The segregation of Ge due to oxygen flooding is quantified by comparative measurements using different measurement conditions.

3:40pm **AS-ThA6 Nitrogen Incorporation and Trace Element Analysis of Nanocrystalline Diamond Thin Films by SIMS***, **D. Zhou,*** University of Central Florida*; F.A. Stevie, J. Mckinley,* Cirent Semiconductor*; H. Gnaser,* University of Kaiserslautern, Germany

Nitrogen has been recognized as an important impurity in diamond, and the nature of its electronic states has been a central concern in elucidating the electronic and the optical properties of both natural and synthetically grown diamond. Although substitutional nitrogen in diamond is a deep donor impurity, it can affect that optical transparency, thermal conductivity, and electron field emission characteristics of diamond. We report that nitrogen has been successfully incorporated into nanodiamond films produced from a N@sub 2@/CH@sub 4@ microwave plasma enhanced CVD. High mass resolution SIMS (with a Cs@super +@ source) characterization shows that the concentration of the incorporated nitrogen, monitored via CN@super -@ (26.0031 amu), can be as high as 10@super 21@ atoms/cm@super 3@ depending on the ratio of N@sub 2@ to CH@sub 4@ in the reactant gas and on the substrate temperature used for the film preparation. The SIMS depth profile demonstrates that the incorporated nitrogen is uniform through the diamond films (about 1 micron thick) except for the surface and the interface between the film and substrate. Furthermore, SIMS (with an O@sub 2@@super +@ source) analysis reveals that alkali elements such as Na, K and Li appear to be the major trace metallic impurities and/or contamination for the diamond thin films produced from CH@sub 4@/N@sub 2@, CH@sub 4@/Ar, or CH@sub 4@/H@sub 2@ discharge, but they are the bulk impurities only for the thin films prepared from CH@sub 4@/N@sub 2@ plasma. These alkali impurities could also play important roles in electronic properties such as electron field emission of nanodiamond thin films. The authors would like to acknowledge the support from the Advanced Materials Processing and Analysis Center and UCF/Cirent Materials Characterization Facility at University of Central Florida. D. Zhou also specially acknowledge valuable discussion with D. M. Gruen and A. R. Krauss at Argonne National Laboratory.

4:00pm **AS-ThA7 Quantitative ToF-SIMS Analysis of Industrial Polymers***, **A.A. Galuska,*** *D.W. Abmayr,* Exxon Chemical Co. **INVITED**

In recent years, ToF-SIMS has been developed as a tool for surface (top 10 Å) and microscopic (= 60 µm) polymer analysis. The technique is most commonly used to qualitatively identify chemical species on polymer surfaces. However, quantitative methods can also be routinely performed on polymer articles. In fact, much of the real power of the technique for industrial polymer analysis is associated with the quantitative information that can be obtained from the ToF-SIMS mass spectra. In this presentation, we will discuss quantitative ToF-SIMS methods for the analysis of comonomers, sequence distributions, MWs, and trace elements in various polymers. Issues associated with microscopic bulk analysis will also be discussed. When possible, quantitative methods will be demonstrated using industrially meaningful analyses.

4:40pm **AS-ThA9 Secondary Ion Emission from Molecular Surfaces and Overlayers under Noble Gas and Molecular Primary Ion Bombardment***, **D. Stapel,*** *A. Benninghoven,* Universität Münster, Germany

By changing from atomic to molecular primary ions, considerable increases in secondary ion yields Y(X@sub i@@super q@) are achieved, in particular for molecular surfaces and overlayers. In an earlier paper@footnote 1@ we report on yield increases up to a factor of 1000 for polymer surfaces under 10 keV SF@sub 5@@super +@ bombardment. The corresponding increase of damage cross sections @sigma@(X@sub i@@super q@) is relatively small, so that the increase in ionization efficiencies E(X@sub i@@super q@) = Y(X@sub i@@super q@)/@sigma@(X@sub i@@super q@) remains high. This has important consequences for the analytical application of molecular SIMS - for spectroscopy as well as for imaging and microarea analysis. For further yield optimization and for a better understanding of this yield enhancement by the use of molecular primary ions, we carried out systematic investigations for different polymers, metals and semiconductor materials, covered by a variety of molecular overlayers as biomolecules, additives, LB- and SA-layers, etc. Comparing molecular (SF@sub 5@@super +@ , C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 10@@super +@, ...) and atomic (Ar@super +@, Kr@super +@, Xe@super +@) primary ion bombardment we found for nearly all of the investigated molecular surfaces and overlayers a strong increase in molecular ion yields, a much smaller increase in the corresponding damage cross sections, and smaller secondary ion emission depths. Experimental results will be presented and will be compared with model calculations. @FootnoteText@ @footnote 1@ F. Kötter, A. Benninghoven, Appl. Surf. Sci., in press

5:00pm **AS-ThA10 Coincidence Counting in Highly Charged Ion Based Time-of-Flight Secondary Ion Mass Spectrometry***, **A.V. Hamza**, T. Schenkel, A.V. Barnes, D.H. Schneider,* Lawrence Livermore National Laboratory

The high (>1) secondary ion yield per incident primary ion, which is produced when slow, highly charged ions impinge on a surface, affords the collection of time-of-flight secondary ion mass spectra in coincidence mode. In coincidence mode a spectrum may be acquired in which a particular secondary ion is required for each recorded primary ion event. Primary ion events that do not exhibit the required secondary ion are discarded. Since the primary highly charged ion induces the emission of secondary ions from a localized area of ~20 nm, the coincidence measurement insures that secondary ion emission be from within 20 nm of the coincident secondary ion emission. Hence localized (20nm scale) chemical information is obtained. An example of the power of this technique with highly charged ions is presented for a tungsten/SiO@sub 2@ patterned silicon sample wafer. Details of the wafer processing steps can be discerned from the coincidence spectra. By this coincidence method trace impurities can be associated with tungsten features. This work was performed under the auspices of the U. S. Department of Energy at Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Electronic Materials and Processing Division
Room 314/315 - Session EM1-ThA

Dielectrics

Moderator: E. Garfunkel, Rutgers University

2:00pm **EM1-ThA1 Short Range Order and Electronic Structure of Amorphous Silicon Oxinitride***, **V.A. Gritsenko**,* Siberian Branch of Russian Academy of Science, Russia*; R.W.M. Kwok, Y.H. Ng, J.B. Xu,* The Chinese University of Hong Kong, China*; I.H. Wilson,* The Chinese University of Hong Kong, Hong Kong

The short range order and electronic properties (electronic structure, energy diagram, and charge transport) of bulk amorphous silicon oxynitride (a-SiO@sub x@N@sub y@) were reviewed for the further understand of a-SiO@sub x@N@sub y@ the properties of gate oxynitride of MOS devices on the atomic scale. Amorphous SiO@sub x@N@sub y@ consists of Si-O and Si-N bonds and involves five types of tetrahedra: SiO@sub@nu@@N@sub 4-@nu@@ for @nu@ = 0, 1, 2, 3, 4. The local bonding in SiO@sub x@N@sub y@ is governed by the Mott rule as shown in the equation 4=2x+3y. From x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, x-ray emission spectroscopy and the simulation of the electronic structure, we concluded that Si-O bonds in a-SiO@sub x@N@sub y@ are created by O 2s, 2p and Si 3s, 3p, 3d bonding states, and Si-N bonds are created by N 2s, 2p and Si 3s, 3p, 3d bonding states. Barriers for electron and hole injection at Si-SiO@sub x@N@sub y@ interface also gradually change with composition. The nature of the removal of hole traps from the SiO@sub 2@/Si interface during oxide nitridation was understood from the removing of Si-Si defects. The origin of Si-Si bond creation near the top surface of gate oxynitride after re-oxidation are understood on the basis of the Mott rule through the oxidation of nitride species Si@sub 3@N to form Si-Si bonds.

2:20pm **EM1-ThA2 Cathodoluminescence Spectroscopy of Nitrided Si-SiO@sub 2@ Interfaces***, **R. Bandhu**, J. Schäfer, A.P. Young, L.J. Brillson,* The Ohio State University*; H. Niimi, G. Lucovsky,* North Carolina State University

We use cathodoluminescence spectroscopy (CLS) to probe the electronic states at ultrathin gate dielectrics with nitrided Si-SiO@sub 2@ interfaces, known to improve reliability in advanced CMOS devices. The 5 nm-thick oxide at plasma-processed interfaces were: i) as-deposited (at 300 °C) structures, ii) 400 °C 30 min post-metallization annealed (PMA) in H2/N2, iii) 30 s 900°C rapid thermal annealed (RTA) in argon, and iv) a combination of both anneals. CLS emission energies and relative intensities vs. excitation energy (0.6-4.5 keV) were essentially unchanged for the as-deposited interface as reported for non-nitrided plasma-processed interfaces.@footnote 1@ In the near-IR (Ge detector), peaks appear at 0.8 and 1.0 eV, with the 1.0 eV peak intensity increasing with increasing electron energy. In the visible and near-UV (S-20 photocathode), features were observed at 1.9, 2.7 and 3.4 eV. From the depth variations, the 2.7 eV peak is generated near the surface of the oxide film, the 3.4 eV peak arises from the Si substrate, and the 1.9 eV feature comes from the near-interface region. After the PMA, CLS is essentially the same as for non-nitrided interfaces, except for an increase of the relative intensity of the 1.9 eV feature; after the RTA, analogous spectral features appear. However, the combination of the RTA and PMA does not completely suppress the 1.9 eV feature as for non-nitrided interfaces. CLS for as-deposited structures parallels optical second harmonic generation (OSHG); there are no differences with and without nitridation. However, as with OSHG, after the combined RTA/PMA, CLS reveals a substantial difference between nitrided and non-nitrided interfaces. The behaviors of the CLS features clearly distinguishes between interfacial defects (0.8 and 1.0 eV) and bulk defects (2.7 eV) which are significantly reduced by the combined RTA/PMA, and features that are intrinsic to the bonding chemistry, such as the 1.9 eV nitrided interface feature and the 3.4 eV Si substrate feature. @FootnoteText@ @footnote 1@A. P. Young, J. Schäfer, G. Jessen, R. Bandu, L. J. Brillson, H. Niimi, and G. Lucovsky, J. Vac. Sci. Technol. B, submitted. @footnote 2@G. Lucovsky, A. Banerjee, B. Hinds, C. Claflin, K. Koh and H. Yang, J. Vac. Sci. Technol. B15, 1074 (1997).

2:40pm **EM1-ThA3 Reliability of Ultra-thin Gate Dielectric formed with Nitrogen Implantation and Thermal Oxidation***, **Y. Ma**, M.S. Carroll, F. Li,* Bell Laboratories, Lucent Technologies*; C.T. Liu,* Bell Laboratories, Lucent Technologies, US*; C.Y. Sung, M.M. Brown,* Bell Laboratories, Lucent Technologies

Traditionally nitrogen was incorporated into oxide through oxidation or post-oxidation annealing in N@Sub 2@O or NO. With a well engineered process, a thin layer of oxide containing nitrogen forms at SiO@Sub 2@/Si interface. The gate oxide reliability can be improved in terms of device lifetime. Recently, nitrogen incorporation with nitrogen implantation has been studied. In this paper, ultra-thin gate dielectric was thermally grown on nitrogen implanted silicon substrates. The advantages of this technique are (i) the oxide growth rate can be significantly suppressed and (ii) a multiple gate dielectric thickness on same chip can be realized. However, previous reports showed that gate oxide quality is degraded. In this paper, we demonstrated that higher thermal budget is needed to remove the implantation induced damage and to improve the gate oxide reliability. The gate oxides were either grown or post-oxidation annealed at higher temperature. We also will present that the gate oxide reliability are nitrogen dose dependent. Gate oxide quality was evaluated with three different techniques: current ramp breakdown, time dependent dielectric breakdown and hot carrier aging test. Both current ramp and TDDB indicate that the gate oxide was degraded with nitrogen implant. However, the hot carrier aging test showed that the device lifetimes were longer for the nitrogen implanted ones. CMOS transistors were also fabricated. Device performances such as channel mobility, drive current, device yield will also be reported.

3:00pm **EM1-ThA4 Effect of Substrate Temperature in SiO@sub x@N@sub y@ Films Deposited By Electron Cyclotron Resonance***, **A. del Prado**, F.L. Martinez,* Universidad Complutense de Madrid, Spain*; M. Fernandez,* Instituto de Ciencia de Materiales, Spain*; I. Martil, G. Gonzalez Diaz,* Universidad Complutense de Madrid, Spain

High quality silicon oxynitride films for ULSI applications can be deposited at low temperatures using plasma assisted processes like the ECR-CVD technique.@footnote 1,2@ Physical properties of SiO@sub x@N@sub y@ films have been studied. The films have been deposited from mixtures of

SiH@sub 4@, O@sub 2@ and N@sub 2@, using the ECR-CVD technique, with substrate temperature ranging from room temperature to 200°C. FTIR spectroscopy, AES and ellipsometric measurementes have been performed in order to characterize the films. Low bonded hydrogen content is observed along the entire composition range from Si@sub 3@N@sub 4@ to SiO@sub 2@. N-H bonds are present in all the films, while Si-H bonds are detected only for those films deposited under high SiH@sub 4@ partial pressure. No O-H bonds are detected. When substrate temperature is increased, a slight decrease in total bonded H concentration is observed. A small shift (7-20 cm@super -1@) in the main FTIR absorption peak (Si-N/Si-O stretching band) is detected. This behavior is attributed to hydrogen release from N-H bonds due to the substitution of H for Si, with no signicant change in the film composition. FWHM of the main FTIR peak decreases as temperature is increased for all the composition range, indicating an improvement in the film quality, as this parameter is related to the structural order of the film. Silicon oxide films (SiO@sub 2.0@) deposited at 200°C show improved properties with respect to those deposited at room temperature. FWHM decreases from 96 cm@super -1@ to 88 cm@super -1@, and shoulder-to-peak ratio from 0.30 to 0.25. The position of the Si-O stretching band (1072 cm@super -1@) is unaffected. These values are very close to those obtained for thermally grown oxides,@footnote 2@ while the thermal budget of the process is reduced. @FootnoteText@ @footnote 1@S. V. Hattangady, H. Niimi, G. Lucovsky. J. Vac. Sci. Tech. A 14 (6) 3017 (1996) @footnote 2@D. Landheer, Y. Tao, J. E. Hulse, T. Quance, D. -X. Xu. J. Electrochem. Soc. 143 (5) 1681 (1996)

3:20pm **EM1-ThA5 Roughness at Si/SiO@sub 2@ Interfaces and Silicon Oxidation*, X. Chen,*** Argonne National Laboratory*; J.M. Gibson,* University of Illinois, Urbana **INVITED**

Roughness at Si/SiO@sub 2@ interfaces and silicon oxidation With a plan-view transmission electron microscopy technique to directly image buried Si/SiO@sub 2@ interfaces, we studied the interface roughness resulting from the oxidation process. Our results show that thermal annealing in nitrogen at 900 C can dramatically remove the interface roughness for Si(100)/SiO@sub 2@ interfaces.(Xidong Chen and J. M. Gibson Appl. Phys. Lett. 70, 1462 (1997)) In contrast, Si(111)/SiO@sub 2@ interfaces, which tend to be smoother than Si(100)/SiO@sub 2@ interfaces, are not affected by annealing. A model to link interface roughness and silicon oxidation kinetics was developed. This model not only qualitatively explains the difference between Si(111) and Si(100) interfaces that we saw but also shows that oxidation kinetics is the origin of the interface roughness. Hence, it might be a new approach to understand oxidation kinetics by studying interface roughness.

4:00pm **EM1-ThA7 Energy Dispersion of the Conduction Band Mass in Ultrathin SiO@sub 2@ Gate Oxides*, R. Ludeke,*** IBM T.J. Watson Research Center*; A. Schenk,* Swiss Federal Institute of Technology, Switzerland

The effective conduction band mass m@sub ox@ of a-SiO@sub 2@ has been the subject of extensive studies and considerable controversy, with a defacto value of 0.5m@sub 0@ having been adopted by most researchers.@footnote 1@ The STM based technique of Ballistic Electron Emission Spectroscopy (BEEM) has recently been used to obtain a value of m@sub ox@=(0.63±0.09)m@sub 0@, which was deduced from quantum interference (QI) oscillations in the BEEM current through a 2.8 nm oxide.@footnote 2@ However, the more fundamental issue of the energy dependence of m@sub ox@ has not yet been properly addressed experimentally or theoretically. We report here pronounced QI effects in the BEEM current through 2.2 nm oxides and an assessment of the energy dependence of m@sub ox@(E) obtained from simulations of the transport process. Up to five QI peaks were observed over a kinetic energy range of 2 eV relative to the conduction band minimum (CBM). Peak positions were reproducible to within 0.1 eV for injections at sites previously not exposed to the electron beam. Transmission coefficients (TC) for over-the-barrier injection were calculated by numerically solving the Schrödinger equation, which included both image force effects and an energy dependent m@sub ox@(E). The gradients of m@sub ox@(E) at the energies of the TC maxima were adjusted until a match to the maxima in the data was obtained. With the assumption of a 2.2 nm oxide thickness (measured by ellipsometry, with other measurements in progress), the fits show that m@sub ox@ increases rapidly from 0.60m@sub 0@ near the CBM to 0.86m@sub 0@ 2 eV above the CBM. An expected trend toward m@sub ox@=1m@sub 0@ for larger energies is suggested as well by the results. @FootnoteText@ @footnote 1@A. Schenk and G. Heiser, J. Appl. Phys. 81, 7900 (1997) and references therein. @footnote 2@H.J. Wen, R. Ludeke and A. Schenk, J. Vac. Sci. Technol. B 16, to be published

4:20pm **EM1-ThA8 Ultra Thin Silicon Oxide Film on Si(100) Fabricated by High Purity Ozone at Atmospheric Pressure*, K. Nakamura,*** *S. Ichimura, A. Kurokawa,* Electrotechnical Laboratory, Japan*; K. Koike, G. Inoue, T. Fukuda,* Iwatani International Corporation, Japan

Microstructure of electronic devices requires much thinner silicon oxide film so that alternative oxidants must be developed to lower substrate temperature during oxidation. High purity ozone is expected as one of such oxidants because of its higher reactivity not only for adsorption on surfaces@footnote 1,2@ but also for thin film growth@footnote 3@ in comparison with that of molecular oxygen. However, lowering oxidation temperature also needs high dose of ozone to compensate decreasing oxidation rate. We investigated growth kinetics of oxide film under different ozone pressure conditions and succeeded in formation of oxide with the thickness >2nm at room temperature. First we fabricated oxide by exposing Si(100) with the substrate temperatures between 300°C and 700°C to 8x10@super -4@Pa ozone for 90 min. in an UHV chamber. Etching rates by 0.1wt% hydrofluoric acid solution of these SiO@sub 2@ films are equivalent to that of device-grade thermally grown oxide. Etching rate is so sensitive to film density that oxide films made by use of high purity ozone at lower substrate temperatures are expected to be as dense as thermally grown oxide. However, the oxidation rate, especially at oxide thickness >5Å, decreased as oxidation temperature decreased. So we utilized another ozone generator system giving an atmospheric pressure for much higher ozone dose. In this processing, oxide film >2nm was successfully grown on Si(100) even at room temperature. Etching rate of SiO@sub 2@ fabricated on Si(100), for example, at 350°C by this method is almost the same as that of thermally grown oxide or as those with lower ozone dose mentioned above. Effects of such treatment as preoxidation or hydrogen termination on oxidation kinetics and film quality will also be discussed. @FootnoteText@ @footnote 1@ K. Nakamura, A. Kurokawa and S. Ichimura, J. Vac. Sci. Technol. A 15, 2441 (1997). @footnote 2@ K. Nakamura, A. Kurokawa and S. Ichimura, Surf. Interface Anal. 25, 88 (1997). @footnote 3@ A. Kurokawa, S. Ichimura and D. W. Moon, Mat. Res. Soc. Symp. Proc. 477, 359 (1997).

4:40pm **EM1-ThA9 Mixed Silicon Dioxide / Tantalum Oxide Layers for High k MOS Gate Dielectrics Formed by Plasma Oxidation of Si and Ta Using a rf Remote N@sub 2@O Plasma Source*, J.J. Chambers,*** North Carolina State University, U. S. A.*; G. Lucovsky, G.N. Parsons,* North Carolina State University

High dielectric constant gate insulators will be needed to minimize gate tunneling in sub-100 nm integrated circuit devices. High k will allow the gate capacitance to scale with gate length without a significant reduction in gate dielectric thickness. Mixing SiO@sub 2@ with high k metal oxides (including Ti or Ta oxides) is expected to increase the dielectric constant without losing the beneficial properties of the Si/SiO@sub 2@ system. We have developed a rf plasma source capable of concurrent remote plasma CVD and separately controlled d.c. sputtering of metals. The motivation of this work is to establish an in-situ process for controlled silicon/high-k interface formation that will be stable during subsequent high-k dielectric deposition. Using an Ar plasma, Ta was sputtered for 1 to 10 minutes leading to controlled coverage onto a cleaned silicon surface. The Ta target was removed from the plasma zone, and the surface was exposed to a remote N@sub 2@O plasma for 10 minutes. After oxidation, XPS and AES were used to characterize Ta, Si and O bonding on the surface. XPS of the oxidized surface shows Ta 4f peaks at 28.4 and 30.3 eV indicative of Ta-O bonds. Si 2p peaks at 101.1 and 104.7 eV are also observed, indicating Si and Si-O bonding. As the surface coverage of tantalum increases, XPS of the oxidized surface shows the O 1s peak at 533.9 eV developing a shoulder at lower binding energy characteristic of O-Ta bonding. This data indicates, for the studied range of small tantalum surface coverage, that the tantalum is completely oxidized forming tantalum oxide and silicon oxide layers. Ellipsometry results indicate the oxide thickness is less than 20 Å. We will discuss the effect of initial Ta layer thickness on oxide formation, and experiments of co-deposition of metal and SiO@sub 2@ to form thin mixed metal oxide / silicon dioxide high dielectric constant films.

5:00pm **EM1-ThA10 Thermal Stability of a-SiNx:H Films Deposited by Plasma Electron Cyclotron Resonance***, F.L. Martinez,* ***A. del Prado,*** Universidad Complutense de Madrid, Spain*; D. Bravo, F.J. Lopez,* Universidad Autonoma de Madrid, Spain*; I. Martil, G. Gonzalez-Diaz,* Universidad Complutense de Madrid, Spain

Amorphous hydrogenated silicon nitride is widely used in semiconductor devices. Its higher dielectric constant compared to silicon dioxide results in a larger gate insulator capacitance, which in its turn means a larger transconductance and a smaller threshold voltage shift for a given defect charge concentration. A Rapid Thermal Annealing (RTA) post-treatment can improve significantly the properties of the dielectric and the interface. We have analyzed the influence of RTA on Al/SiN@sub x@:H/Si structures with x=1.55. The silicon nitride is deposited by the Electron Cyclotron Resonance plasma method and the films were annealed at temperatures ranging from 300ºC to 1050ºC. Determination of the dangling bond density in the insulator was done with Electron Paramagnetic Resonance, while the density of interface states was obtained from the high-low frequency capacitance method. Resistivity and breakdown field were deduced from current measurements in accumulation. A pronounced dip in the density of dangling bonds is obtained for moderate annealing temperatures, from 1.85E18 cm@super -3@ for the as-deposited film down to 9.58E16 cm@super -3@ at the point of inversion of the trend between 500 and 600ºC. The density of interface states is also reduced in this range of temperatures from 3.6E11 eV@super -1@cm@super -2@ to 1.2E11 eV@super -1@cm@super -2@. Resistivity and breakdown field are maintained in the range 5E14-5E15 @OMEGA@cm and 6.4-6.6 MV/cm respectively up to a temperature of 600ºC. We attribute the improvement of the film properties and interface characteristics to a thermal relaxation and reconstruction of the silicon nitride lattice and its interface with the silicon substrate. In this range of temperatures we did not observe hydrogen evolution from the SiN@sub x@:H lattice. For temperatures above this threshold the electrical properties suddenly deteriorate and the density of dangling bonds increase. At even higher temperatures (above 800ºC) a release of hydrogen from N-H bonds takes place.

Electronic Materials and Processing Division
Room 316 - Session EM2-ThA

Non-destructive Testing and In-situ Diagnostics

Moderator: C.J. Palmstrom, University of Minnesota

2:00pm **EM2-ThA1 In-Situ IR Spectroscopic Study of the Chemical Process of Si-Related CVD Thin Films***, **T. Wadayama**,* Tohoku University, Japan **INVITED**

A comprehensive understanding of the molecular process of thin films growing under the chemical vapor deposition (CVD) conditions is quite of importance from a technological point of view. In-situ molecular vibrational study of the dynamic behavior of surface species under such conditions should give us an important clue to the understanding of the process and, further, a useful guide in developing new thin film devices. However, there exist few techniques available for the in-situ observation of the process. The polarization modulation IR spectroscopy (PM-IR), which is based on the difference in absorption intensity of surface species upon the change in the polarization state of the incident IR light, is a powerful tool for detecting signals from surface species over wide ranges of the substrate temperature and gaseous pressure. We have been successful in applying this method to observing in-situ the photo-CVD process of the Si-related thin films as well as the reaction of the films with the metal-organic and the etchant molecules. In the present talk, we will mention (1) the basis of the PM-IR method, the results obtained through the in-situ IR observation of (2) the growing process of the a-Si:H and the a-SiN@sub x@ thin films, and (3) the reaction of the a-Si:H/dimethylaluminum hydride ((CH@sub 3@)@sub 2@AlH) and the a-SiN@sub x@/F@sub 2@. The results suggest that the hydrogen-rich and the Si-rich layers are present on the growing surface of the a-Si:H and the a-SiN@sub x@ film, respectively, illustrating the feasibility of the PM-IR method to the in-situ molecular vibrational study of the chemical process of the CVD thin films.

2:40pm **EM2-ThA3 Integrated Real-Time Spectroscopic Ellipsometric and Reflectance Difference Measurements on a Commercial OMCVD Reactor***, **M. Ebert**,* Technical University Berlin, Germany*; K.A. Bell, S.D. Yoo, G.D. Powell, D.E. Aspnes,* North Carolina State University

Comprehensive monitoring of epitaxial growth by organometallic chemical vapor deposition (OMCVD) requires not only near-surface measurements for compositional analysis of the most recently deposited material and bulk measurements for determining layer thicknesses, but also surface analysis for information about growth chemistry. Here, we describe the first unified optical system that meets all 3 needs simultaneously. This system is a multichannel, parallel acquisition and processing, combined reflectance-difference (RD) spectrometer and rotating-polarizer spectroscopic ellipsometer (SE). It is built around a commercial rotating-spindle OMCVD reactor and a state-of-the-art high-speed 16-bit photodiode array (PDA) and allows data to be taken from 200 to 800 nm at a repetition rate of 600 ms to a precision of ±0.0001. These capabilities are realized by the PDA detector, synchronization of the spindle to the polarizer in a 3-to-1 ratio, and a spindle design that allows wobble to be reduced to less than 0.02° during rotation. RD measurements on a test (011) Si wafer, when transformed to normal incidence, are in excellent agreement with normal-incidence data. In addition to the diagnostic capabilities of SE, updating complete RD spectra at 0.6 s intervals allows surface reconstructions to be interpreted by pattern recognition as in RHEED.

3:00pm **EM2-ThA4 Real-Time Optical Control of Ga@sub 1-x@In@sub x@P Film Growth by P-Polarized Reflectance***, **N. Dietz**, K. Ito, V. Woods,* North Carolina State University

The engineering of advanced optoelectronic integrated circuits implies the stringent control of thickness and composition. These demands led to the development of surface-sensitive real-time optical sensors that are able to move the control point close to the point where the growth occurs, which in a chemical beam epitaxy process is the surface reaction layer (SRL), built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In this contents, we explored the application of p-polarized reflectance spectroscopy (PRS) for real-time monitoring and control of pulsed chemical beam epitaxy (PCBE) during low temperature growth of epitaxial Ga@sub 1-x@In@sub x@P heterostructures on Si(001) substrates by PCBE. Using a 'reduced order kinetic model' we demonstrate the linkage of the PRS response towards surface reaction chemistry, composition, film growth rate, and film properties. Mathematical control algorithms are introduced and applied that link the PR signals to the growth process control parameters to control composition and growth rate of epitaxial Ga@sub 1-x@In@sub x@P heterostructures.

3:20pm **EM2-ThA5 Electron Cyclotron Resonance Induced Surface and Subsurface Defects in GaAs Exposed to a Chlorine/Ar Plasma***, **O.J. Glembocki**, R.T. Holm, W.E. Carlos, D. Leonhardt,* Naval Research Laboratory*; C.R. Eddy,* Boston University*; K.K. Ko, S.W. Pang,* University of Michigan*; D.S. Katzer,* Naval Research Laboratory

The detection and control of dry etched induced electronic damage is critical to the formation of high quality semiconductor devices. In order to avoid ambient contamination, we have used in-situ photoreflectance (PR) to study the behavior the surface electric fields and surface photovoltage in both n-type and p-type GaAs exposed to a chlorine/Ar plasma generated by an electron resonance cyclotron source. By monitoring the desorption of the Ga and As chlorides, we find that the removal of Ga is the rate limiting step. This leads to a surface that is Ga rich and decorated by Ga vacancies which change the surface pinning position in both n- and p-GaAs. In addition, the etched surfaces show a decreased surface photovoltage. By using in-situ chemical etching/passivation with chlorine, we are able to uncover subsurface damage and show that it is distinctly different from the Ga vacancies formed on the surface. We find that the bulk etch damage has an exponential profile and that it is amphoteric, behaving as a very deep donor in n-GaAs and a deep acceptor in p-GaAs. Our experiments further indicate that both states of this defect lie below midgap. Possible candidates are point defects such as interstitials. Spin resonance results will be used in discussing the nature of the defects.

3:40pm **EM2-ThA6 Reciprocal-Space Analysis of Optical Spectra***, **S.D. Yoo**, N.V. Edwards, D.E. Aspnes,* North Carolina State University

Reciprocal-space analysis of optical spectra yields significant improvements in determining critical point energies in comparison to conventional real-space analysis. Enhanced diagnostic power is realized because, among other aspects, baseline effects, spectral information, and noise are localized in the low, middle, and high Fourier coefficients, respectively, allowing information to be extracted largely independent of baseline and noise artifacts. We use reciprocal-space analysis to address several issues regarding spectroscopy of electronic materials, both in real-time and off-line applications. Among these are the determination of optimal slit widths and numbers of data points that allow data to be taken at the fastest rate for a given signal-to-noise ratio and a simple analytic expression that describes the apparent shift of apparent critical point energies with overlayer thickness. We apply reciprocal-space analysis to various problems in electronic materials. The binding energies of the A, B, and C excitons of various GaN layers epitaxially grown on sapphire and SiC substrates have been determined to within 1 meV from low temperature reflectance data, which allows the in-plane strain and upper valence band parameters to be determined to similar accuracy. Apparent bulk critical point energies and broadening parameters of (110) Ge samples with and without a thin (~30 Å) Ni overlayer show substantial (~10 meV) differences, providing further evidence of photon-induced localization of optically excited electron and hole states. Finally, analysis of photoluminescence and photoluminescence excitation (PLE) spectra of GaAs/AlGaAs single quantum wells shows that exciton energies can be obtained independent of baseline artifacts to a wavelength uncertainty of 0.1 Å, which is particularly important for PLE where baselines cannot be determined unambiguously.

4:00pm **EM2-ThA7 Observation of Adsorption and Reaction of NH@sub 3@ on Al@sub 2@O@sub 3@, AlN and AlON Under Steady-State Conditions Using IRRAS***, **V.M. Bermudez,*** Naval Research Laboratory

The surface chemistry of Al@sub 2@O@sub 3@, AlN and Al oxynitride ("AlON") with NH@sub 3@ is important in the MOCVD growth of GaN on these substrates. Thin films of Al@sub 2@O@sub 3@, AlN and AlON have been grown by reacting a NiAl(111) surface with O@sub 2@, NH@sub 3@ or NO, respectively.@footnote 1@ The resulting buried-metal-layer structures have then been employed as substrates for studies of NH@sub 3@ adsorption under steady-state conditions, at 300 K and up to 200 Torr, using polarization-modulated fourier-transform infrared reflection absorption spectroscopy. For Al@sub 2@O@sub 3@ evidence is seen, in the form of a change in the LO phonon, for incorporation of N into the surface to form a dilute "AlON-like" phase. The @delta@@sub s@ symmetric deformation mode of adsorbed NH@sub 3@ is easily detected under high (@>=@25 Torr) static pressures. For AlN, no evidence of adsorbed NH@sub 3@ is seen in a 200 Torr ambient. For AlON, distinct surface and volume LO phonon modes are seen, with the former responding reversibly to chemisorbed NH@sub 3@. The @delta@@sub s@ frequency indicates a lesser degree of Lewis acidity on AlON vs. Al@sub 2@O@sub 3@ surfaces, which may favor 2D GaN growth on AlON by increasing the surface mobility of NH@sub x@ species. For each of the three materials, IRRAS also provides useful information about the structural quality of the films prior to NH@sub 3@ exposure. @FootnoteText@ @footnote 1@Franchy et al., Appl. Phys. A 65 (1997) 551.

4:20pm **EM2-ThA8 Time of Flight Mass Spectroscopy of Recoiled Ions Comparative Studies of Gallium Nitride Thin Film Deposition By Various Molecular Beam Epitaxial Methods***, E. Kim, I.E. Berishev, **A. Bensaoula,*** University of Houston*; K.L. Waters, J.A. Schultz,* Ionwerks

GaN thin films were successfully grown by electron cyclotron resonance molecular beam epitaxy (ECR-MBE), gas source MBE (GSMBE), and chemical beam epitaxy (CBE). Time of flight mass spectroscopy of recoiled ions (TOF-MSRI) and RHEED were used in-situ to determine the surface composition, the crystalline structure, and the growth mode of GaN thin films deposited by the three MBE methods. The substrate nitridation and the buffer layers were characterized by TOF-MSRI and RHEED. In GSMBE, the Ga/N ratio is found to correlate well with ex-situ optical properties. In the case of CBE, the carbon incorporation determines the surface morphology, the crystalline quality and the optical activity of the epilayers. In the case of CBE, no nucleation was possible until a combination of ECR nitrogen and TEG was used for the low temperature buffer. The carbon and oxygen levels were found to depend greatly on the TeGA flow and substrate temperature. A model describing the main experimental observations will be presented. The model explains both the chemical dissociation of ammonia at low temperatures and the Ga to N TOF-MSRI peak ratio for various Ga and ammonia fluxes.Our study shows that under optimized conditions crystalline epilayers with good optical and surface morphologies can be obtained with all three methods. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061.

4:40pm **EM2-ThA9 Near-Surface Variation of Gallium Nitride Cathodoluminescence with Annealing***, **T. Levin**, J. Schäfer, A.P. Young, L.J. Brillson,* The Ohio State University*; J.D. MacKenzie, C.R. Abernathy,* University of Florida, Gainesville

Er-doped GaN with its promising luminescence yield is of considerable importance for optical communications. However, interfaces can induce significant changes in Er efficiency for optical pumping. Here we report on low energy cathodoluminescence spectroscopy (CLS) to probe the emission of GaN:Er as a function of distance from the semiconductor surface. CLS reveals order-of-magnitude emission variations of Er dopants and related Er-defect complexes vs. depth. Variable incident beam energies (0.5 - 5 keV) provided a strongly depth-dependent excitation from ca. 4 to 40 nm. GaN was grown by metal-organic molecular beam epitaxy at 925°C and doped to 3 x 10@super 18@ cm@super -3@. The primary spectral feature observed was the 0.8 eV (1554 nm) Er emission, which increases by over an order of magnitude with increasing excitation depth. Relative to the broad 'yellow' luminescence between 1.5 and 2.5 eV, which exhibits little or no increase away from the GaN surface, the variation in 0.8 eV emission suggests a depletion of Er within the outer 10 nm. The CLS also reveals three sharp spectral lines at 1.8, 2.2, and 2.3 eV which have been associated with Er 4f transitions from excitation spectroscopy.@footnote 1@ However, the intensities of these features do not scale directly with the 0.8 eV line as a function of depth or processing, but reflect the sensitivity of these additional transitions to near-surface defects and impurities. Annealing the GaN:Er to 500°C for 5 min extends the otherwise bulk emission from these levels to a more uniform distribution extending to within 10 nm of the surface. Further annealing to 700°C promotes even stronger near-surface as well as bulk emission from these lines. However, it produces no significant change in the depth distribution of the 0.8 eV emission but enhances its yield by over a factor of two. Overall, the contrast in intensity variation of specific Er 3+ emission lines with depth reveals the sensitivity of dopant intra-shell transition strengths to near-surface defects. @FootnoteText@ @footnote 1@M. Thaik, U. Hommerich, R.N.Schwartz, R.G.Wilson, and J.M.Zavada, Appl. Phys. Lett. 71, 2641 (1997).

5:00pm **EM2-ThA10 In-situ Formation, Reactions, and Electrical Characterization of MBE Grown Metal/Semiconductor Interfaces***, **L.C. Chen**, D.A. Caldwell,* University of Minnesota*; T.G. Finstad,* University of Oslo, Norway*; C.J. Palmstrom,* University of Minnesota

An in-situ probe station is used for the determination of the electronic properties of interfaces being modified in an MBE system. After MBE growth of the semiconductor structures, contacts were formed by metal deposition through a removable molybdenum shadow mask. An abrupt change in doping profile serves as a marker layer to allow doping density versus depth profile measurements obtained from capacitance-voltage (C-V) to be used to measure the position of the electrical metal/semiconductor interface relative to the marker layer, allowing metal/semiconductor reaction kinetics to be determined electrically in-situ. C-V measurements on n/n@super +@ GaAs structures were used to monitor the Ni/GaAs reaction and subsequent GaAs regrowth. The measurements indicated that 500Å of Ni consumes 700Å of GaAs during Ni@sub 3@GaAs formation, which is in excellent agreement with RBS and cross-sectional TEM measurements. Exposure of Ni@sub 3@GaAs to As@sub 4@ at 300°C results in the formation of NiAs at the surface and epitaxially regrown GaAs at the Ni@sub 3@GaAs/GaAs interface. The doping profiles indicated the complete regrowth of the 700Å GaAs beneath the contact. In-situ current-voltage (I-V) measurements of the NiAs/regrown-GaAs interfaces showed good Schottky behavior (V@sub bn@=0.87 V, n=1.08). C-V measurements showed further that the net electrically active donor density 2000Å beneath the contact changed during the different stages of reaction; it was 9.0x10@super 16@ (after Ni deposition), 6.5x10@super 16@ (after complete Ni@sub 3@GaAs formation), 5.Ox1O@super 16@ (after subsequent GaAs regrowth), and 9.0xl0@super 16@ (after an additional 585°C anneal). This results from the formation of point defects in the underlying GaAs during the reactions, which are eliminated by a 585°C anneal. In-situ electrical measurements on MBE-grown epitaxial metallic compound/Ga@sub 1-x@Al@sub x@As heterostructures grown on various surface terminations before and after annealing with emphasis on Sc@sub x@Er@sub 1-x@As structures will also be presented.

Magnetic Interfaces and Nanostructures Technical Group Room 324/325 - Session MI-ThA

Structure & Magnetism of Surfaces & Interfaces

Moderator: J.G. Tobin, Lawrence Livermore National Laboratory

2:00pm **MI-ThA1 Exchange Coupling in Co/Au/Co Sandwiches***, **T. Duden**, E. Bauer,* Arizona State University

The evolution of the magnetic domain structure during the growth of the Co layer on top of (111)-oriented Au spacer layers deposited onto a W(110) surface is studied by spin-polarized low energy electron microscopy. Pronounced biquadratic coupling is found not only at the nodes of the bilinear coupling but generally above the spin reorientation transition in the top layer. This produces a wrinkled magnetization or magnetization waves in the top layer. The results are discussed in the light of the various mechanisms which can lead to biquadratic coupling.

2:20pm **MI-ThA2 Experimental and Model Theoretical Dispersions of Unoccupied Metallic Quantum Well States in Cu/fccCo/Cu(100) and Related Systems***, **A.G. Danese**, F.G. Curti, R.A. Bartynski,* Rutgers University

The dispersion with parallel momentum (k @sub ||@) of unoccupied metallic quantum well (MQW) states in the Cu/fccCo/Cu(100) system has been measured using inverse photoemission and modeled using a phase accumulation approach. For Cu films in the 2 - 4 monolayer range, a state close to the Fermi level is observed to have a flat dispersion near the neck of the Cu Fermi surface along the @GAMMA@-BAR X-BAR direction of the two dimensional Brillouin zone. Appearance of this state coincides with a hybridization gap in the Co minority spin bands. The calculation shows that the large effective mass of this state is the result of the rapid change in the scattering phase shift across the gap. The periodicities with which MQW states cross the Fermi level at the center and at the neck of the Cu Fermi surface, which correspond to the long and short period oscillatory magnetic coupling in this system, are well reproduced by the calculation. Furthermore, the observed phase shift of the short period magnetic coupling when the ferromagnetic layer is changed from Fe to Co to Ni layers can be attributed to changes in the position of this hybridization gap with respect to the Fermi level across this series. The effect of this behavior on the strength of the short period magnetic coupling in these systems is discussed.

2:40pm **MI-ThA3 Spin-Polarized Quantum Well States***, **K.N. Altmann**, W.L. O'Brien, D.J. Seo, J. McKay,* Synchrotron Radiation Center, Univ. of Wisconsin, Madison*; F.J. Himpsel,* University of Wisconsin, Madison*; P. Segovia, A. Mascaraque, E.G. Michel,* Univ. Autonoma Madrid, Spain*; A. Naermann, J.E. Ortega,* Univ. del Pais Vasco, San Sebastian, Spain

Quantum well states are intimately connected to the oscillatory magnetic coupling observed in magnetic multilayers.@footnote 1,2,3@ The spin-polarization of these states is non-trivial since they reside in a non-magnetic spacer material. We have grown Cu/Co/Cu-(100) quantum wells in a chamber containing RHEED, SMOKE, MBE, and sputtering facilities. The high quality of our fcc-Co(100) layers is evidenced by the extremely low coercivity of < 1 Oe, which indicates minimal pinning of the domains at defects. These films were transferred in situ to a spin-polarized, angle-resolved photoemission system that uses undulator radiation from the SRC. Quantum well states with s,p and d character were observed when depositing films with sharp interfaces at low temperature and annealing them to room temperature. Also, a surprisingly-strong photon energy dependence was observed, even at energies of 70-80 eV, which needs a rethinking of the excitation process for "two-dimensional" quantum well states. Some of the quantum well states appear to be split, either due to multiple layer thicknesses, or due to a highly-unusual "inverted" magnetic splitting. Scanning tunneling spectroscopy measurements are in progress to find the layer-by-layer change in the energy of quantum well states. @FootnoteText@ @footnote 1@J.E. Ortega and F.J. Himpsel, Phys. Rev. Lett. 69, 844 (1992). @footnote 2@P. Segovia, E.G. Michel, and J.E. Ortega, Phys. Rev. Lett. 77, 3455 (1996). @footnote 3@F.J. Himpsel, J.E. Ortega, G.J. Mankey, and R.F. Willis, Adv. Phys., in press.

3:00pm **MI-ThA4 Systematic Measurement of Exchange Coupling Across the Periodic Chart of 3-d Transition Elements to Understand Magnetization In Ferromagnetic Mn Alloys@footnote 1@***, **W.L. O'Brien**,* University of Wisconsin, Madison*; S. Banerjee, B.P. Tonner,* University of Wisconsin, Milwaukee

Ultrathin films of Mn alloyed with Fe, Co and Ni have magnetic properties quite distinct from their bulk counterparts with same composition. Even the sign of exchange coupling in the ultrathin films are opposite to those of bulk alloys. For example, Mn impurities in bulk Fe are ferromagnetic with the magnetization of Mn parallel to the Fe magnetization, while we find that ultrathin alloys of the same composition are ferrimagnetic with an antiparallel coupling between Mn and Fe. Bulk Mn-Co alloys with dilute Mn concentration are ferrimagnetic with antiparallel coupling between Mn and Co whereas ultrathin films of same composition have the magnetization of Mn parallel to the Co. Finally, bulk 1:1 MnNi is an antiferromagnet, while the ultrathin alloys of same composition are ferromagnetic with Mn magnetization parallel to the Ni magnetization. To explore how widespread are these substantial differences in the magnetic phase diagrams of the ultrathin films, as compared to bulk, we performed a systematic measurement of the magnetic coupling for V, Cr, Mn, Fe, Co and Ni overlayers to Fe, Co and Ni substrates. The sign of the exchange coupling can be summarized by a simple electron counting rule. In this analysis of the periodic chart, we do not find parallel magnetic coupling when the sum of the formal atomic number of d electrons per atom (overlayer plus substrate) is less than 12. Considering this d=12 rule, Mn is located in a special position in the periodic table near the transition region between parallel and antiparallel coupling with Fe, Co and Ni. This rule works both for atomically clean surfaces, and surfaces modified by chemisorption. @FootnoteText@ @footnote 1@Work supported by the National Science Foundation, DMR, and performed at the Wisconsin Synchrotron Radiation Center.

3:20pm **MI-ThA5 Epitaxial Fe and Co Layers on Cu Crystals***, **J. Kirschner**,* Max-Planck-Institut für Mikrostrukturphysik, Germany **INVITED**

Fe and Co exhibit a multitude of structural and magnetic phases when deposited on to high-index planes of fccCu. Much work has been done on films made by thermal deposition or sputter deposition. We added pulsed laser deposition (PLD) in UHV and chemical deposition, and studied similarities and dissimilarities. Most striking effects are observed for pulsed laser deposition, which may alter the growth mode (from 3D growth for thermal deposition (TD) to layer-by-layer growth for PLD), magnetic anisotropies (from perpendicular (TD) to in-plane (PLD) for Fe/Cu(100), and magnetic moments (from low-spin (TD) to high-spin (PLD) for Fe/Cu(111). Co deposited electrochemically on to Cu(100) grows pseudomorphically up to 5 monolayers and non-pseudomorphically beyond. This has been found by in-situ surface x-ray diffraction. Effects of reduced dimensionality ocurr at surfaces and at steps. In the former case an oscillatory behaviour of the surface magnetization with one monolayer period has been observed by magneto-optical second harmonic generation. Magnetic nano-wires may be created by step edge decoration on stepped Cu(111). These resemble one-dimensional Ising chains (which has no net magnetization at thermal equilibrium), but show magnetic hysteresis at low temperature.

4:00pm **MI-ThA7 Fermi Surface Study of Pseudomorphic Fe@sub 1-x@Ni@sub x@ and Co@sub 1-x@Ni@sub x@ Thin Films on Cu(100)***, **M. Hochstrasser**, F.O. Schumann*, R.F. Willis,* Pennsylvania State University*; T.R. Cummins, G.D. Waddill,* University of Missouri, Rolla*; S.R. Mishra, J.G. Tobin,* Lawrence Livermore National Laboratory*; E. Rotenberg,* Lawrence Berkeley National Laboratory

We report angle resolved photoemission studies of the electronic behavior of ultrathin epitaxial layers of fcc structured binary alloys, Fe@sub 1-x@Ni@sub x@ and Co@sub 1-x@Ni@sub x@, deposited by molecular beam epitaxy on Cu(100) substrates. In particular, we have used Fermi surface mapping to monitor changes in the Fermi surface with increasing magnetization density. Fermi surface mapping has shown to be a valuable method to investigate for example the collapse of the exchange splitting between the upper and lower d-band in Ni@footnote 1@ and surface electronic states of hydrogen adsorbed on W(110).@footnote 2@ Co@sub 1-x@Ni@sub x@ and Fe@sub 1-x@Ni@sub x@ binary alloys show a different behavior in the bulk. Co@sub 1-x@Ni@sub x@ is structurally and magnetically well-behaved. In particular the magnetic moment varies linearly as a function of concentration. This is in sharp contrast to fcc Fe@sub 1-x@Ni@sub x@ which displays a magnetic instability at ~65% Fe content. An extended regime of fcc stability is possible via epitaxy on Cu(100).@footnote 3@ We investigated the changes in the Fermi surfaces of Fe@sub 1-x@Ni@sub x@ and Co@sub 1-x@Ni@sub x@ pseudo-morphic film alloys depending on various concentrations of Ni in a large photon energy regime and compared these measurements with the known Fermi surface of Ni(100), Cu(100) and Co(100). We observe a change in the Fermi surface with increasing magnetization density e.g. number of holes in the d-band by changing the stoichiometry of our samples. @FootnoteText@ *present address: Department of Chemistry and Material Science, Lawrence Livermore National Laboratory, U.S. @footnote 1@T. Greber et al., Phys. Rev. Lett. 79, 4465 (1997). @footnote 2@E. Rotenberg et al., Phys. Rev. Lett. 80, 2905(1998). @footnote 3@F.O. Schumann et al., Phys. Rev. Lett. 79, 5166 (1997).

4:20pm **MI-ThA8 Growth Study of FePt(001) L1_0 ordered alloys using a Temperature Wedge Method***, **M.M. Schwickert**,* Ohio University*; M.F. Toney, M.E. Best, J.-U. Thiele, L. Folks,* IBM Almaden Research Center*; G.R. Harp,* Ohio University*; D. Weller,* IBM Almaden Research Center

The L1_0 ordered phase of FePt has unique properties like enhanced magneto-optical Kerr effects and large magnetic anisotropy. Of particular interest is the formation temperature and growth kinetics of this phase. Fully ordered material has been synthesized using MBE growth at temperatures as low as 500oC. Spontaneous ordering induced by surface diffusion with a 0.2 eV barrier height was found.@footnote 1@ The present study aims at a combinatorial mapping of growth temperatures and seed techniques of MBE type, (001) and (110) oriented FePt films on MgO substrates. We have developed a temperature wedge technique in which temperature gradients of several hundred Kelvin can be established.

Respectively, electron beam evaporated films show systematic dependencies of magnetic, magneto-optic and structural properties as function of "wedge" position, corresponding to temperature. Magnetic hysteresis properties and anisotropy fields were characterized with a polar and transverse Kerr looper with spatial resolution. Structural data including quantification of the long range chemical ordering S as function of temperature were obtained from x-ray diffraction measurements. Finally we report on a combined AFM/MFM study of these films, revealing the equilibrium magnetic domain structure in correlation with topographic features. @FootnoteText@ @footnote 1@R.F.C. Farrow et al., Appl. Phys. Lett. 69, 116 (1996)

4:40pm **MI-ThA9 The Effect of Oxygen on the Growth and the Surface Magnetism of Iron Films***, R. Moroni, F. Bisio, M. Salvietti, M. Canepa,* ***L. Mattera,*** University of Genova, Italy

The effect of oxygen on the growth and the surface magnetism of iron films has been investigated by Helium Reflectivity (HR) and Spin Polarized Metastable Deexcitation Spectroscopy (SPMDS) during the growth of Fe on an O(1X1)-Fe adlayer. HR and SPMDS measurements are performed contemporarily, providing real time information on defect density (HR) and electronic and magnetic properties (SPMDS) at surface as the growth proceeds. At room temperature, on O(1X1)-Fe, iron grows layer-by-layer, the oxygen atoms acting as surfactants. The intensity of the features induced by O@sub 2p@ and Fe@sub 3d@ states in the electron distribution curves detected following the deexcitation of metastable atoms remain unchanged during the growth indicating that the surface composition is constant: the oxygen atoms remain segregated at surface by position exchange with incoming iron atoms. Helium reflectivity and magnetization intensity oscillate in-phase during growth: significant oscillations of the magnetization intensity are observed in perfect phase with the cyclic order/disorder transitions. Such a behaviour provides a real time, direct experimental evidence of the strong correlation between structural order and magnetization intensity.

5:00pm **MI-ThA10 Magnetic Properties of Ultrathin Fe/Gd and Gd Thin Films***,* ***C.S. Arnold,*** National Institute of Standards and Technology, US*; D.P. Pappas,* National Institute of Standards and Technology

Ultrathin films of magnetic transition metals are known to grow amorphously on rare-earth substrates. Magnetically, these films exhibit a strong perpendicular anisotropy and antiferromagnetic coupling of the transition metal to the rare earth atoms at the interface. Fe films 1- 4 monolayers thick grown on Gd substrates conform to this behavior, but also exhibit a reorientation phase transition (RPT) with temperature. This RPT is unlike those of ultrathin films on non-magnetic substrates because it is driven by the loss of magnetic order in the substrate as the bulk Gd Curie temperature is approached. Spin-polarized secondary electron polarimetry and SMOKE susceptibility measurements are employed to study the surface, bulk and interfacial magnetization as a function of temperature and Fe thickness. A partial thickness-temperature phase diagram is constructed. A second focus of the work is a comparison of surface and bulk magnetization vs. temperature in thin Gd films. The existence of a magnetic surface state is well established by spin-polarized spectroscopies, but direct comparisons of surface and bulk macroscopic magnetizations are rare in the literature. An earlier experiment using MOKE and electron spin-polarimetry to measure M(T) for the bulk and surface respectively is repeated.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS-ThA

Nanoscale Manipulation and Chemical Modification

Moderator: R.J. Hamers, University of Wisconsin, Madison

2:00pm **NS-ThA1 Nanomanipulation for Material Properties, Interactions and Devices***,* ***R. Superfine,*** University of North Carolina, Chapel Hill **INVITED**

We have pursued the study of nanometer-scale materials, including colloids, viruses, DNA and nanotubes, through the use and development of an advanced interface for scanning probe microscopy (SPM). The ability to manipulate objects efficiently on surfaces makes available a wide variety of experiments on the interactions between the sample and substrate, on the physical properties of individual objects and on the creation of unusual devices incorporating the nanometer objects. For example, the simple pushing of an object with the AFM tip, with the measurement of the applied lateral force, measures the surface adhesion and friction. Dynamical phenomena such as stick/slip, sliding and rolling has been observed. Manipulation can be used to deform objects, and the response of the objects to large strain reveals phenomena such as buckling and fracture. Finally, manipulation allows us to begin the study of unusual device structures incorporating nanometer samples such as nanotubes. Making these experiments possible is the nanoManipulator, an interface for SPM's. The interface allows for real time control of the AFM tip while simultaneously recording topography, lateral forces, as well as device features such as conductivity. In addition, the data is rendered as 3-d, directionally illuminated surfaces providing immediate, intuitive interpretation of the SPM data.

2:40pm **NS-ThA3 Monitored Mechanical Nano-Manipulation***,* ***B.E. Koel,*** *C. Baur, A. Bugacov, A. Madhukar, N. Montoya, T.R. Ramachandran, A.A.G. Requicha, R. Resch, P. Will,* University of Southern California

We have investigated the mechanical positioning of colloid particles deposited on a flat substrate. The positioning is achieved by pushing the particles with the tip of an Atomic Force Microscope (AFM). We gained fundamental insight into this manipulation process by monitoring the tip deflection and other signals during the pushing event. We also developed a procedure that allows the operator to compensate for instrument errors such as creep, hysteresis and thermal drift, especially important for operation in ambient air and at room temperature. This has lead to manipulation with high spatial certainty and increased the reliability considerably. We demonstrate precise positioning of arrays of colloidal particles and building and manipulating 3-D and linked 2-D structures of nanoparticles. It is possible to adapt this generic type of manipulation to a variety of environments and materials promising a high potential for fabrication of nano-scale devices such as those required in applications ranging from high-density data storage to single-electron electronics and nanoelectromechanical systems (NEMS) prototyping and fabrication.

3:00pm **NS-ThA4 Field-Induced Manipulation of Ag Clusters for Tailoring of Nano-Structures on Silicon Surface***,* ***K.-H. Park****, J.S. Ha, W.S. Yun, E.-H. Lee,* ETRI, Republic of Korea

A precise nano-fabrication method was devised by using field-induced manipulation of Ag clusters with a tip of scanning tunneling microscope(STM). After deposition of Ag on Sb-terminated Si(100) surface, we were able to selectively desorb(redeposit) Ag clusters from(to) the surface by applying a voltage pulse. The manipulation of metal clusters was found to be precisely controlled due to the weak bonding strength between the clusters and an Sb-terminated Si(100) surface. We investigated those field-induced manipulation by varying bias voltage, pulse duration, and distance between tip and sample. Under suitable conditions for manipulation, we could fabricated various kinds of metallic nanostructures on the Sb-passivated silicon surface. Of interest, single electron charging and tunneling behaviors were observed in the local current-voltage (I-V) measurements on top of Ag clusters at room temperature. We have found that Coulomb staircases in tunneling spectroscopy at Ag nano-clusters sensitively depended on the distribution of surrounding clusters, indicating that the lateral conduction channel through neighboring Ag clusters was very important for the tunneling I-V characteristics. This result can be further utilized for the construction of single electron devices operating at room temperature by means of lateral conduction channels.

3:20pm **NS-ThA5 Probe Induced Manipulation of Bromine, Iodine, and Sulfur on Si (100)***,* ***C.F. Herrmann****, J.J. Boland,* University of North Carolina, Chapel Hill

Scanning tunneling microscopy was used to study probe induced manipulation of the chemisorption sites of molecules on the Si (100) 2x1 surface. Specifically, the behaviors of bromine, iodine, and sulfur were studied. These adsorbates initially adsorb to the room temperature surface on adjacent dimers of the same row. Using the probe tip, one of the atoms can then be shifted to another dimer in this row, leaving one or more bare Si dimers in between them. This relocation occurs due to an increase in the field between the probe tip and the Si surface, which is induced by applying a voltage pulse to the probe tip. The separation efficiency as a function of probe tip voltage was measured for each adsorbate and it was found that each adsorbate exhibited a different threshold voltage. The diatomic molecules can also adsorb to the surface along a single dimer unit. A comparison study of the behaviors of the two different adsorption configurations was also conducted.

3:40pm **NS-ThA6 Two Mechanisms of Nanostructure Growth for STM Assisted CVD@footnote 1@**, ***I. Lyubinetsky****, S. Mezhenny,* University of Pittsburgh, U.S.*; J.T. Yates, Jr.,* University of Pittsburgh

A large Cu-containing organometallic molecule, [CuI (hfac)(vtms)],@footnote 2@ has been employed to produce nanostructures under the action of the STM tip on Si(111) exposed to the molecular flux in a UHV system at room temperature. The nanostructure growth mechanism, induced by dissociative electron attachment, exhibits an electron energy threshold of 4.5 eV. A second growth mechanism is related to an electric field-assisted activation process, which takes place in a narrow sample voltage bias range from +6 to +10 V. The topology of the deposited structure produced by the two mechanisms is strikingly different. Electron-induced growth leads to flat and broad structures which extend up to 100 nm laterally with an increase of electron energy to +15 eV. Field-induced growth leads to column-like structures with a HWHM down to 4 nm and a high aspect ratio up to 3. Comparative studies of the electron attachment mechanism have been carried out using a broad beam electron gun and x-ray photoelectron spectroscopy of the deposit on Si(111) to confirm the 4.5 eV energy threshold observed under the STM tip, and to measure elemental composition of the deposit. @FootnoteText@ @footnote 1@Work supported by the Office of Naval Research; @footnote 2@Hexafluoroacetylacetonate Cu (I) vinyltrimethylsilane, a CVD precursor for Cu deposition.

4:00pm **NS-ThA7 Nano Scale Selective Al Growth on the Si(001)-H Surface using Dimethylethyamine Hydride***,* ***T. Mitsui****, E. Hill,* University of Minnesota, US*; E. Ganz,* University of Minnesota

I will discuss nano-scale selective growth of Al on a hydrogen patterned Si(001) surface. We have studied Al growth on the clean and mono-hydride terminated Si(001) surface over a range of temperatures using Dimethylethyamine Hydride (DMAH). We have found that Al growth occurs upon dosing the clean Si(001) surface heated above 150 °C but does not occur on a mono-hydride Si(001) surface up to 300 °C. Patterning a mono-hydride terminated Si(001) surface with the STM tip,@footnote 1@ we have created nano-scale regions of bare Si(001). Heating this surface to 200 °C and dosing with DMAH, we observe the selective growth of Al from DMAH on the clean silicon region. The mechanism for selectivity will be discussed. @FootnoteText@ @footnote 1@Lyding et al, Science. 268 (1995) 1590

4:20pm **NS-ThA8 Modifications of Thioaromatic Monolayers by Low Energy Electrons***, W. Geyer, V. Stadler, W. Eck, M. Zharnikov,* ***A. Gölzhäuser****, M. Grunze,* Universität Heidelberg, Germany

Electron induced modifications of aromatic self-assembled monolayers (SAMs) were investigated by x-ray photoelectron (XPS) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy. SAMs of 1,1'-biphenyl-4-thiol (BP), 4'-nitro-1,1'-biphenyl-4-thiol (NBP) and 4'-amino-1,1'-biphenyl-4-thiol (ABP) were prepared on (111) textured gold surfaces. The subsequent characterization indicated that the films were well ordered. The films were then irradiated with low energy electrons (20 - 300 eV) and changes were observed in situ. Biphenyl SAMs are generally more stable to low energy electrons than alkanethiols exposed under similar conditions. The functionalized biphenyls (NBP, ABP) showed distinct differences in the reactions of their end groups with the incident electrons. Mechanisms of interactions between the electrons and the SAMs as well as possible applications in the tailoring of surfaces for electron beam lithography will be discussed.

4:40pm **NS-ThA9 Selective Etching of the SiO@sub 2@/Si Surface with Low Energy Electron Stimulated Reaction by using STM***,* ***N. Li****, T. Yoshinobu, H. Iwasaki,* Osaka University, Japan

Nano-fabrication on the SiO@sub 2@/Si surface is such an important subject that it may relate directly to the silicon industry. It has been shown that with focused high energy (tens to a few hundreds keV) electron beam, such as employed in TEM or SEM, nanometer scale windows can be cut through the SiO@sub 2@ overlayer and nano-structures can be formed on the exposed Si surface in a subsequent growth.@footnote 1,2@ However, large scale applications of this technique has been prevented by the relatively low efficiency of the high energy e-beam in etching the SiO@sub 2@ layer, particularly compared to the cost to build and maintain such a high energy accelerating system. Here we report an experimental study on selective etching of the SiO@sub 2@/Si surface with a low energy electron stimulated surface reaction by using STM. The investigation was carried out on Si(001) surface either with a thin native oxide overlayer or with a thermal oxide overlayer prepared in the UHV chamber. By applying a voltage of ~70 to 150 V across the tip-surface vacuum gap in the STM setup, while the tip-surface separation was adjusted to ~100 to 200 nm, a field emission current of ~5 to several hundred nA can be obtained, with which the SiO@sub 2@/Si surface was irradiated. Subsequent STM imaging shows that within the exposed area, the SiO@sub 2@ overlayer can be effectively evacuated by a thermal annealing of the surface at a temperature of ~650 to 700 °C. This can be shown evidently in the STM images by the obvious contrast change and clear atomic steps appeared within the exposed areas. By adjusting the beam energy, beam current and tip-surface separation, windows down to tens of nanometers in diameter can be etched through the SiO@sub 2@ overlayer. This result demonstrates the possibility of fabricating the SiO@sub 2@/Si surface with a low energy electron stimulated surface etching, and also presents another possibility of conducting such a nano-fabrication in a well controlled way with the STM. @FootnoteText@ @footnote 1@D.R. Allee, C.P. Umbach, and A.N. Broers, J. Vac. Sci. Technol. B9, 2838, (1991) @footnote 2@S. Fujita, S. Maruno, H. Watanabe, and M. Ichikawa, J. Vac. Sci. Technol. A15, 1493, (1997)

5:00pm **NS-ThA10 Current-Induced Local Oxidation: Mechanism, Quantum-Size Effects, and Applications***,* ***R. Martel****, T. Schmidt, Ph. Avouris,* IBM T.J. Watson Research Center

A novel method is introduced for locally oxidizing thin metal films with nanometer-scale resolution. Simply by subjecting Ti and Nb films in air to local current densities of 10@super 7@ A/cm@super 2@, metal-oxide tunneling barriers of 10-50 nm width can be fabricated in a self-limiting fashion. The high spatial resolution of the process results from its strongly non-linear dependence on the current density. Our experiments suggest that the oxidation involves current-induced atomic rearrangements and local heating. At the final stages of the barrier formation, when only atomic-scale channels remain unoxidized, the oxidation rate decreases drastically while the conductance drops in steps of about 2e@super 2@/h. This behavior gives evidence of conductance quantization and a superior stability of such metallic nanowires against current-induced forces compared with the bulk metal. This current induced local oxidation (CILO) process can be used in nanofabrication. Single electron transistor structures exemplifying Coulomb staircases at room temperature were fabricated in this manner.

Partial Pressure Measurements and Process Control Topical Conference

Room 317 - Session PC-ThA

RGA Characteristics and Calibration

Moderator: S.A. Tison, Millipore Corporation

2:00pm **PC-ThA1 Semiconductor Applications of a Quadrupole Mass Spectrometer***,* ***R.K. Waits,*** MKS Instruments **INVITED**

Commercial quadrupole mass spectrometers (QMSs) became available in the late 1960s and have been popular in R&D labs, but until recently have found limited use in semiconductor manufacturing. To sample at pressures above 10@super -5@ Torr with ppm sensitivity or better (relative to the total process pressure), differential pumping is usually required. The newly-available, small, high-pressure QMS sensors can operate as high as 10 to 20 mTorr without differential pumping, but provide somewhat lower mass resolution and partial pressure sensitivity than a standard QMS. Applications in the semiconductor fab include equipment monitoring, process monitoring and effluent analysis. Equipment monitoring can include qualification after preventative maintenance, rate-of-rise tests, and leak identification and detection. Usually the burning question is: Why won't the vacuum chamber pump down? Other uses that are not usually considered include the qualification of replaceable parts: sputter cathodes, electrodes, lamps, shields, etc. The trend to smaller features and thinner layers on larger, more expensive wafers requires better in-situ monitoring of fabrication processes. In process monitoring, the key question is: Is this process running normally? A manufacturing monitor can be useful simply by providing a comparison between a well-behaved high-yield process and a marginal or failing process. Experience mixed with a little process expertise can link the symptoms, as shown by QMS spectra, with the root cause of the disease, result in a prompt cure, and lead to continuous process improvement. Examples will be given for physical vapor deposition (sputtering) processes, chemical vapor deposition and plasma etching. The effluent from chemical vapor deposition and plasma etch processes can be analyzed to measure the efficiency of process gas utilization or to monitor the efficacy of abatement methods used for the removal of global warming gases.

2:40pm **PC-ThA3 In Situ Monitoring of Semiconductor Reactive Gas Processes using Partial Pressure Analyzers*, L.C. Frees,*** Leybold Inficon, Inc. **INVITED**

As semiconductor fabrication is pushed towards narrower linewidths utilizing new materials, processes such as chemical vapor deposition (CVD) and etch increasingly employ reactive gases. These gases, along with high temperatures and/or plasmas, and process pressures ranging over six orders of magnitude (1E-1 to 1E+5 Pa) present considerable challenges to the partial pressure analyzers (PPAs) and systems used to monitor them. Techniques used in the design and construction of the sample inlet system, the differential pumping system and the PPA itself which result in a viable in situ process monitor will be discussed. Emphasis will be given to the ion source itself. Choices concerning the place on the process tool to connect the PPA, and their effects on the data obtained, will also be covered. Applications examples will include CVD of the metals Cu, Ti (and TiN), and W and Al. Also included will be the CVD of dielectrics such as silicon nitride and phosphosilicate glass. Sampling methods for monitor etch processes for both metals and dielectrics will be presented, with a focus on the lifetime of the ion source.

3:20pm **PC-ThA5 Emission Free Measurement of Residual Gas in XHV Using Ionization by Trapped Electrons in Magnetic Field*, A. Yamamoto***, *S. Kato,* KEK, Japan

One problem associated with partial pressure measurement in an extremely high vacuum (XHV) region is outgassing from an ion source of a residual gas analyzer (RGA) itself. In order to reduce the outgassing, an improvement of its structural materials of the ion source was reported previously.@footnote 1@ However there still remains a problem of thermal outgassing from the ion source as far as a hot filament is used. Therefore, it is required for suppressing thermal outgassing to limit a time of electron emission from a filament. In this work we used a hot filament for a limited time in the beginning of the measurement. Adopting an axial magnetic field to a cylindrical anode to make a flight time of emitted electrons long, we could keep electrons trapped inside. These trapped electrons allowed us to ionize the residual gas without the thermal outgassing. But dwindling of the number of electrons due to the electron - gas collisions leads to decreasing of ion currents. We measured a dependence of the decay of ion currents for He, Ne, N2 and Xe on a gas pressure in a range of 10@super -7@ to 10@super -8@ Pa. And we also compared the decay of ion currents for the different gas species in the same pressure range. We verified that the decay time decreased with an increase of the pressures or the molecular diameters. @FootnoteText@ @footnote 1@S.Watanabe, M.Aono, S.Kato, J. Vac. Sci. Technol. A 14, 3261 (1996).

3:40pm **PC-ThA6 Residual Gas Analyzer Ion Current Measurement, Calibration and Partial Pressure Detection Limits*, R.E. Ellefson***, *A.J. Kubis, L.C. Frees,* Leybold Inficon, Inc.

Ion detection in a residual gas analyzer (RGA) is by faraday detector with electrometer and/or a secondary electron multiplier detector that use the same or separate electrometer. The minimum detectable partial pressure (MDPP) measured by these detectors is a ratio of noise(A) of the detection system to the sensitivity(A/Torr) of the RGA for each detector type. Critical to the statement of MDPP is the inclusion of the integration (dwell) time interval used to determine the noise value. Usually the MDPP reported is the longest integration time period of the RGA which produces the lowest number. However, the user normally uses integration times of the order of 0.25 s or less to rapidly get data for timely observation of the process. In this paper we present a model for predicting MDPP as a function of integration times from 8 ms to 4 s based on detector noise and ion statistics. Separately we present ion current measurements of the @super 36@Ar and @super 38@Ar minor isotopes of argon as a function of pressure to demonstrate practical detection limits of a RGA as a function of integration time. Additionally, we present data from the systematic dilution of standard gas mixtures and from a fixed composition flow standard that validate the low ppm detection limits for impurities in Ar.

4:00pm **PC-ThA7 Practical Quadrupole Theory: RGA Characteristics*, R.E. Pedder,*** ABB Extrel **INVITED**

Residual Gas Analyzers (RGA's) are commonly used to monitor the partial pressures of contaminants, process gases and reaction gases in various vacuum processes. Quadrupole mass filters can be used as RGA's through the application of RF and DC voltages in such a way as to make ions of a single mass or narrow range of masses to transmit through the quadrupole to the detector. The physics that describes the trajectories of these ions through this electrodynamic field is well studied. The performance characteristics that can be inferred from such trajectories have been predicted through both analytical and numerical methods. Unfortunately, the mathematics involved, while straightforward, is often beyond the comfort level of the practical experimentalist. This presentation will include a broad review of practical quadrupole theory, utilizing graphical means to illustrate the indicators to quadrupole performance, and avoiding all but the most straightforward equations. The goal of this presentation is to provide a more intuitive understanding of quadrupole operation, with emphasis on practical issues. Key performance figures of merit will be identified along with a practical analysis of the theoretical indicators to performance (e.g. transmission/sensitivity is proportional to the square of the rod diameter, resolution and abundance sensitivity increase with increasing RF frequency). Performance characteristics of a wide spectrum of analyzers will be compared. The performance compromises that are inherent in the optimization of quadrupole analyzer characteristics for a given application will be reviewed.

4:40pm **PC-ThA9 Residual Gas Analyzer Performance Characteristics*, C.R. Tilford,*** National Institute of Standards and Technology*; T. Gougousi,* University of Maryland

Reliable process monitoring and control require reliable instrumentation. Residual gas analyzers (RGAs) are promising candidates for these applications, but only if they are properly adjusted and used. The National Institute of Standards and Technology's (NIST) earlier work on the performance characterization and calibration of conventional, or open-source RGAs, is being extended in collaboration with the University of Maryland. This new work includes the characterization of closed-source RGAs, the development of in situ RGA calibration techniques for use in a CVD tungsten deposition tool, and the application of the calibrated RGAs in the monitoring and control of the tungsten deposition process. This talk describes fundamental characteristics of RGAs that limit their performance, and techniques to detect and minimize these undesirable characteristics. Particular attention is paid to operating conditions that cause the sensitivity for one gas to depend on the pressures of other gases.

5:00pm **PC-ThA10 Calibration of Gas-Analytic Mass Spectrometers for Gases and Vapors*, R. Dobrozemsky,*** *G.W. Schwarzinger,* Vienna University of Technology, Austria

The demand to quantify pressure-, density-, and flow-rate-readings is steadily growing, e.g. for quality control. By many reasons, simple and reliable in-situ calibration methods for pressure-reading instruments (e.g. BA-gauges) and partial pressure analyzers (e.g. quadrupole mass spectrometers) are required. In this contribution, the potential of in-situ methods for calibration of vacuum instruments is discussed, with special attention on admitting gas bursts, defined by expansion of known quantities of gases and vapors. Ten years ago, a "gas-burst calibration" procedure for non-reactive gases has been introduced at Seibersdorf.@footnote 1@ Recent demands in geological research and space technology led to new calibration procedures for water- and oil-vapors (thermal decomposition method - TDM and crack-product calibration - CPC, respectively). By these methods, in-situ calibrations can be done with an accuracy of 1 to 3% for non-reactive gases (e.g. H@sub 2@, N@sub 2@, CO, CO@sub 2@, CH@sub 4@, He, Ar, etc.), of about 10% for water vapor and of about 20 to 40% for oil vapors. Moreover, calibrations can be repeated several times a day, if necessary (e.g. under harsh conditions), and ca be performed in a wide pressure range down to uhv. @FootnoteText@ @footnote 1@ R. Dobrozemsky, Vacuum 41, 2109 (1990)

Plasma Science and Technology Division
Room 318/319/320 - Session PS-ThA

Diagnostics II

Moderator: G.L. Bell, Sematech

2:00pm **PS-ThA1 In Situ Surface Diagnostics in Plasma Processing: Present Status and Future Challenges*, E.S. Aydil,*** University of California, Santa Barbara **INVITED**

Understanding and controlling plasma-surface interactions in plasma etching and deposition is a prerequisite for achieving process goals. Towards that end, the last decade has witnessed a steady growth of research activity both in developing new plasma and in situ surface diagnostic methods and using them to address key problems in plasma processing.@footnote 1@ In this talk, we will review the recent progress in diagnostic methods with emphasis on in situ surface diagnostic techniques, their current limitations, and challenges for the next decade. Specifically, we will describe applications of techniques such as multiple internal reflection Fourier transform infrared spectroscopy,@footnote 2@ spectroscopic ellipsometry, and laser induced thermal desorption@footnote 3@ to problems in plasma etching and deposition. Simultaneous use of in situ surface diagnostics in conjunction with ex situ surface characterization methods such as X-Ray photoelectron spectroscopy and plasma gas phase diagnostic techniques such as optical emission spectroscopy has led to improved understanding of plasma etching and deposition processes. Examples from plasma etching of Si and SiO@sub 2@ and plasma deposition of hydrogenated amorphous silicon, fluorinated SiO@sub 2@ and silicon nitride will be reviewed. Despite the recent successes, major challenges remain both in advancing the capabilities of the existing surface diagnostics and applying the knowledge acquired to date to develop simple predictive models of surface processes. While some of the sophisticated surface diagnostic methods provide valuable information on surface reactions and species during process development, their use in manufacturing for real time process control is almost impossible due to their complexity. Inventing robust sensors and diagnostic tools for use in manufacturing remains a major challenge for the next decade. @FootnoteText@ @footnote 1@G. S. Oehrlein, Surf. Sci. 386, 222 (1997). @footnote 2@E. S. Aydil and R. A. Gottscho, Solid State Technol. 10, 181 (October 1997). @footnote 3@I. P. Herman, V. M. Donnelly, C. C. Cheng, K. V. Guinn, Jpn. J. Appl. Phys. 35, 2410 (1996).

2:40pm **PS-ThA3 Comparison of Surface Wave Plasma with ICP used in Oxide Etching***, H. Kokura, S. Yoneda, K. Nakamura,* Nagoya University, Japan*; N. Matsumoto,* Sumitomo Metal In., Ltd., Japan*; M. Nakamura,* Fujitsu Ltd., Japan*;* ***H. Sugai,*** Nagoya University, Japan

High-density large-diameter SWP (surface wave plasma) is produced by microwave discharge at 2.45 GHz, without magnetic field. With application to SiO@sub 2@ etching in mind, comparison of SWP to ICP (inductively coupled plasma) at 13.56 MHz is made in such a way as to replace the antenna on the quartz plate from a slot type (SWP) to a single loop (ICP) in the identical plasma vessel where the discharge electron density, pumping speed and wall temperatures are kept at the same values. In order to set the electron density at the same value, a novel probe technique is developed, which enables reliable measurement of electron density even when the probe surface is contaminated by polymer deposition. First, impurity (CO@sub 2@, SiF@sub 2@) monitoring shows considerable sputtering of quartz window in case of ICP due to electrostatic antenna-plasma coupling. Second, a degree of dissociation of source gas (10% C@sub 4@F@sub 8@ + 90% Ar) at the same electron density is higher in ICP than in SWP. Third, the neutral radical densities (CF@sub 3@, CF, F) at the same electron density are ten times higher in SWP than in ICP. Fourth, as for the ionic composition, ICP contains CF@super +@ more than 90% while SWP has less CF@super +@ and more CF@sub 3@@super +@, C@sub 2@F@sub 4@@super +@ and C@sub 3@F@sub 5@@super +@. As a consequence, ICP is more highly dissociated than SWP at the same electron density. The origin of this difference is tentatively attributed to the high-energy electron population :optical emission spectroscopy of ArI line suggested 1.5 - 2 times more high-energy electron in ICP than SWP. The physical process leading to a difference in the electron energy distribution functions between ICP and SWP will be discussed, together with etching results. Finally, a radical composition of plasmas produced by an alternative etching gas, C@sub 3@HF@sub 7@O (HFE227), for environmental issue is measured in comparison to conventional gas C@sub 4@F@sub 8@.

3:00pm **PS-ThA4 An ICP Source Design with Improved Azimuthal Symmetry@footnote 1@***,* ***M.H. Khater***[1]*, L.J. Overzet,* University of Texas, Dallas*; B.E. Cherrington,* University of Dayton

The geometry of an inductively coupled plasma (ICP) source impacts the plasma and processing uniformity. A reasonably uniform source design does not always guarantee uniform plasma, however, because transmission line effects also impact its performance.@footnote 2@ These cause the current to vary along the coil length producing azimuthal asymmetries in the RF fields of planar sources, a non-uniform power deposition in the plasma and non-uniform processing rates. The azimuthal uniformity for planar coils can be improved somewhat but with significant drawbacks. A source geometry that is inherently uniform and is not adversely impacted by transmission line effects would be preferred. We will present what we think is just such an ICP source design. The geometry is three dimensional rather than planar and consists of two (or more) layers of full and semicircular loops with the RF current generally flowing in opposite directions. Typically, the "bottom" layer consists of full circular loops, while the "top" layer consists of semicircular loops. The length of the new source is greater than that of a similarly sized planar coil, nevertheless, both have inductances near 3 µH. We have measured the free space magnetic fields produced by one of these sources in the (r,@theta@) plane using a B-dot probe. It generated fields of higher azimuthal symmetry than the planar coil despite a larger current variation (I@sub out@/I@sub in@) along the source length. The average value of the peak azimuthal electric field for the new source was E@sub theta@/I@sub out@=0.24 V/(cm A) with a standard deviation of @sigma@=0.0085. The planar coil produced 0.32 V/(cm A) with @sigma@=0.027. The new source has been used to produce high density (10@super 11@-10@super 12@ cm@super -3@) Ar and SF@sub 6@ discharges at low pressures (5-20 mTorr) and to etch poly silicon. @FootnoteText@ @footnote 1@ This material is based upon work supported by Beta Squared Inc. under Grant No. UTD96-56 and by the State of Texas Advanced Research Program under Grant No. 009741-043. @footnote 2@ M. Kushner, et al., J. Appl. Phys. 80, 1337 (1996).

3:20pm **PS-ThA5 Characterization of 100 MHz Inductively Coupled Plasma (ICP) by Comparison with 13.56 MHz ICP***,* ***H. Nakagawa****, S. Morishita, S. Noda, M. Okigawa, M. Inoue, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The effect of the excitation frequency on gas dissociation was investigated using a multi-spiral coil in inductively coupled plasma (ICP). The same apparatus except for wave generators and matching circuits was used in the 100 MHz@footnote 1@ and 13.56 MHz excitation wavelength experiments. The electron density (Ne) and electron temperature (Te) in the Ar plasma were measured using a Langmuir probe. In both cases, the value of the Ne was around 2 e+11 cm@super -3@ at the excitation power of 2 kW in 3 Pa (Ar = 400 sccm). Although the Ne in 13.56 MHz plasma is a little higher than that in the 100 MHz plasma, Te (~3) in the 13.56 MHz plasma is higher than that (~2) in the 100 MHz plasma. From the dependence of the radial distribution of the Ne on the ICP source power, it was found that the 13.56 MHz-ICP was produced in a space under the coil area, and that the 100 MHz-ICP was generated throughout the reactor. This is because of the strong capacitive coupling in the 13.56 MHz-ICP, and because the inductive coupling in the 100 MHz-ICP is stronger than that in the 13.56 MHz-ICP. In the C@sub 4@F@sub 8@ / Ar plasma, CF@sub X@ (x=1, 2, 3) radical densities in the reactor wall were measured by appearance mass spectrometry (AMS),@footnote 2@ and the F radical density was evaluated using actinometry through optical emission spectroscopy of Ar (750.4 nm) and F (703.7 nm).@footnote 3@ The degree of dissociation of C@sub 4@F@sub 8@ in the 100 MHz-ICP was higher than that in the 13.56 MHz-ICP, but the CF@sub 2@ / F density ratio in the 100 MHz-ICP was 3 ~ 5 times as large as that in the 13.56 MHz-ICP. This result indicates that the dissociation of a high order (ex. CF@sub 2@ + e --> CF + F + e) in the 13.56 MHz-ICP is larger than that in the 100 MHz-ICP. Thus, it was demonstrated that the 100 MHz-ICP has a greater ability to suppress F radical generation than the 13.56 MHz-ICP. @FootnoteText@ This work was supported by NEDO. @footnote 1@H. Nakagawa et al.: Proc. 14th Symp. on Plasma Processing,136 (Hamamatsu, 1998). @footnote 2@M. Goto et al.: Jpn. J. Appl. Phys. 33 (1994) 3602. @footnote 3@J. S. Jenq et al.: Plasma Source Sci. Technol. 3 (1994) 154.

3:40pm **PS-ThA6 Multi-Frequency Operation of RIE and ICP Sources@footnote 1@***,* ***S. Rauf****, M.J. Kushner,* University of Illinois, Urbana-Champaign

In both inductively and capacitively coupled rf discharges, the source frequency strongly influences the plasma and electrical properties. Multiple sources at different frequencies are often simultaneously used to combine their attractive features. For example, the goal of dual-frequency RIE plasmas is to separately optimize the magnitude and energy of ion fluxes to the substrate. If the source frequencies are significantly different from each other, the resulting plasma properties can generally be characterized in terms of the separate contributions of the individual sources. However, when the frequencies are close to each other (e.g., 6.78 MHz and 13.56 MHz), the sources interact through the nonlinear plasma medium, thereby complicating this additive relationship. The dynamics of rf plasma processing reactors with multi-frequency sources have been investigated using a coupled plasma equipment-circuit model. In capacitively coupled Ar and Ar/CF@sub 4@ discharges, the addition of a high frequency source (27.12 MHz) on the opposing electrode decreases the magnitude of the dc bias at the substrate (13.56 MHz) due to nonlinear interaction between the

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

separately powered sheaths and a reapportionment of current. In ICP reactors, the dc bias on the substrate has a strong dependence on the rf bias frequency (becoming more negative at higher frequencies) due to the differences in sheath impedance at the powered substrate and the grounded walls. This relationship can be altered by repositioning the antenna which, in turn, reapportions the current collected on biased and grounded surfaces. It was also found that by adding rf sources at remote locations from the substrate in ICP reactors, such as small areas of the wall, one can control the dc bias at the substrate without appreciably changing the ion flux or electron temperature. @FootnoteText@ @footnote 1@Work supported by AFOSR/DARPA, SRC and NSF.

4:00pm **PS-ThA7 Diagnostics in a Novel Capacitively Shielded, Inductively Coupled Plasma Source***, **V.A. Shamamian**, J.E. Butler, D. Leonhardt,* Naval Research Laboratory*; J.L. Giuliani,* Naval Research Laboratory, US

An electrostatic shield in the form of a slotted metal cylinder is often placed between the exciting coil and the dielectric discharge tube of an inductively coupled plasma system in order to screen the electric field generated by the coil. Such fields can, under some circumstances, have a deleterious effect on the process for which the plasma is being used. For very high power systems, the dielectric discharge tube can be replaced by a thick-walled, water-cooled, slotted metal cylinder (i.e., a cold crucible). It is not generally realized that the electrostatic shield can also lead to a significant reduction of the r.f. magnetic fields inside the tube as well as altering its axial distribution. This effect needs to be considered in detailed modeling of inductively coupled plasma systems and is of practical importance in determining the impedance the plasma presents to the r.f. generator. In this combined experimental and theoretical work, we have employed induction probes to study the effect by measuring the r.f. magnetic field inside hydrogen discharges. We interrogated the level to which the plasma screens the field as a function of pressure and coupled power. In addition, we have employed optical emission imaging techniques and a radiation transport model to extract the axial and radial dependence of the electron and neutral temperatures, and plasma spatial extent in the axial direction. We have found that the electron temperature is constant in the axial direction but strongly dependent in the radial dimension, and the plasma extent is self-similar with respect to the value of power divided by pressure. Finally, we have developed electromagnetic models that give good agreement with the plasma induction probe observations. We are currently developing a global 2D model which incorporates electromagnetics, gas phase chemistry and transport, and surface recombination. Work supported by IST/BMDO, DARPA, and ONR.

4:20pm **PS-ThA8 Volume/Surface Effects on Dissociation Processes in Ar/C@sub 4@F@sub 8@ Plasma***, **K. Kinoshita**,* Association of Super-Advanced Electronics Technologies (ASET), Japan*; S. Morishita, S. Noda, M. Okigawa, M. Inoue, M. Sekine,* ASET, Japan

We clarified that the control of multistage dissociation in Ar diluted C@sub 4@F@sub 8@ plasma via the total number of collisions, @tau@ N@sub e@ <@sigma@v>,@footnote 1@ is essential in establishing a high-performance SiO@sub 2@ etch process in a narrow-gap parallel plate reactor. For the scaling of the reactor to a larger wafer size in the near future, a wider gap space will be required to assure uniformity of the gas supply and exhaust. Changing the gap space (i.e, volume/surface ratio) must affect the gas dissociation process by changing total number of collisions. Here, @tau@ and N@sub e@ can be controlled by the pumping speed and source power. Therefore, we examined the change in <@sigma@v> on the gap space and its effect on the dissociation process. Two kinds of UHF (500 MHz) plasma sources were used. One source had a spoke antenna coupled with plasma through a quartz top plate and the other had a carbon top plate antenna with a magnetic field of ECR condition. In both systems, when the gap space was widened, the N@sub e@ increased and <@sigma@v> for the C@sub 4@F@sub 8@ dissociation decreased, when @tau@ was constant. <@sigma@v> for excitation for ArI emission also decreased with increasing gap space. Kinetic analysis through rate equations indicated that the reaction rate constant <@sigma@v> for the F generation reaction decreased with increase in gap space in both plasma sources. These results suggest that changing the electron energy distribution by changing the gap space significantly influences the reaction rate constant of the dissociation reactions in the Ar/C@sub 4@F@sub 8@ plasma. @FootnoteText@ This work was supported by NEDO. @footnote 1@ T. Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998) to be published

4:40pm **PS-ThA9 Investigation of the Gasphase of Expanding Ar/C@sub x@H@sub y@ Plasmas***, A. de Graaf, M.F.A.M. van Hest, **K.G.Y. Letourneur**, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

An expanding argon plasma into which several C@sub x@H@sub y@ precursors are injected was used for the deposition of diamond-like carbon films. The argon plasma is created in a cascaded arc and expands into a low-pressure vessel, where precursor gases, such as CH@sub 4@, C@sub 2@H@sub 2@, C@sub 2@H@sub 4@ and C@sub 2@H@sub 6@ are injected into the beam. The gasphase of these plasmas was investigated by means of Fourier Transform Infrared (FTIR) absorption spectroscopy and Mass Spectrometry (MS). The consumption of the different precursor gases was derived from both FTIR and MS measurements for several arc currents, pressures and flows. The results from the two techniques are compared in order to eliminate the effect of temperature and to distinguish whether reaction products are formed in the background or in the plasma beam. By correlating the depletion measurements with the growth rate measured in situ by ellipsometry, information is obtained on the reactions taking place inside the plasma and during deposition. Assuming that only argon ions are contributing to the dissociation of the C@sub x@H@sub y@, the electron energy being too low (typically 0.2 eV in these plasmas), the ionization degree of the arc can be deduced as function of arc current and argon flow. The measurements also prove that other stable monomers are produced in the plasma phase, i.e. polymerization is taking place. The possible polymerization reactions, occurring either in the gasphase or at the reactor walls, will be discussed for the different precursor gases.

5:00pm **PS-ThA10 Electrical Control of Spatial Uniformity of Chamber-Cleaning Plasmas Investigated using Planar Laser-Induced Fluorescence***, **K.L. Steffens**, M.A. Sobolewski,* National Institute of Standards and Technology

Fluorocarbon plasmas are widely used by the semiconductor industry for in situ cleaning of PECVD chambers. Control and optimization of chamber-cleaning processes are critical for reduction of both the emission of greenhouse gases and chamber-cleaning time. Also the spatial distribution of chemically reactive species in the plasma should be tailored to maximize the cleaning rate at appropriate surfaces. Previous studies in parallel-plate reactors have indicated that reactive species density distributions, plasma emission, and cleaning rates are correlated to the rf current measured at the upper, grounded electrode. In this study, the current at the upper electrode was varied by adjusting the impedance between the upper electrode and ground, and the resulting changes in plasma uniformity were investigated using optical techniques. Measurements were made in O@sub 2@/CF@sub 4@ and O@sub 2@/C@sub 2@F@sub 6@ plasmas in the capacitively-coupled Gaseous Electronics Conference Reference Cell at pressures from 0.1 to 1 Torr. The 2-dimensional density distribution of the reactive radical, CF@sub 2@, was measured using planar laser-induced fluorescence (PLIF), and the regions where reactive species were generated were determined using spatially-resolved, broadband optical emission. As the current at the upper electrode was varied, changes were observed in the axial symmetry of the broadband emission and in the radial uniformity of the CF@sub 2@ PLIF. These results suggest that electrical control of the current paths through the plasma could be used to control the spatial distribution of reactive chemical species, aiding in the optimization of chamber-cleaning plasmas and other fluorocarbon plasmas.

Selected Energy Epitaxy Topical Conference
Room 327 - Session SE-ThA

Seeded Supersonic Beam Epitaxial Growth

Moderator: R. Bickness-Tassius, Jet Propulsion Laboratory

2:00pm **SE-ThA1 Selected Energy Epitaxial Deposition of GaN and AlN on SiC(0001) Using Seeded Supersonic Free-Jets of NH@sub 3@ in Helium***, V.M. Torres,* Arizona State University*; **R.B. Doak**,* Fulbright Senior Scholar, Ruhr-Universitaet-Bochum, Germany*; B.J. Wilkens, David J. Smith, I.S.T. Tsong,* Arizona State University **INVITED**

By expanding a gas mixture into vacuum through a supersonic nozzle, a heavy "seed" species in a light diluent can be aerodynamically accelerated to suprathermal translational energies, tunable by adjusting the mixture and temperature of the nozzle. Such "seeded" beams retain the high intensity, directionality, and narrow energy distribution characteristic of a supersonic free-jet. They thus offer promise in selectively promoting specific gas-surface reactions, a matter of much current interest in the growth of III-N semiconductor thin films. We report the use of 10%

NH@sub 3@ in He seeded beams to grow GaN and AlN epitaxially on 6H-SiC(0001) and to grow GaN on AlN buffer layers deposited on SiC(0001). The substrate temperature was 800° C in all cases and the incident NH@sub 3@ translational energy was varied from 0.034 to 0.44 eV. Deposition was made with the beam incident at 0°, 30°, and 75° with respect to the surface normal. Ga was supplied from a simple evaporator and all growth was carried out under Ga-rich conditions. The thickness and morphology of the resulting films was characterized ex situ using RBS, Auger, TEM, and AFM. Of particular relevance to the growth of III-N compounds are the following results: (1) Selected energy epitaxial growth was observed, evidently via a direct reaction channel over a barrier of 0.3 ± 0.1 eV and mediated by the NH@sub 3@ translational energy. (2) A low energy reaction channel was also identified and ascribed to physisorption of the incoming NH@sub 3@ molecule followed by dissociative attachment of NH@sub x@ fragments. (3) Comparison of growth at 0° and 30° beam angles revealed total energy scaling, possibly due to rotational coupling of the above two reaction channels. (4) Deposition at grazing angle (75°) yielded faceting oriented towards the beam, indicating minimal mobility of the incident NH@sub 3@ and the attached NH@sub x@ fragments. The experimental evidence will be presented and the implications for III-N growth examined. Supported by ONR grant # N00014-95-1-0122

2:40pm **SE-ThA3 Homoepitaxial Growth of GaN Using Seeded Supersonic Molecular Beams*, H.H. Lamb,*** North Carolina State University **INVITED**

The optoelectronics applications of the Group III-nitrides have stimulated great interest in low-temperature epitaxial growth of GaN. As the quality of heteroepitaxial GaN films is limited by lattice mismatch between the film and typical substrates (e.g., sapphire and 6H-SiC), we have chosen to focus on homoepitaxial growth of epilayers on high-quality MOVPE-grown GaN substrates. Hyperthermal beams of neutral molecules (e.g., NH@sub 3@) are employed as alternatives to plasma and/or ion sources for low-temperature growth. Hyperthermal molecular beams with narrow energy distributions are generated by seeding heavy species in a supersonic expansion of a lighter gas (typically He or H@sub 2@). In this presentation, homoepitaxial growth of GaN using dual seeded supersonic molecular beams of NH@sub 3@ and triethylgallium (TEG) will be described. The results will be compared to those obtained using an NH@sub 3@-seeded supersonic molecular beam and a conventional Ga effusion cell. The influence of precursor kinetic energy on growth kinetics and film morphology will be discussed.

3:20pm **SE-ThA5 The Effect of Scaling Precursor Duty Cycles on Pulsed Supersonic Molecular Beam AlN Growth Rates*, V.W. Ballarotto,*** *M.E. Kordesch,* Ohio University

The effect of varying the precursor duty cycles for AlN grown on Si (100) at 650 °C with pulsed supersonic molecular beams is reported. The duty cycle is defined as the on-time of the valve multiplied by the driving frequency. The Al precursor was trimethylaluminum (130 meV) and the N precursor was 5 percent ammonia seeded in He (220 meV). The duty cycle was varied by changing the driving frequency. The growth rate of AlN films increases linearly (0.09 µ/h to 0.50 µ/h) with an increase in driving frequency. However, the growth rate in terms of thickness per pulse is roughly constant (1 Å/pulse). Total film thickness is on the order of 1-2 µ. A comparison of the growth rates when the duty cycle is varied by changing valve on-time will be presented. The films are predominantly oriented with the non-polar (10-0) plane parallel to the substrate plane. Preliminary results from x-ray diffraction @phi@ scans show that the films exhibit a preferred orientation that does not depend on substrate orientation or film thickness. The nucleation and growth of the non-polar (10-0) film face on polar (0001) MOCVD AlN will be discussed. Support provided by BMDO/ONR N00014-96-1-0782 and -1060.

3:40pm **SE-ThA6 In-Situ Surface Cleaning of GaN Using Hyperthermal Molecular Beams*, A. Michel,*** North Carolina State University, US*; E. Chen,* North Carolina State University*; O. Nam, D. Thomson, R.F. Davis,* North Carolina State University, US*; H.H. Lamb,* North Carolina State University

Selected energy epitaxy (SEE) of GaN on MOVPE-grown GaN/6H-SiC substrates requires in-situ surface cleaning techniques that are effective at removing carbon and oxygen contamination without roughening or otherwise damaging the surface. Remote hydrogen plasma cleaning has been used to remove contaminants from GaN substrates prior to RF plasma-assisted MBE growth; however, the effects of hydrogen plasma exposure on surface roughness and substrate electrical properties have not been reported.@footnote 1@ Nitrogen plasma exposure can destroy surface steps on GaN/6H-SiC substrates, as evidenced by in-situ low energy electron microscopy (LEEM).@footnote 2@ Energetic beams of neutral atoms and molecules provide an alternative to plasma sources for in-situ cleaning and subsequent growth. Hyperthermal molecular beams are generated by seeding heavy species (e.g., NH@sub 3@, Kr) in a supersonic expansion of a lighter gas (e.g., He, H@sub 2@). In this work, in-situ cleaning of MOVPE-grown GaN/AlN/6H-SiC substrates using hyperthermal molecular beams was investigated. Removal of surface carbon and oxygen contaminants was achieved by heating at 730°C under a hyperthermal NH@sub 3@ beam. Oxygen is removed primarily by thermal desorption; however, carbon removal occurs only under an NH@sub 3@ flux. We infer that adsorbed H atoms produced by NH@sub 3@ decomposition react with carbonaceous species on the GaN surface to produce volatile hydrocarbons. Ex-situ atomic force microscopy (AFM) indicates that atomically smooth surfaces with regular steps are produced by NH@sub 3@ beam cleaning. In on-going work, we are investigating the use of dual hyperthermal Kr and NH@sub 3@ beams for GaN cleaning. The effects of kinetic energy on surface contamination removal and surface morphology will be discussed. @FootnoteText@ @footnote 1@W.C. Hughes, W.H. Rowland, Jr., M.A.L. Johnson, S. Fujita, J.W. Cook, Jr., J. Ren, and J.A. Edmond, J. Vac. Sci. Tech. A, 13, 1571 (1995).@footnote 2@E. Bauer, private communication.

4:20pm **SE-ThA8 Controlling Thin Film Morphology and Selectivity using Collimated Monoenergetic Molecular Beams*, J.R. Engstrom,*** Cornell University **INVITED**

Over the past several years we have been investigating the fundamental aspects of thin film growth using energetic neutral molecular beams produced by supersonic expansions as sources. Our focus has been on Group IV systems-- Si, Ge and Si@sub 1-x@Ge@sub x@. This work has ranged from detailed investigations of the gas-surface chemical dynamics of dissociative adsorption, to thin film deposition and growth emphasizing morphological aspects, to computer simulations of both the thin film morphology and gas-surface fluid dynamics. We will present an overview of this work, focusing on more recent developments, which will include (i) the growth of thin films at grazing angles of incidence; (ii) the selectivity of growth (e.g., Si vs. SiO@sub 2@) as a function of beam energy, beam composition and substrate temperature; and (iii) the exploration of scale-up strategies (experiment and computer simulation) for deposition over large areas.

5:00pm **SE-ThA10 Three Dimensional Modeling of Silicon Deposition Process Scale-up Employing Supersonic Jets***, G. Chen,* ***I.D. Boyd****, J.R. Engstrom,* Cornell University

A new technique to deposit silicon thin films employing supersonic beams is examined. Our previous studies involved both experimental and numerical approaches, in which the thin films were deposited at high growth rates but over relative small areas. The current studies are focused on the process scale-up by using multiple discrete supersonic jets. 1% disilane/hydrogen mixture is heated to 350 °C and ejected through nozzles to a 700 °C substrate. Three dimensional simulations are conducted to investigate the geometrical effects of the molecular beam sources. One source configuration involving multiple jets is found to successfully deposit uniform silicon films over an area of 18 cm in diameter, with a growth rate higher than 200 @Ao@/min. The molecular beam energy obtained under these conditions is approximately 1.3eV. A configuration is also designed to increase the deposition area in a laboratory facility for experimental verification.

Surface Science Division

Room 308 - Session SS1-ThA

Surface Diffusion

Moderator: G.L. Kellogg, Sandia National Laboratories

2:00pm **SS1-ThA1 A Novel Real-time Technique for Monitoring Adatom Surface Diffusion and Island Nucleation*, P.M. DeLuca,*** *S.A. Barnett,* Northwestern University

The surface diffusion coefficient of Ga adatoms, along with two-dimensional (2D) island nucleation and coarsening were measured in real-time on vicinal GaAs(001) 2x4 surfaces using specular ion current measurements (SICM). In this new technique, 3 keV Ar ions were incident upon the surface at a glancing angle (typically 1° to 3°), and the specularly scattered ion current measured. Since specular scattering requires a locally-flat surface, surface defects cause a decrease in the scattered ion current, providing a measure of average adatom and/or step-edge density. The time dependence of the Ga adatom population was measured during and after the deposition of 0.1 monolayers of Ga on vicinal GaAs(001)2x4. The scattered ion current dropped with an exponential dependence upon opening the Ga shutter and increased exponentially upon closing the shutter, in good agreement with a simple model for adatom diffusion across terraces to step edges. Diffusion coefficients, D, were obtained using the measured adatom lifetimes,@tau@, and the 70Å terrace width, x, (the miscut was 2.3 ° towards (1 1 0)) in the expression D=x2/@pi@ 2 @tau@, yielding D=(8.89x10-10 cm@super 2@/sec) exp (0.74/kT) for an As@sub 4@ ambient over the temperature range 450 to 570°C. For larger Ga coverages and/or lower substrate temperatures, deviations from simple exponentials and much longer time constants were observed, suggesting that 2D islands had nucleated. The island nucleation and coarsening behaviors will be described.

2:20pm **SS1-ThA2 Direct Measurement of Adsorbed Si Dimer Dynamics on Si(001)***, **J.M. Carpinelli**, B.S. Swartzentruber,* Sandia National Laboratories

Silicon atom deposition onto a clean, well-ordered Si(001) crystal surface results in the formation of adsorbed dimers. This presentation details the use of atom-tracking scanning tunneling microscopy to determine the detailed energetics of such species in a variety of local environments at elevated temperatures (~ 100°C). Dimer diffusion along a buckled A-type step edge is found to be weakly asymmetric, indicating that the adsorbed dimer does not strongly perturb the underlying substrate bonding. A dimer adsorbed onto the middle of a terrace is attracted at only a single lattice site to a 2+1 defect in an adjacent diffusion channel, pinpointing the probable location of subsurface contamination responsible for defect formation. Additionally, a linear dependence between the activation barrier for diffusion and perpendicularly applied electric field magnitude is measured. These results provide valuable insight into the bonding and interaction of dimers with surface features prevalent during homoepitaxial growth. The quantitative measure of lattice-site specific energy parameters not only serves as input to realistic simulations, but also enables the validation and refinement of such calculations. 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 **SS1-ThA3 Ion-Induced Surface Diffusion of Ge on Si(111)***, **E.G. Seebauer**, R. Ditchfield,* University of Illinois, Urbana

In thin film deposition, bombardment of the surface with low-energy (10-100 eV) ions during growth has been shown to improve film quality in a variety of applications. In many cases, the improvement is attributed to enhancements in surface diffusion of the depositing species. However, such effects have never been quantified in a direct way, and the mechanisms for energy transfer from the ions to the mobile atoms remain unclear. Here we report for the first time the direct quantification of ion-influenced surface diffusion, using Ge on Si(111) as the adsorption system and second harmonic microscopy as the measurement probe. The effects are significant and fall into two regimes of temperature. Below about 700 C, the activation energy E@sub diff@ remains unaffected, but the pre-exponential factor D@sub o@ increases. The increase varies as the square root of ion energy and mass (going from He to Ar to Xe), culminating in a factor of 10 increase for Xe near 60 eV. Simulations by molecular dynamics reproduce this effect nearly quantitatively, and point to an increase in the average jump length due to billard-ball-like collisions as the governing mechanism. At higher temperatures, both E@sub diff@ and D@sub o@ decrease dramatically, again according to a square-root energy and mass dependence. E@sub diff@ falls by 75%, while D@sub o@ falls by 8 orders of magnitude. Molecular dynamics simulations again reproduce the effects, and point to ion-mediated changes in the number of mobile adatoms as the governing mechanism. In both temperature regimes, the effects set in only above a threshold energy of about 15 eV.

3:00pm **SS1-ThA4 Schwoebel Barriers on Stepped Pt(111)@footnote 1@***, **P.J. Feibelman**,* Sandia National Laboratories

The ab-initio Schwoebel barrier calculated for downward self-diffusion across A-type steps on Pt(111) is E@super S@(A) ~ 0.02 eV. This is too small to be consistent with the notion that lowering E@super S@(A) is how O promotes layer-by-layer epitaxy on Pt(111). Geometric arguments explain why E@super S@(B), the Schwoebel barrier at B-type steps, is more than an order of magnitude larger than E@super S@(A), a result in conflict with the observation of three-dimensional Pt islands on Pt(111) bounded by A-type steps. The first-principles downward-transport barriers are vindicated by new observationsof Pt growth morphology, in which the CO background has been greatly reduced. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company for the U. S. Department of Energy.

3:20pm **SS1-ThA5 Diffusion and Island Formation of Water Molecules on Ice Ih Surfaces***, E.R. Batista, **H. Jonsson**,* University of Washington **INVITED**

We present theoretical calculations of the deposition, adsorption, diffusion, and island formation of water admolecules on the basal face of ice Ih. The calculations are based on both pairwise additive interaction potentials as well as a polarizable model. The sticking coefficient is found to be near unity for vapor deposition, but drops to 0.9 for incident energy of 1.5 eV and 60 degree angle of incidence. At low coverage, an admolecule prefers to sit at non-crystallographic sites (i.e. not fitting into the ice lattice) with a large binding energy. Since ice Ih is proton disordered, there is a range of binding energies, and for some local environments the binding energy is on the order of (and even larger than) the cohesive energy. The proton disorder also results in a range of activation energies for diffusion. After mapping out a large number of diffusion barriers using the Nudged Elastic Band method, a kinetic Monte Carlo calculation of the diffusion at 140 K was performed. At short time, the mean squared displacement has anomalous scaling with time as is common for diffusion on random lattices. From the long time scaling a diffusion barrier is obtained which is not inconsistent with recent upper bound found by Brown and George. The simulated diffusion is also reasonably consistent with earli! er estimates of the diffusion leng th by Mason. Paths and energy barriers for the formation of small islands have also been studied. It is found that islands up to and including pentamer are non-crystallographic, but the hexamer is crystallographic. The dominant activation energy barrier to the formation of the hexamer is the admolecule diffusion barrier.

4:00pm **SS1-ThA7 H and O promoted Self-Diffusion of Pt(110)***, **S. Horch**, S. Helveg, I. Stensgaard, E. Laegsgaard, F. Besenbacher,* Aarhus University, Denmark

The surface self-diffusion of Pt adatoms on the Pt(110)-(1x2) surface is studied using variable-temperature Scanning Tunneling Microscopy. Exposing the surface to Hydrogen or Oxygen leads to an enhancement of the mobility of the adsorbed Pt adatoms. Atomically resolved STM movies provided the first experimental evidence that in the case of H this is due to the existence of H-Pt ad-dimer skyhooks diffusing several orders of magnitude faster than normal Pt adatoms. These movies allow us to analyse the lifetime distribution of these ad-dimers which gives a surprisingly high binding energy of about 0.8 eV. Nevertheless, only a small fraction of all Pt adatoms form these ad-dimers at the same time. A tentative model will be presented to explain these findings and compare them to the case of O.

4:20pm **SS1-ThA8 Adsorption of N on Fe(100): Diffusion and Adatom-Adatom Interactions Studied with Scanning Tunneling Microscopy***, **M.O. Pedersen**, L. Österlund, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

The dynamics and adsorbate-adsorbate interactions of N adatoms on a Fe(100) surface have been studied using variable temperature Scanning Tunneling Microscopy (STM). By recording a sequence of STM images as a film, we can track the individual N atoms at low coverage, and study their mobility. From these STM films, the diffusion constant of the N atoms can be derived, and by varying the sample temperature from 299 K to 323 K, a diffusion barrier of 0.92 eV ± 0.04 eV and a prefactor of D@sub 0@ = 2.4 10@super -3@ cm@super 2@/s are found. This value of the diffusion barrier is in good agreement with the diffusion barrier calculated using Density Functional Theory.@footnote 1@ From the STM images, the N adatom pair correlation function can also be deduced, from which an ensemble interaction potential can be found. Measuring the ensemble interaction potential at two different coverages (0.034 ML and 0.10 ML), allows us to quantify the entropic contributions and thus find the direct pair interaction potential between the N atoms. As expected, the nearest neighbour interaction is found to be strongly repulsive, whereas the next nearest neighbour interaction is attractive. From the STM images, the N atoms are found to adsorb in the four-fold hollow site, confirming previous LEED experiments. Due to the attractive interactions between the N adatoms, island nucleation is observed, even at sub-monolayer coverage. @FootnoteText@ @footnote 1@J.J. Mortensen, L.B. Hansen and J.K. Norskov, private communication

4:40pm **SS1-ThA9 Novel Diffusion Channel Parallel to Steps: CO on Pt(111)***, **X.D. Xiao**, J.-W. Ma, M.M.T. Loy,* The Hong Kong University of Science and Technology, China

Surface diffusion parallel to steps for CO on Pt(111) has been studied by an optical diffraction technique. With a large accessible dynamic range for diffusion coefficient measurement from 10@super -12@ to 10@super -8@ cm@super 2@/sec, we could cover a wide range of temperatures from 120 to 320 K, within which non-Arrhenius processes can be unambiguously identified. For steps along [110] direction (B-type steps in the present experiment) with a density of one-step/30-atoms, it was found that diffusion at low temperatures are controlled by terrace diffusion and at high temperatures controlled by diffusion along step edges. At 0.3 ML CO coverage, the terrace diffusion was measured with an activation energy of 4.2 kcal/mol and a prefactor of 6x10@super -7@ cm@super 2@/sec. The diffusion along step edges was measured with an activation energy of 10.9 kcal/mol and a prefactor of 0.2 cm@super 2@/sec. It is this large prefactor that compensates the respect high activation barrier for step edge diffusion to take control at high temperatures. As we change the step direction to along [112], a novel diffusion channel was observed. Now, with the same step density as in the previous case, the diffusion is enhanced by a factor of ~10 over the entire temperature range as compared to the terrace diffusion. At 0.3 ML CO coverage, this new channel is characterized by a simple Arrhenius behavior with E@sub D@=3.2 kcal/mol and D@sub o@=5x10@super -7@ cm@super 2@/sec. At 0.5 ML CO coverage, the diffusion is dominated by this new channel only at low temperatures but still by along step edge diffusion at high temperatures. Discussion on how the new channel is formed will be presented.

5:00pm **SS1-ThA10 Potassium Surface Diffusion by Optical Techniques***, **W. Zhao**, M. Asscher,* The Hebrew University, Israel

Coverage grating-optical second-harmonic diffraction method has been used to measure the diffusion of pure potassium and coadsorbed with CO on Re (001) surface in the potassium coverage range of 0.6-1 ML. The activation energy (E@sub d@) and the preexponential factor (D@sub 0@) for diffusion in both show a clear compensation effect. For the pure potassium case, E@sub d@ and D@sub 0@ change quadratically with the coverage, having a minimum in the potassium coverage of 0.75 ML. The activation energies for diffusion are determined to be 5.0±0.2, 3.9±0.7, 3.6±0.2, and 5.0±1.0 kcal/mol, the preexponentials are 5.6x10@super -3±0.3@, 3.5x10@super -4±1.1@, 5.8x10@super -4±0.3@, and 3.7x10@super -1±1.9@ cm@super 2@/s corresponding to potassium coverages of 0.93, 0.84, 0.73, and 0.59, respectively. The results are discussed in terms of electrostatic dipole-dipole repulsive interactions among neighboring adsorbates. In the coadsorption case, it is found that CO hinders potassium surface diffusion significantly, with the effective activation energy for 0.8 ML K rising to 15 kcal/mol for CO average coverage of 0.06 ML. The attractive interaction and complex formation (observed by TPD) of CO-K are proposed as the main reasons for the increasing E@sub d@.

Surface Science Division
Room 309 - Session SS2-ThA
Oxide Growth and Structure

Moderator: W. Hebenstreit, Tulane University

2:00pm **SS2-ThA1 Structural and Pt Adsorption Properties of Ultrathin Al@sub 2@O@sub 3@(001) Films on Al(111), Mo(110), and Ru(001)@footnote 1@***, **D.R. Jennison**, C. Verdozzi*, P.A. Schultz, M.P. Sears,* Sandia National Laboratories

Using first-principles LDA calculations, we explore Al@sub 2@O@sub 3@ ultrathin films on a variety of metallic substrates. A general principle of interface structure is proposed, which then affects the film-surface termination (i.e., Al or O) and the degree of surface polarity. Several film thicknesses are compared. In the thinnest films, we find a favored phase not observed in bulk crystals, having only four-fold coordinated Al-ions. For all studied substrate materials, this indicates that a structural transformation could occur during film growth, as the film bulk and interfacial energies compete. Large differences, ~50%, are found in the adhesion of a metallic overlayer (Pt) with two vs. three O-layer thicknesses. This is due to greater surface polarity in the latter, which in turn is related to decreased stability of the thinnest film phase. Diffusion barriers are presented for isolated Pt adatoms and predictions made of hop length and symmetry. Huge coverage dependences (five-fold) in the adsorption energy of Pt occur between 1/3 and 1 ML, the binding being ionic when the Pt atoms are isolated (Pt@super +1@ or greater), but image-polarization driven at 2/3 ML and higher coverages. Our results agree with experimental ISS and HREELS data on the thinnest films.@footnote 2@ @FootnoteText@*Current address: Univ. of Edinburgh, Edinburgh EH9 3JX, UK. @footnote1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000. @footnote 2@J. Libuda, et al., Surf. Sci. 318 (1994) 61.

2:20pm **SS2-ThA2 Interaction and Growth of Rh on Hydroxylated Alumina Model Substrates***, **J. Libuda**, S. Stempel, M. Heemeier, M. Frank,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; A. Sandell,* Lund University, Sweden*; S. Andersson, P.A. Brühwiler, N. M@ao@rtensson,* Uppsala University, Sweden*; M. Bäumer, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

In contrast to simple model surfaces, alumina supports employed in technical catalysis exhibit a variety of complex surface structures. In particular, depending on preparation, their surface can be covered to a large extend by hydroxyl groups, affecting the chemical behaviour not only with respect to adsorption of gases but also the interaction with the catalytically active metal component. In order to study the dependence of metal growth and metal oxide interaction on the surface properties of an alumina support, we have established a hydroxylation procedure based on Al deposition and subsequent water exposure, which is applied to a well ordered Al@sub 2@O@sub 3@ film grown on NiAl(110). The hydroxylated surface is characterized with respect to morphologic (Scanning Tunneling Microscopy (STM) and Spot-Profile Analysis-LEED (SPA-LEED)) and electronic properties (High Resolution Photoelectron Spectroscopy (PES)). Upon Al deposition, uniformly distributed small metallic aggregates are formed, which can be transformed to larger two-dimensional patches and three-dimensional islands by annealing. The small aggregates can be completely oxidized by water exposure. Following this treatment, characteristic features in the Al 2p and O 1s regions are observed. The growth of Rh on the modified surface has been investigated by STM and SPA-LEED and compared to previous results for the non-modified alumina support. In contrast to the non-modified support, no decoration of characteristic one-dimensional oxide defect structures is found. Instead, the formation of a high density layer of uniformly distributed aggregates is observed. The dissappearance of the characteristic O 1s and Al 2p features upon metal exposure points to a direct chemical interaction between the surface hydroxyl groups and the Rh deposided.

2:40pm **SS2-ThA3 Growth of Ultrathin ß-MnO@sub 2@ on TiO@sub 2@(110) by Oxygen-Plasma-Assisted Molecular Beam Epitaxy***, **S.A. Chambers**, Y. Liang,* Pacific Northwest National Laboratory

We have used oxygen-plasma-assisted MBE to grow epitaxial rutile films of pyrolusite (@beta@-MnO@sub 2@) on TiO@sub 2@(110) for thicknesses of 1 to 6 bilayers (BL). We define a BL to be a layer of Mn and lattice O and an adjacent layer of bridging O within the rutile structure. The resulting surfaces have been characterized in-situ by RHEED, LEED, XPS, XPD, and AFM. Well-ordered, pseudomorphic overlayers form for substrate temperatures between 400C and 500C. Mn-Ti intermixing occurs over the time scale of film growth for substrate temperatures in excess of 500C. Films grown at 400-500C exhibit classic Stranski-Krastanov growth whereas those grown at higher temperatures are atomically flat. 1-BL films grown at 450C form a well-ordered surface cation layer of Mn on the rutile structure with at most 10% indiffusion to the second cation layer. Thicker films rapidly disorder due to the simultaneous formation of pyrolusite and ramsdellite (@gamma@-MnO@sub 2@), which is orthorhombic and not lattice matched to TiO@sub 2@(110). However, thin films of rutile pyrolusite are preferentially stabilized by the TiO@sub 2@ substrate. @FootnoteText@ Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research - Environmental Management Science Program.

3:00pm **SS2-ThA4 Ordered Cerium Oxide Thin Films Grown on Ru(0001) and Ni(111)@footnote 1@***, **D.R. Mullins**, P.V. Radulovic, S.H. Overbury,* Oak Ridge National Laboratory

Ultrathin oxide films grown on single crystal metal substrates are advantageous for studying the adsorption and reaction of gases on oxide surfaces. Ultrathin films have a high surface area relative to their bulk volume. Their composition can be controlled during growth. They can be grown as nearly single crystals, can be readily removed and replenished in situ and they don't suffer from sample charging when using electron or ion probes. Cerium oxide thin films between 1 - 10 ML thick have been grown in situ on the Ru(0001) and Ni(111) surfaces. Well ordered films were grown by dosing metallic Ce in an oxygen ambient of 10@super -8@ - 10@super -7@ torr while the substrate was at 700K. Fully oxidized films could be grown by using a higher oxygen pressure while substoichiometric films were grown by reducing the oxygen pressure. The relative amounts of Ce@super +3@ and Ce@super +4@ were determined by soft x-ray photoelectron spectroscopy. Ion scattering spectroscopy (ISS) and LEED indicate that the cerium oxide films have the same symmetry as the substrate on which they are grown, i. e. six-fold on Ru(0001) and three-fold on Ni(111). The principal azimuths of the oxide films are aligned parallel to the principal azimuths of the substrates. The lattice constant of the cerium oxide is nominally the same as cubic CeO@sub 2@. Angle resolved ISS indicated that the fully oxidized films were predominantly terminated by an oxygen layer, whereas the substoichiometric films had a significant amount of cerium in the top layer. The structure and composition of the films grown on Ru(0001) were stable at temperatures up to 1000K. The films grown on Ni(111) lost oxygen upon annealing to 1000K. @FootnoteText@ @footnote 1@ 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.

3:20pm **SS2-ThA5 Evolution of Surface Morphology and Growth Modes for Epitaxial alpha-Fe@sub 2@O@sub 3@ on alpha-Al@sub 2@O@sub 3@**, ***I. Yi***, *A. Chambers,* Pacific Northwest National Laboratory

We have investigated how the surface morphology of epitaxial alpha-Fe@sub 2@O@sub 3@ evolves with film thickness on alpha-Al@sub 2@O@sub 3@ as a function of growth rate and surface orientation. The lattice mismatch of this materials system is 5.7%. The growth technique used was oxygen-plasma-assisted molecular beam epitaxy. Film surfaces were characterized as a function of thickness in situ using reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy and diffraction, and non-contact atomic force microscopy. Island formation is observed upon relaxation of the Fe@sub 2@O@sub 3@ film to its bulk lattice spacing. Relaxation begins at coverages of only ~1 full monolayer. Furthermore, the shape and size distributions of the islands are critically dependent on growth rate during the early stages of film growth. Sparsely populated, high-aspect-ratio islands form at higher growth rates, whereas more densely populated islands with lower aspect ratios form at lower growth rates. The former surface morphology is found to be a very poor template for further epitaxy, and gives rise to poorly ordered material, whereas subsequent epitaxy on the latter morphology produces very well ordered films and surfaces. The low-aspect-ratio islands formed at the initial stages of film growth coalesce within the first 50 Å. With a reduced number of islands, the surface becomes smoother. With additional growth, the surface morphology is greatly improved and the island-to-island height variation is reduced to few Ångstroms.@footnote 1@ @FootnoteText@ @footnote 1@Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research Environmental Management Science Program.

3:40pm **SS2-ThA6 The Nature, Growth and Stability of Vanadium Oxides on Pd(111)**, ***F.P. Leisenberger***, *M.G. Ramsey, S.L. Surnev, F.P. Netzer,* Karl-Franzens-Universität Graz, Austria

The study of metal - oxide interfaces is at the cutting edge of present day surface science. This particular study is inspired by the fact that the vanadium oxide - palladium phase boundary is an important system in practical heterogeneous catalysis. In this work high resolution XPS and NEXAFS have been used to characterise the growth and stability of vanadium oxide on a Pd(111) single crystal surface as a model system. The vanadium oxides have been prepared by reactive evaporation of vanadium in p@sub O2@ = 2 x 10@super -7@ mbar at 250°C from submonolayer to 15 ML coverages. The oxide morphology has been gauged by the C 1s XPS following the adsorption of CO as a probe molecule for the bare palladium sites. The stoichiometry of the oxide phase varies as a function of coverage, V@sub 2@O@sub 5@ / VO@sub 2@ - like at low coverages to V@sub 2@O@sub 3@ for the thicker oxide layers as indicated by the characteristic NEXAFS fingerprints at both the V 2p and O 1s edges. The thermal stability of the oxides is dependent on the coverage: the decomposition onset temperatures range from 300°C for submonolayer coverage to @>=@600°C for 15 ML. The V 2p XPS data indicate that the oxides disproportionate into higher and lower oxidation state phases. For nominal oxide coverage of 1 ML two different LEED patterns are observed on annealing between 250°C to 350°C. The surface formed below 300°C has a complex pattern and allows the uptake of CO, while on heating to 300 - 350°C a simple p(2x2) structure evolves, on which CO cannot be accommodated. This behaviour suggests that initially ordered oxide island structures are formed with bare palladium in between. At the higher temperature (300 - 350°C) a more homogeneous passive surface layer evolves.

4:00pm **SS2-ThA7 Photoemission Study of Ultra-thin NiO(111) Films Grown on Au(111)**, *B.R. King, M. Howard, P.S. Robbert, H. Geisler,* ***C.A. Ventrice, Jr.***, University of New Orleans; *D.A. Hite, P.T. Sprunger,* CAMD/Louisiana State University

Only a few systems are known where the polar surface of an ionic metal-oxide crystal can be grown without the introduction of surface impurities. One example of a stable polar surface is the growth of NiO(111) on Au(111) by evaporation of Ni in an O@sub 2@ atmosphere at ~300 °C.@footnote 1@ STM analysis of this surface has shown that the NiO(111) surface consists of a p(2x2) array of four-atom tripods with several missing-atom point defects on the surface as well as regions of bare Au.@footnote 1@ Angle-resolved photoelectron spectroscopy and x-ray absorption measurements have been performed to better understand the growth morphology and the resulting electronic structure of this system. Significant changes in the Au-5d photoemission intensity features are observed after the growth or the NiO which indicates that the Au regions observed with STM result from segregation, not NiO three-dimensional island growth into the Au substrate. The photoemission results also show a 1 eV shift in the Ni-3d emission to lower binding energy when compared to previously published results for single-crystal NiO(100).@footnote 2@ Since Ni deficient NiO results in a p-type substrate, this shift and the observation of missing-atom point defects with STM provide evidence that the (111) surface is Ni terminated. Analysis of structural changes in the Ni coordination upon oxidation is currently being performed by comparison of x-ray absorption features of Ni/Au(111) and NiO(111)/Au(111) systems. @FootnoteText@ @footnote 1@C. A. Ventrice, Jr., et al., Phys. Rev. B 49, 5773 (1994). @footnote 2@S. Hüffner et al., Z. Phys. B 83, 185 (1991).

4:20pm **SS2-ThA8 The Effects of High Temperature Annealing on the Surface Reconstruction of NiO(111)**, ***M.A. Schofield***, *A.K. Hicks, M. Gajdardziska-Josifovska,* University of Wisconsin, Milwaukee

NiO is an ionically bonded solid with a rocksalt structure. In the crystallographic direction, NiO consists of alternating close-packed planes of nickel and oxygen. The bulk terminated (111) surface, therefore, is a polar surface with theoretically predicted infinite surface energy. Consequently, adsorption of charged species at the surface or a considerable rearrangement of the atomic ordering is expected to occur to stabilize the surface. While microscopic faceting into neutral planes has been the accepted model for polar oxide surfaces, recent theoretical and experimental studies have reported a 2x2 reconstruction as a stabilization mechanism for the NiO(111) surface. In essence, the 2x2 structure (also known as octapolar, or nanofaceting structure) is the smallest possible scaling of the faceting model. In the present work we report two new reconstructions of annealed NiO(111) surfaces which cannot be readily explained by nanofaceting. Electron transparent single-crystal NiO samples were prepared for study of the (111) surface in plan view by transmission electron microscopy (TEM) and diffraction (TED) techniques. Annealing experiments were performed under high vacuum and atmospheric conditions over a wide range of temperatures and times. Under high vacuum annealing conditions a preferential desorption of oxygen from the sample surface resulted in the formation of epitaxial nickel islands. Conversely, for annealing experiments performed under atmospheric conditions, the NiO(111) samples exhibited surface reconstructions. Two reconstructions were observed and identified as having (@sr@3x@sr@3)R30° and (2@sr@3x2@sr@3)R30° surface periodicities from TED patterns obtained after annealing above 800°C in air. Both reconstructions were stable in air even after prolonged exposure of several weeks to atmospheric conditions.

4:40pm **SS2-ThA9 Morphology of MgO (111) Surfaces: Artifacts Associated with the Faceting of Polar Oxide Surfaces into Neutral Surfaces**, *R.A. Plass, J. Feller,* ***M. Gajdardziska-Josifovska***, University of Wisconsin, Milwaukee

We have found using optical, atomic force, scanning and transmission electron microscopies that the polar ionic MgO (111) surface does not facet into neutral (100) type planes upon high temperature annealing, as has been commonly believed, rather it appears to be stabilized by surface reconstructions containing cyclic ozone. The triangular pyramidal pits which Henrich@footnote 1@ associated with this presumed faceting turn out to be artifacts of the acid etch used in the sample preparation process. We have determined that the pits have walls sloped at 10.8° ± 2.8 ° with respect to the (111) surface, not the 54.7° expected for faceting to (100) type planes. The pit edges were confirmed by transmission electron microscopy to be along the three equivalent type directions. The morphology of this surface before and after annealing as well as transmission electron diffraction data and proposed atomic structures of three native surface reconstructions seen after annealing will be discussed. @FootnoteText@ @footnote 1@V.E. Henrich, Surf. Sci., 57 (1976) 385

5:00pm **SS2-ThA10 Surface Phonons and Surface Phase Transitions in KTaO@sub3@ (001)**, ***J.A. Li,*** *E.A. Akhadov, T.W. Trelenberg, S.A. Safron, J.G. Skofronick,* Florida State University*; L.A. Boatner,* Oak Ridge National Laboratory

Phase transitions of the (001) surface of KTaO@sub3@, prepared by cleaving a single crystal sample in situ, have been investigated by high-resolution Helium Atom Scattering (HAS). Angular distribution measurements of the diffractive scattering show that thermal cycling of the sample from room temperature to low temperatures (@<=@140 K) and back to @>=@220 K induces the (1x1) surface found after cleaving at ~300 K to reconstruct to a (2x1) surface. The reconstruction appears to occur much more rapidly, minutes vs. days, when the temperature is cycled to above ~250 K. The (2x1) phase appears to be stable until ~365 K at which point the surface reverts partially to the (1x1) structure. A time-of-flight technique was employed to measure the helium atom-single phonon creation/annihilation scattering events in order to examine the surface phonon dispersion of this surface. Experiments were carried out over the temperature range of 80 to 220 K. For bulk KTaO@sub3@ considerable softening near the Brillouin zone center of the transverse optical phonon branch had been reported as the temperature was reduced. For the surface, the observed softening in the surface phonon branches is not as great, but it appears to become more pronounced as the temperature is raised from 80 to 220 K. The implications of the temperature behavior of the surface lattice dynamics and the surface phase transitions are discussed.@footnote1@ @FootnoteText@ @footnote1@ Work supported in part by US DOE grant No. DE-FG02- 97ER45635.

Thin Films Division

Room 310 - Session TF-ThA

Ex-situ Characterization of Thin Films

Moderator: P. Ruzakowski Athey, PPG Industries Inc.

2:00pm **TF-ThA1 Ex-situ Characterization of Polycrystalline Thin Films***, K. Barmak,* ***J. Rickman,*** Lehigh University **INVITED**

The granular nature of polycrystalline thin films is an increasingly important consideration in modern high technology applications as grain and structural dimensions become comparable. This realization has prompted a renewed interest in understanding those factors which affect the evolution of grain structure in both as-deposited and reacted thin films. This presentation will address the ex-situ characterization of thin films that are of relevance to microelectronics interconnects and magnetic storage media. Experimental evidence from differential scanning calorimetry, x-ray diffraction and transmission electron microscopy studies will be reviewed and details of transformation kinetics and grain structure evolution will be discussed. Theoretical models and computer simulations of these processes will also be presented. Finally, results of algorithm development for automated grain size measurement from transmission electron micrographs will be highlighted.

2:40pm **TF-ThA3 TEM Study of Defects, Domains and Vacancy Ordering in Ga@sub 2@Se@sub 3@/GaAs(100) and Ga@sub 2@Se@sub 3@/Si(111) Thin Films***,* ***Z.R. Dai,*** *S.R. Chegwidden, S. Meng,* University of Washington*; K. Ueno, A. Koma,* University of Tokyo, Japan*; M.A. Olmstead, F.S. Ohuchi,* University of Washington

Ga@sub2@Se@sub3@ belongs to a class of M2(III)X3(VI) compounds (where M=AL, Ga or In and X=S, Se or Te) that is largely unexplored, but which has potential applications in novel optoelectronic devices. The crystal structure of Ga@sub2@Se@sub3@ is based on tetrahedral atomic coordination as in the zinc-blende structure, but in which one third of Ga sites on the average are left as vacancies to preserve charge balance in the crystal. The existence of vacancies complicates the Ga@sub2@Se@sub3@ crystal structure, with their arrangement leading to a variety of polymorphs and possible defect structures, but the arrangement of vacancies also strongly influences the properties of Ga@sub2@Se@sub3@. In particular, the vacancy ordering in the crystal structure likely results in the unique optical and electronic properties of Ga@sub2@Se@sub3@. In this work, the Ga@sub2@Se@sub3@ films were grown on GaAs(100) and Si(111) substrates, respectively, by Molecular Beam Epitaxy (MBE). The microstructure of the Ga@sub2@Se@sub3@ films were characterized by transmission electron microscopy (TEM). For the case of Ga@sub2@Se@sub3@/GaAs(100), a single crystal Ga@sub2@Se@sub3@ film was obtained, in which a number of plane boundaries parallel to [111] crystal planes were observed, as well as some micro-twins. The electron diffraction analysis indicates that the vacancies are ordered to distribute into the domains separated by the boundaries in some equivalent orientations of the zinc-blende structure. For the case of Ga@sub2@Se@sub3@/Si(111), the Ga@sub2@Se@sub3@ film consists of domains forming a twin relationship each other, relative to the [-110] crystal planes of the Si substrate. The vacancy ordering occurs in the [111] crystal planes and the periodicity of atomic stacking along crystal direction is two times of that for the cubic zinc-blende structure. The ordered arrangement of the vacancies is associated with the surface structure of the substrates. The attribute of the boundaries and formation mechanism of the domains and vacancy ordering will be discussed.

3:00pm **TF-ThA4 Sputtered Deposition of Ni@sub 3@Al Thin Films***, G.B. Thompson, X.D. Zhang, R. Grylls,* ***R. Banerjee****, P.M. Anderson, H.L. Fraser,* Ohio State University

Monolithic Ni@sub 3@Al films have been deposited using a magnetron sputtering technique. Each film was deposited onto an amorphous SiO@sub 2@ substrate at 25°C (unheated), 200°C, and 400°C. X-ray Diffraction, Transmission Electron Microscopy, and High Resolution Electron Microscopy was used to characterize the microstructure of the thin films. A nonequilibrium structure, which can be common in PVD techniques due to the high quench rates from a vapor to solid state, was observed. The phase transition towards the equilibrium state was seen with increased substrate temperature. X-ray diffraction indicated a strong [111] texture to all the deposited films in the growth direction. Although the elevated temperature samples showed the onset of a slight cubic orientation texturing. TEM/HREM was performed upon cross section and plan view specimens. An equiaxed grain structure, with a typical grain size of 20 nm, was seen in the films. No obvious macroscopic grain growth was observed for the elevated temperature samples. However a high density of planar defects was observed in the cross section of the unheated specimen. Formation of these planer defects will be discussed in terms of phase transition and structural stability in the Ni@sub 3@Al thin films.

3:20pm **TF-ThA5 Roughness Measurements With X-Rays Using an Out-Of-Plane Scattering Geometry***,* ***J.J. Kelly IV****, J. Con Foo, J.F. MacKay, M.G. Lagally,* University of Wisconsin, Madison

Surface and interface morphology plays a dominant role in fields ranging from thin-film magnetism to integrated-circuit production. Of the several techniques that can be used routinely for quantitative determination of the surface morphology, diffuse X-ray scattering provides the widest dynamic range in terms of the lateral scale of roughness that can be sampled, from sub-Angstrom to many micrometers. The use of a grazing-incidence geometry enhances surface sensitivity. In investigations to assess the influence of surface and interface roughness in giant-magnetoresistive films, we have measured the diffusely scattered intensity of soft X-rays (~1 keV) from rough surfaces and interfaces of Si, Co, Ni, and their combinations, using a non-conventional approach, an out-of-plane scattering geometry. An out-of-plane measurement is not limited by the shadow edge of the sample surface, and thus it samples a much wider range of reciprocal space and hence a much larger range of roughness wavelengths than a conventional in-plane rocking curve. We use the Born approximation and the distorted wave Born approximation to fit the data. The bandpass of our experiment allows us to extract all the relevant roughness parameters: the mean square roughness @sigma@, the correlation length @xi@, and the roughness exponent h. We have measured a roughness of bare highest-quality polished silicon wafers of less than 0.5 @Ao@, lower than can be measured by AFM or other techniques. Comparisons to rocking curves measured on the same samples in the same chamber will be presented to show the capabilities of this method. Roughness measurements on epitaxial sputter-deposited Co-on-Cu films will also be shown and, as time permits, compared to magnetic properties of these films. This work is supported by AFOSR and NSF. The Synchrotron Radiation Center is supported by the NSF.

3:40pm **TF-ThA6 Accurate Thin Film Density Measured by Energy-Dispersive X-ray Reflectivity***,* ***W.E. Wallace****, W.L. Wu,* National Institute of Standards and Technology

Recent advances in our group in x-ray reflectivity have shown that this technique, applied in the proper fashion, can be a robust and rapid way to measure thin film density on flat substrates. Density is directly related to most thin film properties: dielectric constant, moisture absorption, thermal diffusivity, etc. Until now, measuring the mass density of thin films less than a 1000 nm thick has not been an easy task. Energy-dispersive X-ray reflectivity,@footnote 1@ performed on a modified x-ray powder diffractometer, has been applied to a variety of organic and inorganic thin film materials. The density can be measured to ±1% in a few minutes. Changes in density of a variety of materials have been followed as a function of processing conditions, for example, annealing time and temperature of spin-on-glasses. A description of the technique and some recent representative examples of low dielectric constant materials for ULSI will be given. @FootnoteText@ @footnote 1@W.E. Wallace and W.L. Wu, Applied Physics Letters 67(1995)1203

4:00pm **TF-ThA7 Structure and Electronic Properties of the Novel Semiconductor Alloy Cd@sub 1-x@Cu@sub x@Te**, *S. López-López, G. Torres-Delgado,* ***S.J. Jiménez-Sandoval****, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Cinvestav-IPN, Mexico

In this work is presented an investigation of the structural and electronic properties of the novel semiconductor alloy Cd@sub 1-x@Cu@sub x@Te. The samples were prepared as thin films by rf sputtering on substrates made of Corning glass. X-ray diffraction patterns showed that the incorporation of Cu into CdTe did not affect significantly its lattice parameter. The band gap of the alloys measured by optical transmission spectroscopy was smaller than that of pure CdTe by only 50 meV, approximately. Due to its sensitivity to local atomic order, the samples were studied by micro-Raman spectroscopy. The transverse and longitudinal optic modes regularly observed in CdTe were also found in the Cd@sub 1-x@Cu@sub x@Te samples with frequency variations lower than 2 cm@super -1@, and no additional modes were observed. From the Raman experiments it was also determined that the incorporation of Cu precluded the formation of Te aggregates, which are commonly detected in CdTe thin films and bulk samples. The Cd@sub 1-x@Cu@sub x@Te films were p-type and, remarkably, it was found in some cases resistivity reductions by seven orders of magnitude with respect to pure CdTe films grown under the same conditions. This is opposite to the observed behavior on Cu-doped CdTe samples where copper acts detrimentally for electronic transport. Our studies indicated that the samples with the best properties were those in which the copper content was below ca. 7.0 at%.

4:20pm **TF-ThA8 Thickness-Dependence of Infrared Reflection-Absorption Spectra from Thin Film of Anatase-type TiO@sub2@ Grown on Polished MgO(001) Substrate by Ar-ion Beam Sputtering**, *D. Osabe, T. Uchitani,* ***K. Maki,*** Yokohama City University, Japan

The structure of thin film of TiO@sub2@ grown on air-cleaved surface of MgO(001) by Ar-ion beam sputtering on a Ti target is controlled by adjusting the partial pressure of O@sub2@ vapour (P@subO@) flowing near the substrate, which has previously been published in J.Vac.Sci. Technol., A, 15, 2485(1997). In the present study we will show that the preferred oriented anatase-type thin film of TiO@sub2@ with its c-axis parallel to the surface is grown on polished MgO(001) substrate held at 550 °C in P@subO@ = 1.1 x 10@super-2@ Pa. The polished substrate was used for studying optical property after X-rays diffraction. The diffraction peak height from the (200) lattice plane of the anatase TiO@sub 2@ film increases sigmoidally with increasing its thickness, d, below 20 nm, and linearly with d above 20 nm. The relationship between infrared reflection-absorption peak height near at 510 cm@super-1@ and d also shows the similar one between the diffraction peak height and d. Some discussion is given how to determine the dielectric function, @epsilon@, as a function of the angular frequency, @omega@, from the infrared reflection-absorption(IR-RAS). @epsilon@(@omega@) is determined by comparing the measured IR-RAS with the calculated one which is performed by evaluating from the Fresnel coefficient for the anisotropic materials on isotropic substrate by adopting the Lorentz model for the dielectric constant. After determining the dielectric function, the ratio of @omega@ for exciting of the longitudinal optical phonon, @omega@@subL@, to the transverse one, @omega@@subT@, that is, so called Lyddane-Sachs-Teller relation, is determined, which equals to the square root of @epsilon@(0)/@epsilon@. For this aim IR-RAS at 100 @<=@ @omega@ @<=@ 1000 cm@super-1@ is required which is shown for rutile-type single crystal of TiO@sub2@. However, IR-RAS at 400 @<=@ @omega@ @<=@ 1000 cm@super-1@ in the present study will be available for judging whether epitaxially-grown thin film is prepared or not and will show that the dielectric property of crystalline regions in thin films of TiO@sub2@ at d > 20 nm are similar to the bulk single crystal.

4:40pm **TF-ThA9 Rutherford Backscattering and Channeling Studies of Al and Mg Diffusion in Iron Oxide Thin Films**, ***S. Thevuthasan****, W. Jiang, D.E. McCready, S.A. Chambers,* Pacific Northwest National Laboratory*; N.R. Shivaparan, R.J. Smith,* Montana State University

There is growing interest in the epitaxial growth of model oxides on various oxide and metal substrates to obtain high-quality surfaces and films. This interest is being fueled by the utility of these materials in magnetic recording, surface geochemistry, heterogeneous catalysis and integrated microwave devices. A number of single crystal iron oxide films with various stoichiometries and orientations have recently been synthesized in our lab using oxygen-plasma-assisted molecular beam epitaxial growth. In the present work, we have used Rutherford backscattering and channeling techniques to investigate the crystalline quality of epitaxially grown @alpha@-Fe@sub 2@O@sub 3@(0001) on Al@sub 2@O@sub 3@(0001), Fe@sub 3@O@sub 4@(001) on MgO(001), and @gamma@-Fe@sub 2@O@sub 3@(001) on MgO(001). The nature of the film-substrate interface, the crystallographic quality of the films, and Al, Mg, and Fe interdiffusion were investigated. The minimum backscattering yields obtained from channeling and random spectra show that in general the film crystal quality is reasonably good. However, @alpha@-Fe@sub 2@O@sub 3@(0001) grown on Al@sub 2@O@sub 3@(0001) show some disordering at the interface due to the 5.7% lattice mismatch. In contrast, no disorder was seen at the Fe@sub 3@O@sub 4@(001)/MgO(001), and @gamma@-Fe@sub 2@O@sub 3@(001)/MgO(001) interfaces, in keeping with their respective lattice mismatches of -0.36% and -0.89%. Mg appears to outdiffuse into @gamma@-Fe@sub 2@O@sub 3@ film at a lower temperature than that at which Al outdiffusion occurs into epitaxial @alpha@-Fe@sub 2@O@sub 3@. Interestingly, Fe indiffusion was not observed for the @gamma@-Fe@sub 2@O@sub 3@/MgO system until higher temperatures (~800°C) were reached. @FootnoteText@ Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research - Environmental Management Science Program and NSF Grant DMR-9409205

5:00pm **TF-ThA10 Advances in the Characterization of Thin (<30 nm) TiN Films Using SIMS*****, A.V. Li-Fatou****, G.R. Mount, V.K.F. Chia,* Charles Evans & Associates

Titanium and titanium nitride films are widely used as barrier stacks to prevent junction spiking. It is also an important material for anti-reflection coatings (ARCs) on aluminum films to facilitate lithography processes during multilevel metallization for the manufacture of integrated circuits on silicon-based semiconductor devices. SIMS (secondary ion mass spectrometry) is a very capable tool for characterizing films because of its excellent detection sensitivities for transition elements and atmospherics. However, as films become thinner (<30 nm) quantitative analysis by SIMS also becomes more challenging. This is because a larger fraction of the film is now located in the transient region of the depth profile where the ion yields are not yet constant. In this paper we describe the effects of various analytical conditions (primary beam energies, incidence angles, and oxygen flooding using quandrupole and magnetic sector mass spectrometers) on the sputter rate at the near-surface and ion yields at the film/substrate interface. The samples used in this study were CVD grown samples of Ti (10 nm) /Si and Ti (3x10 nm)/Si. Our preliminary study shows that oblique angle bombardment with oxygen flooding can result in both accurate quantification and depth calibration in the upper 15 nm of the sample; there appears to be a dependence between the incidence angle and the primary beam energy. Interfacial mixing is reduced by using a lower primary beam energy. Ion yield enhancements are reduced using oblique incidence bombardment and oxygen flooding. Difficulties still exist when using SIMS to determine the exact the film thickness.

Thursday Evening Poster Sessions, November 5, 1998

Applied Surface Science Division
Room Hall A - Session AS-ThP

Aspects of Applied Surface Science Poster Session

AS-ThP1 Mass Spectral Frequency Plots: A New Tool For Static SIMS Data Interpretation*, **A.M. Spool,*** IBM Corporation

The experienced Static SIMS Analyst will examine common peak mass differences in addition to common peak positions in attempting to interpret a spectrum of a new or unknown sample. Mass differences of 44 amu, for example, suggest polymers with an ethylene oxide monomer, common to many surfactants. Many species with biological origins will display peaks differing by 2 methylene groups (28 amu). Fluorinated polymers will often have peaks with mass differences of 50 amu corresponding to a perfluorinated methylene. Spectra of many polymers will have common peak differences that correspond to the mass of their monomers. In this paper I propose a simple algorithm that converts spectra with unit mass resolution to a plot of the "frequency" of peaks in the mass spectrum. The resulting "pseudo-power spectra" or "mass spectral frequency plots" are more indicative of the type of species on the sample than the exact identity of these species. The algorithm proposed simply involves multiplying the intensity of the peak at each mass by the peak intensity at every other mass, and adding each result to the bin corresponding to the difference between the masses. The intensities of the resulting peaks at each "delta" are a function of the number of peaks with those mass differences, and the intensities of the original peaks. Examples of these plots will be shown and their utility demonstrated.

AS-ThP2 The Münster High Mass Resolution Static SIMS Library*, **B.C. Schwede,*** University of Münster, Germany*; T. Heller, D. Rading, E. Niehuis,* ION-TOF GmbH, Germany*; B. Hagenhoff,* TASCON GmbH, Germany*; L. Wiedmann, A. Benninghoven,* University of Münster, Germany

Despite the high mass resolution and accurate mass determination available with high-performance TOF-SIMS instruments, the interpretation of a TOF-SIMS spectrum is a tedious process. This paper describes the "Münster High Mass Resolution Static SIMS Library" which can support the user in this situation. The reference spectra were collected with various state-of-the-art TOF-SIMS instruments at the University of Münster, at ION-TOF and at TASCON. The library contains positive and negative spectra from a large variety of substances, with special emphasis on polymers, additives and semiconductor materials. It is structured in a hierarchical, easily extendable manner. All reference spectra are included in the library as interpreted lists of peaks. This library is embedded in the TOF-SIMS IV software package which offers tools like a reference browser or a facility to list all reference spectra which include specified peaks. The evaluation tools are based on a search algorithm specifically designed for the identification of compounds in mixtures. In order to evaluate the similarity of spectra, a version of the PBM algorithm@footnote 1@ was adapted to the specific needs of TOF-SIMS. The performance of the search algorithm was tested by analyzing mixtures of two substances with known composition. The results will be presented and compared to those achieved using principal component analysis (PCA) and neural networks. @FootnoteText@ @footnote 1@ F.W. McLafferty, R.H. Hertel, R.D. Villwock, Organic Mass Spectrometry 1974, Vol. 9, pp. 690-702

AS-ThP3 Formation of Alkanethiol Self-Assembled Monolayers on Oxidized Gold Surfaces*, **C. Yan,** A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany*; C. Wöll,* Ruhr-Universität-Bochum, Germany

The formation of alkanethiol self-assembled monolayers (SAM) on oxidized gold was studied by x-ray photoelectron (XPS), near edge x-ray absorption fine structure (NEXAFS) and infrared spectroscopy. Different oxidation procedures, exposure of gold to atomic oxygen in vacuum and to UV/ozone in air, lead to different types of surface gold oxides, distinguishable by their oxygen XP spectra. On the gold oxide formed by exposure to atomic oxygen stable SAMs were formed from ethanolic solution as well as via vapor deposition. Two sulfur species were distinguished by XPS, gold thiolate and a species related to the reaction of the thiol with the oxide that was found encapsulated under the self-assembled monolayer. The monolayers adsorbed from ethanolic solution were denser packed and less tilted than the layers formed by vapor deposition and SAMs on clean gold surfaces. The gold oxide produced by exposure to UV/ozone in air was removed during thiol adsorption from ethanolic solution and a monolayer assembled on the bare gold. Chemical vapor deposition on this oxide did not lead to well defined monolayers.

AS-ThP4 XPS and ISS Study of X-ray Damage of Alkanethiol Self-Assembled Monolayers on Gold and Silver*, **D.E. King,** L.S. Dake, A.W. Czanderna,* National Renewable Energy Laboratory

X-ray photoelectron spectroscopy (XPS) has been extensively used to study the chemistry of self-assembled monolayers (SAMs). While XPS is often considered the most non-destructive surface analysis technique, it is known that X-ray exposure and the resulting secondary electron emission can alter the reactivity of many materials. Organic materials can be particularly susceptible to damage resulting from X-ray bombardment during XPS. We have studied the effects of both Mg and Al K-alpha X-ray exposure on acid and methyl functionalized alkanethiol SAMs on gold and silver substrates. In the methyl terminated SAMs, a 20 percent reduction in C 1s peak area results after a 3 hour X-ray exposure. In the acid-terminated SAMs, both carbon and oxygen XPS signals decrease rapidly, with a relatively greater loss in the oxygen signal. Ion scattering spectroscopy (ISS) depth profiles indicate that it takes longer to sputter the irradiated SAMs than non-irradiated SAMs. We conclude that chemical changes in the monolayers result from the X-ray exposure. Although these changes are not detectable with XPS, the increased resistance to sputtering by the ISS beam indicates changes in bonding that are consistent with C-C crosslinking between the chains in the SAMs. XPS and ISS data will be presented for methyl and acid terminated alkanethiols after subjecting the SAMs to increasing times of X-ray exposure. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selinsgrove, PA 17870-1001

AS-ThP5 Identification of Halogen Atoms in STM Images of Substituted Phenyloctadecylethers*, **H.S. Lee,** S. Iyengar, I.H. Musselman,* University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images acquired from these ethers have revealed a bias-dependent contrast which corresponds to calculated electron density contours of various X-POE molecular orbitals. STM images of the X-POEs reflecting the electron density contour of the highest occupied molecular orbital (HOMO) exhibited four bright spots - one for the halogen atom, two representing the pair of lobes of the phenyl ring, and one for the oxygen/alpha-carbon atoms. For each X-POE, a minimum of three sets of four submolecular resolution HOMO images were acquired. The intensities of the spots for the halogen atom and the lobe of the phenyl ring closest to the halogen were measured and their ratio was calculated. The ratios for Cl-POE, Br-POE and I-POE were 0.48 ± 0.05, 0.58 ± 0.05 and 0.75 ± 0.07, respectively. An analysis of variance revealed that the intensity ratios of the X-POEs could be clearly distinguished among all data sets.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

AS-ThP6 Identification of Surface Nitrogen Functionalities Using Gas Phase Derivatization and XPS Analysis*, **Y. Liu,** L.J. Gerenser, P.M. Thompson, J.M. Grace,* Eastman Kodak Company

X-ray photoelectron spectroscopy (XPS) has been widely used as a primary surface analytical technique to determine the surface atomic compositions of polymeric materials. It provides quantitative elemental composition with excellent surface sensitivity. However, quite often, it is very difficult to identify the functional groups when the core-level binding energy shifts of these species are small. We have developed an approach using gas phase derivatization reactions in combination with XPS surface analysis for semi-quantitative determination of nitrogen functional groups. This poster will focus on the studies of two derivatization reagents, trifluoroacetic anhydride and trifluorotolualdehyde, and their applications in the identification of nitrogen functionalities including primary and secondary amines, amides and nitriles.

AS-ThP7 In-situ Characterization of Plasma Polymerized Films Using External Reflection Infrared Spectroscopy*, F.J. Boerio,* ***R.H. Turner,*** University of Cincinnati

External reflection infrared spectroscopy was used for the in-situ characterization of plasma polymerized films of acetylene, hexamethyldisilazane (HMDSZ), and hexamethyldisiloxane (HMDSO) as a function of thickness. The films were deposited onto polished iron and aluminum substrates in an inductively coupled RF reactor interfaced to an FTIR spectrometer. In-situ characterization of the films enabled the effects of oxidation during atmospheric exposure of the films to be reduced or eliminated. Conducting the investigations as a function of film thickness enabled spectral features associated with the bulk of the films and with the film/substrate interface to be identified. Infrared spectra of plasma polymerized acetylene films on iron substrates were characterized by a band near 3325 cm@super -1@ that was tentatively assigned to CH stretching in an acetylide species at the interface and by a band near 3300 cm@super -1@ that was assigned to the CH stretching vibration in mono-substituted acetylene groups in the bulk of the films. In a few cases, infrared spectroscopy was used to investigate adsorption of the neat monomers onto the substrates. Thus, infrared spectra of HMDSZ monomer adsorbed onto iron substrates were characterized by bands assigned to siloxane bonds, indicating some polymerization of the monomer.

AS-ThP8 X-Ray Microanalysis Inverse Modeling@footnote 1@*, **H.W. Wagner**, W.S.M. Werner, H. Störi,* Technische Universität Wien, Austria

The typical electron interaction volume in electron microprobe analysis (EPMA) is in the order of several cubic microns. For a single spot measurement of a sample with complex geometry, the source distribution of characteristic x-ray signals within this volume cannot be determined, therefore making it impossible to gain information on the sample structure. A set of measurements performed under different conditions (e.g. beam energies, incidence angles) does contain structural information, however not in a readily available form. The present work describes an approach for the extraction of structural information from EPMA measurements. The inverse modeling method relies on an efficient way to compute the forward transformation, i.e. the calculation of a generated x-ray signal of a known structure and experimental setup, and the application of appropriate mathematical optimization techniques. The use of simulated annealing as optimization method turned out to be advantageous in this context. The presented approach can be applied to arbitrary 2-D structures and accounts for possible a priori information on the sample structure. @FootnoteText@ @footnote 1@ The authors wish to thank Digital Equipment Corp. for support of this work.

AS-ThP9 Analysis of X-ray Growth Oscillations During Heteroepitaxy*, **J. Baker**,* Risoe National Laboratory, Japan*; F. Berg Rasmussen, M. Nielsen, R. Feidenhans'l,* Risoe National Laboratory, Denmark

Despite recent progress,@footnote 1@ x-ray intensity oscillations recorded during heteroepitaxial growth are an under-exploited source of information on buried interface roughness, growth-front roughness, and inter-layer spacings. We explore some fundamental aspects of growth curve shape and their dependence on the x-ray scattering vector and film properties. In particular, the super-periodic modulation of oscillation amplitudes is demonstrated. Oscillations during the growth KCl/NaCl(001) are shown as a typical example of the phenomenon. @FootnoteText@ @footnote 1@E. Weschke, C. Schüssler-Langeheine, R. Meier, and G. Kaindl, Phys. Rev. Lett. 79, 3954 (1997).

AS-ThP10 Surface X-ray Diffractometer for MOVPE growth at SPring-8*, **T. Kawamura**, Y. Utsumi, M. Sugiyama, Y. Watanabe,* NTT Basic Research Laboratories, Japan*; J. Matsui, Y. Kagoshima, Y. Tsusaka,* Himeji Institute of Technology, Japan

We developed a grazing incidence x-ray diffractometer, installed at the SPring-8 synchrotron facility, to enable the analysis of the initial stage of III-V compound semiconductor homoepitaxial growth in gas-phase. To maintain growth conditions, the z-axis arrangement is used instead of the conventional 4-axes arrangement. The detection range of x-rays is from -5.0 degrees to 135 degrees in 2@theta@, and the incident and the take-off angle ranges from 0 degrees to 15 degrees. To align the goniometer system, additional stages were attached for horizontal and vertical translation, and rotation around the z-axis. The material gases are delivered with a conventional MOVPE gas handling system, consisting of carrier gas supply, material gas handling, and exhaust subsystems. Hydrogen and nitrogen are used for carrier gases, and organometallic vapor sources are selected for material gases. For safety, to avoid the leaks, the whole system, including the goniometer, were installed in an isolated and the cabinet is maintained at lower than atmospheric prresure.

AS-ThP11 Quantitative Wafer Surface Trace Metal Analysis by TXRF and Surface SIMS*, J.M. Metz, S.P. Smith, **M.J. Edgell**, V.K.F. Chia,* Charles Evans & Associates

Ultra-clean Si wafer surfaces are critical to the fabrication of ULSI devices. This is reflected by the stringent contamination limits for polished and epitaxial substrates, and surface preparation (i.e. before gate oxide growth) suggested by the National Technology Roadmap for Semiconductors (NTRS). Today's requirement for surface metals is typically in the range of 10@super 10@ atoms/cm@super 2@. Future needs in the year 2003 are anticipated to be 1x10@super 10@ atoms/cm@super 2@ for Al, Ca, and Zn, and 2x10@super 10@ atoms/cm@super 2@ for Fe, Ni, Cu, and Na. The transition metals Fe, Ni, Cu, and Na are considered to be very damaging at the gate oxide level, and therefore requirements for these are becoming more stringent. It is even considered that surface metals on epi substrates before gate oxidation may have to be as tight as for polished substrates, because the low temperature processing at small design rules leads to less effective gettering in the p+ substrate of p/p+ epi. Al is important to monitor because at concentrations below 10@super 11@ atoms/cm@super 2@ it can increase the oxide growth rate in the very thin gate oxide regime. This is a different effect compared to higher levels of Al (e.g. >10@super 12@ atoms/cm@super 2@) decreasing gate oxide thickness for thicker gate oxides. TXRF and SurfaceSIMS are two of the most powerful analytical techniques available for substrate and interface engineering. Both these techniques provide quantitative trace metal information at the surface of wafers. TXRF is an excellent survey tool capable of analyzing 300 mm wafers to a depth of about 50 Å. Quantification at the Si/SiO@sub 2@ interface is very important and may be performed accurately using SurfaceSIMS. The information provided by these two techniques allows pre-clean technologies used on silicon substrates to be evaluated. This presentation reviews the two techniques and illustrates with examples how they compliment each other.

AS-ThP12 AFM Explanation of the Improved Resolution in Auger Depth Profiles by Using the Zalar Rotation*, **L. Lozzi**, S. Santucci, D. Pacifico, P. Picozzi,* Università dell'Aquila, Italy*; R. Alfonsetti,* Texas Instruments ITALIA, Italy

Auger Microscopy, as a consequence of its high lateral resolution (around 10 nm) and its sensitivity to the surface, is a powerful tool to investigate elemental and chemical composition of surfaces, interfaces and thin films, particularly in microelectronics artifacts with dimensions lower than 200 nm. In this paper we studied the TiN/AlSiCu interface, with interfacial oxygen, of a 500 nm wide metal line of a 64 Mbit DRAM device. The sharpness of this interface and the presence of interdiffused interfacial contaminants may affect the device behaviour. The elemental depth profile of the investigated system has been performed by using the Auger Spectroscopy assisted by Ar ion sputtering. The profiles have been performed using two different methods of sample sputtering: the first one maintaining the sample in a fixed position respect to the ion beam and the second one by rotating the sample with a Zalar rotation accessory. The profiles have been interrupted when the TiN/AlSiCu interface had slightly overcome. The sputtering crater has been observed by using an AFM microscope. For identical samples we observed, in the case of the fixed sputtered sample, a particularly rough TiN/AlSiCu interface with evident finger prints of preferential sputtering which produces a sensibly enlarged interface depth profile. In the case of the rotated sample, we obtained a sharp interface profile which corresponds to a flat surface of the bottom of the crater with a roughness comparable to that of the not sputtered surface. In this case the presence of interfacial oxygen bonded to Al has been carefully localised.

AS-ThP13 Structure of Plasma Polymerized SiO@sub2@Films: Corrosion Protection of Steel and Aluminum Substrates*, **R.G. Dillingham**,* Brighton Technologies Group, Inc.*; F.J. Boerio,* University of Cincinnati

Plasma polymerized organosiloxanes made using excess oxygen as a carrier gas have a silica-like structure, and function as excellent corrosion inhibiting coatings and primers for adhesive bonding and painting. Similar structures can be obtained using a variety of reactor configurations and polymerization conditions, but details of film structure and performance can vary. Infrared spectra of these films show non-bridging Si-O and -OH species. The relative amount of structural imperfection is a strong function of deposition conditions. These structural features provide reactivity necessary for adhesion of paints and adhesives, but limit corrosion protection, probably by increasing electrolyte diffusion. Structures that provide optimum corrosion protection do not necessarily provide optimum overlayer adhesion. This work relates film deposition conditions to structural defects, and shows how these defects affect the electrical impedance spectra and corrosion inhibiting capabilities of plasma polymerized SiO@sub2@.

Electronic Materials and Processing Division
Room Hall A - Session EM-ThP
Electronic Materials and Processing Poster Session

EM-ThP1 Synthesis and I-V Characterization of Tin Dioxide Varistors*, **A. Kale**,* University of Central Florida*; R.N. Barve,* College of Engineering, India*; S.K. Date,* National Chemical Laboratories, India*; P.N. Santhosh,* Indian Institute of Science, India*; S. Seal,* University of Central Florida

Tin dioxide varistors are novel semiconducting ceramics having interesting non-ohmic current-voltage characteristics. They are widely used in consumer and military electronics, industrial protection, communications, transportation, data processing and other applications like medical devices. An overview of the steady state time dependent electrical properties of Tin dioxide varistors is presented. For a quantitative agreement with the experimental data the electronic defect states in the bulk of the Tin dioxide grains and at the interfaces between the grains were studied. The varistors were fabricated in two ways. The normal physical process (ceramic route) of mixing and compaction of Tin dioxide powder with various dopants and the second method being that of sol-gel processing in which dopants were taken in their aqueous solutions. Samples prepared by both the processes were studied for the dopant densification using Scanning Electron Microscope and X-ray diffraction. The effect of various sintering temperatures on their non-ohmic or non-linear characteristics was also studied. The varistors prepared by the sol-gel method showed high non-linearity, high density and high threshold voltage properties than the ceramic route owing to their finer grain structure and better densification of dopants around the grain boundaries. It was shown that the Tin dioxide non-linear properties are a function of grain size and depend upon the factors that influence the course of events at the sintering temperature. It is hoped that in coming years, the research efforts are likely to have path breaking impacts in design and development of better varistors

EM-ThP2 First Principles Calculations of Ge (100) Covered by Up to One Monolayer of Pb*, **N. Takeuchi**,* Universidad Nacional Autonoma de Mexico, Mexico

We have performed first principles total energy calculations to determine the atomic structure of the Ge(100) surface covered with different amounts of Pb. For low coverages, Pb starts growing parallel to the underlying Ge dimers (without breaking them), and it forms asymmetric dimers. This situation continues up to half a monolayer. At this coverage, several structures are possible: (2x2), p(4x2), etc. They are also formed by asymmetric Pb dimers on top of the Ge(100) surface. They differ from each other by the orientation of the buckled dimers. When the coverage is larger, the Ge dimer bonds start to break. >From this coverage,and up to one monolayer, the stable surface shows a c(4x8) reconstruction, similar to the one found in Sn on Si(100) and Pb on Si(100).It consists of rows of Pb ad-dimers, with one missing row out of every four, yielding a coverage of 0.75 of a monolayer.The dimers are also asymetric. Calculated local density of states are in excellent agreement with scanning tunneling microscope images. Surface formation energies show that this configuration is more stable than the full monolayer (2x1) structure.

EM-ThP3 TEM Study of TiAl@sub3@ Formation*, **C.C. Pace**,* University of North Carolina, Chapel Hill and MCNC*; M.K. Lamvik, M.A. Ray,* Microelectronics Center of North Carolina*; A. McTeer,* Micron Technology

Metallizations consisting of Al-Cu alloys and Ti layers are widely used in microelectronic device fabrication, because of their low contact resistance and resistance to electromigration and hillock formation. As device dimensions are reduced, reaction mechanisms between layers must be understood at the atomic level to develop device structures that minimize failures due to resistive heating and stress induced voiding. Structures consisting of 350nm Al-0.5% Cu on 20nm Ti sputter deposited onto SiO@sub2@/Si substrates have been studied using a Philips EM 430 transmission electron microscope (TEM) equipped with a heating stage. TEM specimens of as-deposited samples were prepared and annealed in situ in the TEM. The temperature was varied up to 450 °C and times up to several hours. Within this temperature range the reaction rate for the formation of TiAl@sub3@ in the in-situ experiments agree with the published literature, although the range in published values is quite broad. Cross-sectional TEM micrographs reveal a non-uniform TiAl@sub3@/AlCu interface. The roughness revealed by TEM contradicts interpretations of Rutherford backscattering spectra (RBS). RBS suggest a layer-by-layer growth mechanism, which would produce a TiAl@sub3@ layer of uniform thickness. To show the equivalence of an in situ anneal and a furnace anneal, TEM samples were prepared from a wafer annealed in a furnace at 400 °C for 50 minutes. Cross-sectional micrographs revealed similar interface roughness. For both anneals, less than 10nm of Ti was consumed. An unreacted Ti layer remained even after extended annealing. In-depth profiling with Auger electron spectroscopy (AES) was utilized to confirm the presence of unreacted Ti. A model of the reaction mechanism that results in a non-uniform TiAl@sub3@ layer in contact with unreacted Ti will be proposed. It is critical that this mechanism be understood and controlled as device dimensions are scaled to ever smaller sizes.

EM-ThP4 Side-Wall Damage in a Transmission Electron Microscopy Specimen of Crystalline Silicon Prepared by a Focused-Ion-Beam*, **N. Kato**,* IBM, Japan*; H. Saka,* Nagoya University, Japan*; Y. Kohno,* IBM, Japan

Focused ion beam (FIB) milling has recently been widely used for the preparation of cross-sectional transmission electron microscopy (TEM) specimens. Inevitably, however, such specimens are caused a certain amount of damage by highly accelerated ion beams. The damage to the side-wall of a specimen is visible under TEM as amorphization, and the structure of the undamaged intermediate layer can be observed through the damaged layers. Nevertheless, these damaged layers do pose a serious problem for TEM observation, especially when high-resolution observation is required. Many techniques have been developed for reducing the damage, such as gas-assisted etching. In this study, we experimentally investigated the depth of the side-wall damage in silicon, and the effect of the damaged layer on TEM observation. The depth of damage caused by a 30-keV FIB without gas-assisted etching was 20 nm, which was reduced to 10 nm by lowering the acceleration voltage to 10 kV. Gas-assisted etching with iodine does not markedly reduce the damage, as would be expected from the enhanced etching ratio. We also investigated several methods for reducing the damage after FIB fabrication. Broad-argon-ion-beam milling reduced the damaged layer to 12 nm, and wet-etching the specimen with a mixture of nitric and hydrofluoric acid removed most of the damage. Removal of the amorphous silicon layer significantly improved TEM observation. No amorphous ring such as that observed in the diffraction pattern (DP) of the specimen immediately after FIB fabrication was seen in the DP of the wet-etched specimen, in which a silicon lattice fringe was clearly observed.

EM-ThP5 Heat-Transfer in UHV-Scanning Thermal Microscopy*, **W. Müller-Hirsch**, J.P. Parisi, M.T. Hirsch, A. Kittel,* University of Oldenburg, Germany*; L.V. Govor, A.Yu. Olevanov,* The State University of Belarus

Scanning thermal microscopy (SThM) offers the capability to map temperature distributions of samples with subµm resolution. A wide variety of microscope configurations and sensor designs have been described in literature. However, most experiments have been performed under ambient conditions and the heat-transfer between sensor and sample was attributed to be mostly due to a liquid film-bridge between sensortip and sample.@footnote 1@ In this study we use a Scanning Thermal Microscope to investigate the heat transfer under ultra-high vacuum (UHV) conditions. A needle-shaped Au/Ni-thermocouple-sensor is brought into close proximity of a liquid nitrogen cooled sample. We find an almost linear increase of the heat-transfer with decreasing tip-sample distance on a length-scale in the range of 10nm. Since our experiments are performed at a base-pressure of 10@super -10@ mbar, the heat conduction path via a liquid film-bridge can be excluded. We discuss other mechansims like electron-, phonon- or photon-coupling between tip and sample as an origin of the heat-transfer in the near-field regime of the sample. Additionally, the observed near-field heat-transfer is sensitive with respect to the sample topography. Measurements of the plateau structure of Au-samples with a homogeneous temperature distribution will be presented and exlained by a simple geometric model. Further measurements investigate the joule-heating of a MIS-diode array with diode-dimensions of 2µm. The inhomogeneous temperature distribution due to the joule-heating of the diodes is clearly resolved in the thermal image of the sample. @FootnoteText@ @footnote 1@K. Lou et.al. J. Vac. Sci. Technol B 15(2) p.349 (1997)

EM-ThP6 Boron Phosphide Films Grown by Solid-Source Molecular Beam Epitaxy*, **D. Buchenauer**, D. Dibble, K.F. McCarty, J.C. Lund, R.J. Anderson, M. Clift, D.L. Medlin, J.A. Schneider,* Sandia National Laboratories

A significant improvement in the detection of thermal neutrons could be made through the use of zinc blende boron phosphide (BP) as the detection medium in a solid-state neutron detector. Earlier work on the growth of BP using vapor transport,@footnote 1@ flux growth,@footnote 2@ and chemical vapor deposition@footnote 2@ has produced crystalline material of the required thickness, however, autodoping of the BP has been too high to allow their use in neutron detection. Recent progress on the growth of amorphous films using Molecular Beam Epitaxy (MBE) has led to nearly stoichiometric films with improved electrical properties.@footnote 3@ Here we report on the first growth of BP films using electron beam evaporation of boron and thermal cracking of phosphorus vapor by a three-cell EPI cracker. Stoichiometric films have been grown at substrate temperatures as low as 300°C. The relationship between the electronic and microstructural properties of the BP films and their performance as solid-state neutron detectors will be examined. @FootnoteText@ @footnote 1@T. L. Chu, J. M. Jackson, and R. K. Smeltzer, J. Crystal Growth 15 (1972) 254. @footnote 2@Y. Kumashiro, J. Mater. Res. 5 (1990) 2993. @footnote 3@Y. Kumashiro, T. Yokoyama, T. Sakamoto, and T. Fujita, J. Solid State Chemistry 133 (1997) 269.

EM-ThP7 Effects of Variously Configured Magnets on the Characteristics Of Inductively Coupled Plasmas*, **S.W. Hwang**, Y.J. Lee,* SungKyunKwan University, Korea*; S.W. Joe,* Kyoungki University, Korea*; K.H. Kim,* Hanyang University, Korea*; G.Y. Yeom,* SungKyunKwan University, Korea

Although high density plasma(HDP) sources have been employed for dry etching in microelectronics, their scale-up to process larger wafer size such as the substrates used in flat panel display(FPD) technology is not that easy due to the uniformity problem over a large area wafer size. In this study, to enhance plasma uniformity and density of an inductively coupled plasma source, the effects of variously configured magnets on the characteristics of the plasmas were investigated. As the magnets, Helmholtz type axial electromagnets and multi-dipole magnets composed of 8sets of permanent magnets around the chamber wall were used. The chamber was designed as a square mainly for the FPD application such as liquid-crystal display(LCD), plasma display panel(PDP), etc. To characterize the plasmas as a function of magnetic field strengths and the combination of the magnets, electrostatic probe(Hiden Analytical Ltd.), optical emission spectroscopy(OES: SC Tech. PCM402), and quadrupole mass spectrometer(QMS: Hiden Analytical Ltd. PSM) were used. Ion density, plasma potential, and electron temperature were measured along the chamber diameter and axial direction for Ar and Cl@sub 2@/HBr gas combinations using the electrostatic probe. The results showed that high density plasma(10@super 11@-10@super 12@/cm@super 3@) with excellent uniformity(@<=@3%) near the wafer surface could be achieved along the chamber diameter by the combination of the axial magnets and multi-dipole magnets. Optical emission spectra and mass spectra (positive and negative ions, radicals, and neutrals) were also studied as a function of axial magnetic strengths and with/without multi-dipole magnets for Cl@sub 2@/HBr gas combinations, and showed enhanced ionization and dissociation with the combined magnets. We believe that a suitable combination of axial magnets and multi-dipole magnets would also improve etch uniformities and etch rates of the large size wafers used in FPD.

EM-ThP8 Atomic Order and Electron Affinity at AlN(0001) Surfaces*, **C.I. Wu**, A. Kahn,* Princeton University*; E.S. Hellman, D.N.E. Buchanan,* Bell Laboratories, Lucent Technologies

We have used Auger electron spectroscopy (AES), low energy electron diffraction (LEED), x-ray and ultraviolet photoemission (XPS and UPS) and inverse photoemission spectroscopy (IPES) to investigate the preparation, atomic order and electron affinity of AlN(0001) surfaces. AlN films 0.2µm thick were grown by molecular beam epitaxy on Si(111) substrates. Following ambient transfer to the surface analysis chamber, repeated cycles of nitrogen sputtering (1 keV) and annealing (10 min., 1050 °C) were necessary to obtain ordered surfaces with only a few percent of a monolayer of O contaminant. The resulting surfaces exhibited sharp 1x1 LEED patterns. The UPS (HeI and HeII) spectra exhibited sharp features allowing a clear identification of the valence band maximum (E@sub v@). The position of E@sub v@ was confirmed by XPS measurements of the Al 2p core level and using the known binding energy of this level with respect to E@sub v@.@footnote 1@ The UPS-IPES combination showed the Fermi level at 4.8 eV above EV and 1.6 eV below the conduction band minimum at the surface of our AlN. Given these numbers and in spite of the concomitant observation of a sharp feature at the onset of photoemission, generally associated with the occurrence of negative electron affinity, the electron affinity was calculated to be +2.3 eV. Finally, the deposition of 1-2 monolayer of Al on the (1x1) surface followed by a 5 min. 1250°C anneal led to a structure characterized by a (@sr@3 x @sr@3)-R30° diffraction pattern. This LEED pattern is consistent with RHEED observations for increasing Al surface concentration during growth. @FootnoteText@ @footnote 1@J.R. Waldrop, and R.W. Grant, Appl. Phys. Lett. 68, 2879 (1996).

EM-ThP9 Enhanced Electrical Performance of Au/n-GaN Schottky Diodes by Novel Processing*, **L. He,* Northern Illinois University*; X.J. Wang,* University of Maryland at Baltimore County

GaN has attracted great attention recently for its application in electronic and optoelectronic devices. Applications including in blue lasers, visible light emitting diodes (LED), metal-semiconductor field-effect transistor (MESFET), high electron mobility transistors(HEMT), ultraviolet photodetectors, have been demonstrated. Metal/GaN contacts, both ohmic and Schottky, are of important for device applications. Studies of Schottky contacts on GaN were especially interested. Schottky barrier height is expected to be dependent on the metal work function due to the ionic nature of GaN, though the work function of the contact metal is not the exclusive factor determining the Schottky barrier height. In this study, the low temperature (LT = 77K) metal deposition technique was used to improve the electrical characteristics of Au/n-GaN Schottky diode. The LT deposition technique has been successfully used to fabricate high quality Schottky contacts on InP, GaAs and InGaAs. A comparison of the barrier heights is conducted with previously reported results. The same chip of GaN epitaxial layer was used for room temperature (RT) and LT Schottky diodes. The LT Schottky diodes exhibit excellent performance. The leakage current density as low as 2.55x10@super -11@A×cm@super -2@ was obtained from the LT diodes. The linear region in the I-V curve of the LT diodes at forward bias could extend more than eight orders in the magnitude of the forward current. Current-voltage-temperature (I-V-T) measurements were carried out to study the characteristics of the LT diodes. A typical barrier height of 1.32eV for the LT diode was obtained, which is the highest value ever reported. The obvious enhancement in electrical performance makes the LT processing a high promising technique for GaN device application. Analysis through photoluminescence (PL) and x-ray diffraction measurements were conducted to collaborate with the electrical characteristics.

EM-ThP10 W-Based Ohmic Contacts on p- and n-Type GaN*, **X. Cao**, F. Ren, S.J. Pearton,* University of Florida, Gainesville*; A. Zeitouny, M. Eizenberg,* Technion-Israel Institute of Technology, Israel*; J.C. Zolper,* Office of Naval Research*; C.R. Abernathy,* University of Florida, Gainesville*; R.J. Shul,* Sandia National Laboratories*; J.R. Lothian,* Bell Laboratories, Lucent Technologies

W and WSi ohmic contacts on both p- and n-type GaN have been annealed at temperatures from 300-1000@degree@C. There is minimal reaction (@<=@100@Ao@ broadening of the metal/GaN interface) even at 1000@degree@C. Specific contact resistances in the 10@super -5@ ohm cm@super 2@ range are obtained for WSi@sub x@ on Si-implanted GaN with a peak doping concentration of ~5x10@super 20@cm@super -3@, after annealing at ~750@degree@C. On p-GaN, leaky Schottky diode behavior is observed for W, WSi@sub x@ and Ni/Au contacts at room temperature, but true ohmic characteristics are obtained at 250-300@degree@C, where the specific contact resistances are typically in the 10@super -2@ ohm cm@super 2@ range. The best contacts for W and WSi@sub x@ are obtained after 700@degree@C annealing for periods of 30-120 secs. The formation of @BETA@-W@sub 2@N interfacial phases appear to be important in determining the contact quality.

EM-ThP11 Redistribution and Activation of Implanted S, Se, Te, Be, Zn and C in GaN*, **R.G. Wilson**,* Consultant*; J.M. Zavada,* U.S. Army Research Office*; X. Cao, S.J. Pearton, R.K. Singh,* University of Florida, Gainesville*; M. Fu, J.A. Sekhar, V. Sarvepalli,* Mycropyretics Heaters International*; R.J. Shul, J. Han, D.J. Rieger,* Sandia National Laboratories*; C.R. Abernathy,* University of Florida, Gainesville

We have previously found that implanted Si in GaN shows minimal redistribution after annealing at 1500@degree@C, with an effective diffusion coefficient of @<=@2x10@super -13@cm@super 2.s@@super -1@ at this temperature. In this experiment, common donor (S, Se and Te) and acceptor (Be, Zn and C) dopants were implanted at a typical dose of ~5x10@super 14@cm@super -2@, with a projected range of ~1500@Ao@. Annealing was performed with AlN encapsulation on the GaN, at temperatures up to 1500@degree@C in a novel rapid thermal furnace utilizing intermetallic heating elements. After selective removal of the AlN cap in hot KOH solution, Secondary Ion Mass Spectrometry profiling was performed to measure the redistribution of the different dopant species. Effective diffusion coefficients were obtained from the broadening at full-width-half-maximum of the implanted profile.

EM-ThP12 Etch Characteristics of GaN using Chemically Assisted Ion Beam Etching(CAIBE) and Its Effects on Ohmic Contact Formation to n-type GaN*, W.J. Lee*, *G.Y. Yeom,* Sungkyunkwan University, Korea*; J.W. Lee, Y.J. Park, T.I. Kim,* Samsung Advanced Institute of Technology, Korea

Currently, GaN facets required for GaN laser devices are fabricated using dry etching due to the difference in the cleavage planes of sapphire substrates and GaN epitaxial layers grown on them. Fabrication of GaN facets using dry etching not only requires high GaN etch rates, high selectivity over mask layers, and vertical etch profile with a smooth sidewall, but also requires damage-free etch surface which could be induced due to the energetic ion bombardment during the etching. This induced damage could degrade the electrical performance of the device. Therefore, in this study, we investigated the etch properties, etch-induced damage, and resistances of contacts formed on etched n-type GaN. The GaN samples used in the experiment were grown by metalorganic chemical vapor deposition on sapphire substrates and GaN etching was performed using CAIBE system(RF-350 Etching System, Veeco) having a 210mm diameter ion source, a Meissner trap, and a load-lock chamber. Ar was introduced into the ion source while Cl@sub2@, BCl@sub3@, and HCl were distributed around the substrate through the nozzle. GaN samples patterned with PR or SiO@sub2@ were loaded on the rotational fixture which could be tilted between 0° and 60° and also could be heated up to 300 C or cooled down to 0 C. To determine the etch characteristics, GaN samples were etched as a function of Ar ion beam parameter, gas chemistry, tilt angle, and substrate temperature. Etch characteristics such as etch rates, selectivities, and etch profiles were estimated using a profilometer and scanning electron microscopy(SEM). Variation of surface composition of the etched GaN samples was investigated using X-ray photoelectron spectroscopy(XPS). Contact resistances of the etched n-type GaN samples were measured by transmission line measured(TLM) and physical damage on the etched GaN surface was observed using HRTEM. The relations of surface composition and physical damage on GaN surface to the ohmic contact resistances were also studied.

EM-ThP13 Growth of ß-SiC Thin Films on Si (100) at Low Temperature using Ultra-high Vacuum Electron Cyclotron Resonance Chemical Vapor Deposition*, J.H. Pyo,* Seoul National University, Korea*; K.W. Whang,* Seoul National University, Korea, South Korea

ß-SiC thin films were grown on Si (100) at low temperature using ultra-high vacuum electron cyclotron resonance chemical vapor deposition with gas mixtures of H@sub 2@ / CH@sub 4@ / SiH@sub 4@ and their properties such as crystallinity and stoichiometry were investigated. Care was taken to prepare the clean, damageless Si surface prior to the growth. In situ H@sub 2@ plasma cleaning, as well as conventional wet cleaning, were performed to confirm Si (2X1) reconstruction structure, which seemed to be an essential process to grow the ß-SiC thin films at low temperature. In addition, Si surface was Carburized with H@sub 2@ / CH@sub 4@ plasma at 700 °C before the growth of the film. After the in situ cleaning and the carburization, SiC thin films were grown on the carburized surface with the various ranges of microwave input power, SiH@sub 4@ to CH@sub 4@ flow ratio, and substrate temperature. Reflection high energy electron diffraction (RHEED) patterns of the films which were deposited at the substrate temperature 600 °C showed the changes from textured to ring pattern as the microwave power increased or the flow ratio decreased. Analyses of the films using XPS and spectroscopic ellipsometry showed that the ring and textured patterns were polycrystalline ß-SiC and Si-rich films, respectively. These results implies that stoichiometry of the film is affected by the microwave power and the flow ratio which presumably cause modification of the chemistry in plasmas. On the other hand, the crystallinity was affected by the substrate temperature. As the temperature increased up to 750 °C, the crystallinity was improved.

EM-ThP14 Study of Pulsed versus Continuous Wave Plasma Deposition of Amorphous, Hydrogenated Silicon Carbide (a-Si@sub1-x@C@sub x@:H) from Silane/Methane Mixtures*, P.M. McCurdy,* *J.M. Truitt, E.R. Fisher,* Colorado State University

Hydrogenated amorphous silicon carbide (a-Si@sub 1-x@C@sub x@:H) is an important material because of its current use as a window coating for amorphous Si solar cells and its potential applications in photoelectronics and as a hard coating. Equival ently powered, pulsed and continuous wave (cw) radio-frequency discharges (13.56 MHz) were used to deposit a-Si@sub 1-x@C@sub x@:H films from silane and methane. Deposited films were studied using FTIR, XPS, Raman scattering spectroscopy, scanning electr on microscopy and profillometery. Deposition parameters investigated included pulsed plasma power, duty cycle (d.c.) substrate temperature, substrate bias, and addition of a carrier gas (H@sub 2@, or He). Films deposited from pulsed plasmas show a large decrease in hydrogen incorporation compared to films deposited in equivalently powered CW systems. Notably, there is a significant decrease in modes associated CH@sub 3@ moities. CH@sub 3@ groups have been associated with electrical and mechanical inst abilities of a-Si@sub 1-x@C@sub x@:H films. Grounding the silicon substrate is shown to have a significant effect on both the CW and pulsed plasma deposited films.

Magnetic Interfaces and Nanostructures Technical Group Room Hall A - Session MI-ThP

Magnetic Interfaces and Nanostructures Poster Session

MI-ThP1 Comparison of Cl@sub2@ and F@sub2@ Based Chemistries for the Inductively Coupled Plasma Etching of NiMnSb Thin Films*, J. Hong,* *J.A. Caballero, E.S. Lambers, J.R. Childress, S.J. Pearton,* University of Florida, Gainesville

Plasma etching chemistries based on BCl@sub3@/Ar, BCl@sub3@/H@sub2@ and NF@sub3@/Ar were studies for patterning NiMnSb Heusler Alloys thin films and associated Al@sub2@O@sub3@ barrier layers under Inductively Coupled Plasma. Using BCl@sub3@/Ar discharges, high etch rates (@>=@1µm) were achieved either at high source power (1000W) or high dc self bias (-300V) and etch rates showed a strong dependence upon source power, ion energy and gas composition. Hydrogen addition to the BCl@sub3@ created new species (HCl) in the plasma, leading to the fast etching for NiMnSb, in contrast to the situation of Ar addition. Selectivities of @>=@8 for NiMnSb over Al@sub2@O@sub3@ were obtained in BCl@sub3@-based discharges. On the other hand, NF@sub3@/Ar discharges provided a narrow process window for the etching of NiMnSb and etch rates of NiMnSb were much lower compared to BCl@sub3@. The surface of NiMnSb etched with NF@sub3@/Ar was smoother with RMS surface roughness of 1.4nm measured by Atomic Force Microscopy than the surface produced with BCl@sub3@/Ar. In terms of near surface chemistry, etched surface with NF@sub3@/Ar revealed Mn-enriched, indicating the existence of involatile Mn etch products, whereas Mn-deficiency at the near surface was obtained with BCl@sub3@/Ar.

MI-ThP2 Magnetic Moment of fcc Fe in [Fe/Pd@sub x@Rh@sub 1-x@] Multilayers*, T. Lin,* *M.A. Tomaz,* Ohio University*; W.L. O'Brien,* University of Wisconsin, Madison*; T.K. Sham,* University of Western Ontario, Canada*; G. Retzlaff,* University of Wisconsin, Madison, US*; G.R. Harp,* Ohio University

Results are presented of the magnetic state of fcc Fe in [Fe/Pd@sub x@Rh@sub 1-x@ 10Å] superlattices with x = 0-100%. It was found that 10Å Fe layers have an fcc structure and undergo a magnetic phase transition from paramagnetic to ferromagnetic with increasing x. Its magnetic moment increases to a maximum near x=50%, and then decreases monotonically with increasing x. For thicker Fe layers, a similar behavior is observed, except that the magnetic phase transition can be suppressed. This behavior is explained in terms of small structural variations of the superlattices due to the different lattice constants of Pd and Rh. The sample structures are characterized using x-ray diffraction, and are characterized magnetically using magneto-optic Kerr effect magnetometry and x-ray magnetic circular dichroism.

MI-ThP3 Interface Alloying and Deterioration of the Magnetic Properties in Co/Cu(001)*, S. van Dijken, L.C. Jorritsma,* ***T. de Vries****, B. Poelsema,* University of Twente, The Netherlands

The initial growth of Co-films on Cu(001) and their magnetic properties are studied in a wide temperature range using helium diffraction (TEAS), high resolution low energy electron diffraction (SPA-LEED) and sensitive magneto-optical (SMOKE) measurements. TEAS shows that first an almost perfect bilayer is grown even at relatively low temperatures (250 K). Its microcopic origin is discussed. SPA-LEED data reveal a distinct anomaly in the temperature dependence of the island separation occurring at about 325 K, where the drastic decrease of the separation and a clear broadening of the separation distribution function is attibuted to an increased interface alloying. This morphological change coincides with a substantial decay of the Curie temperature, Tc, of a 2 ML thick Co film as detected with SMOKE measurements and compared to those found for films grown between 250 and 300 K. A lower Tc is also found for different reasons (film roughness!) at deposition temperatures below 225 K.

**MI-ThP4 Unique Photoelectron Spectrometers for Spin-Polarized Photoemission Studies*, G.D. Waddill,* *A. Jones, T.R. Cummins,* University of Missouri, Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory*; S.R. Mishra,* Virginia Commonwealth University*; D.P. Pappas,* National Institute of Standards and Technology*; R. Negri, E. Peterson,* Physical Electronics, Inc.*; R. Gunion,* ESG Consulting*; M. Hochstrasser, R.F. Willis,* Pennsylvania State University

The design and performance of two novel photoelectron spectrometers for elementally-specific spin-polarized measurements of magnetic surfaces and thin films are presented. Both instruments combine a large diameter hemispherical electron energy analyzer with a unique electron detection scheme that can be switched in situ between spin-dependent and spin-independent measurements. Spin-polarization is determined by use of a mini-Mott detector. Spin-independent measurements can be made using an energy dispersive multi-channel electron detection scheme. One instrument has a fixed angle between the incident photons and the detected photoelectrons, while use of a novel electron lens system enables this angle to be varied through a wide range for the second instrument. Both instruments are based at the Advanced Light Source (the fixed angle instrument at the Spectromicroscopy Facility, and the variable angle instrument at the Elliptically Polarized Undulator). Results of preliminary investigations of both magnetic and nonmagnetic materials using variants of magnetic x-ray linear and circular dichroism will be presented. The work at UMR and PSU was supported by the Department of Energy, Office of Basic Energy Sciences (DE-FG02-96ER45595). The work at LLNL was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. The Spectromicroscopy Facility, the Elliptically Polarized Undulator, and the Advanced Light Source were constructed and are operated with the support of the Department of Energy, Office of Basic Energy Sciences.

MI-ThP5 Minor Loops in a Bimodal Magneto-Optical Medium*, R.A. Fry,* *L.A. Bennett, E. Della Torre,* The George Washington University

Bimodal magnetic behavior was recently encountered in a (0.3nm Co/1.2nm Pt)@sub 15@ multilayer magnetic film with perpendicular magnetization by using an automated magneto-optical Kerr effect (MOKE) magnetometer.@footnote 1@ In the two separate magnetic transitions, differences in the ratio of the Kerr rotation to ellipticity were noted. To explain this behavior, it was postulated that there are two different magnetic entities (layers) in this material, each with a characteristic switching field, Kerr rotation, and Kerr ellipticity. To further investigate the magnetization behavior in this material, including magnetic exchange interactions between the two magnetic species, a series of minor loop experiments was performed. From the major loop data, two critical switching field values were observed, H@sub K1@ and H@sub K2@, where H@sub K1@ > H@sub K2@. H@sub K1@ is the smallest reversal field required to fully saturate the material, and H@sub K2@ is the field at which the observed step in the loop occurs. From the minor loops, a third critical field is identified as H@sub K3@. The observed magneto-optical behavior can be explained by defining two interacting magnetic entities, A and B, with intrinsic coercivities, H@sub A@ and H@sub B@. H@sub K1@ is the sum of H@sub A@ and the interaction field (H@sub i@); H@sub K2@ is the sum of H@sub B@ and H@sub i@; and, H@sub K3@ is the sum of -H@sub B@ and H@sub i@. The height of the minor loop is directly related to where on the major loop the reversal is initiated. By using minor loop MO measurements, the observed bimodal magnetization behavior was decomposed into two individual loops which are mutually interacting. From this decomposition, the intrinsic coercivities of the individual magnetic entities, as well as the interaction field between them, was obtained. This paper presents the experimental data and the excellent fit to this proposed model. We thank Dr. R.F.C. Farrow for providing these samples and N.I.S.T. for financial support. @FootnoteText@ @footnote 1@R.A. Fry, L.H. Bennett, E. Della Torre, R.D. Shull, W.F. Egelhoff, Jr., R.F.C. Farrow, and C.H. Lee, to be presented at Seventh International Conference on Magnetic Recording, (1998)

MI-ThP6 X-Ray Magnetic Linear Loops (XMLL)*, M.M. Schwickert,* Ohio University*; W.L. O'Brien,* University of Wisconsin, Madison*; G.R. Harp,* Ohio University

The x-ray magnetic linear dichroism (XMLD) in absorption relies upon the dichroic contrast of two perpendicular magnetization states. We introduce a novel variation to the conventional XMLD experiment which we term XMLL. We have observed the photoabsorption of linearly polarized light while rotating the magnetizaton vector M via an applied magnetic field with frequency w. Extracting the magnetic information from the absorption background leads to the x-ray magnetic linear loops (XMLL). The presented results were obtained by using linearly polarized synchrotron radiation at the L_3 absorption edge of Fe. In accordance with the M^2 dependence of the XMLD effect, we have found that the XMLL frequency spectrum is dominated by 2w, as opposed to possible w or 4w contributions. We applied this technique to Fe/Cr(001) multilayers that are antiferromagnetically exchange coupled. In low magnetic fields when the sample is in the spin-flop state the XMLLs are inverted as compared to ferromagnetic samples, such as Fe thin films. XMLL results for these samples are presented and we discuss applications of XMLL as a characterization tool especially suited to antiferromagnetic materials.

MI-ThP7 Nonlinear Magneto-Optical Kerr Effect in Co-Cu Nanogranular Films*, T.V. Misuryaev,* *E.A. Ganshina, S.V. Guschin, T.V. Murzina, O.A. Aktsipetrov,* Moscow State University, Russia

Magnetic nanostructures and surfaces of magnetic materials have attracted a lot of attention recently because of the observation of new magnetic effects which are not observed in the bulk materials. Apart from magnetic phenomena such as giant magnetoresistance and oscillatory coupling through nonmagnetic spacers magnetic nanostructures can reveal significant nonlinear-optical effects induced by magnetization, e.g. the giant nonlinear magneto-optical Kerr effect (NOMOKE). Magnetization induced optical second harmonic generation (MSHG) has been demonstrated to be effective, sensitive and versatile probe of macroscopic magnetic properties of surfaces and buried interfaces. In this paper both magneto-optical Kerr effect (MOKE) and NOMOKE are studied in granular films composed by nanocrystals of Co in Cu matrix. The samples of Co-Cu granular films were prepared by the co-deposition of Co and Cu on fused quartz substrate. The films thickness is about 200 nm. The mean size of Co nanocrystals is about 60 nm for the Co@sub 0.42@Cu@sub 0.58@ film measured by STM technique. The output of a Q-switched YAG:Nd@super +3@ laser at 1064 nm, with a pulse duration of 15 ns and an intensity of 2 MW/cm@super 2@ is used for the MSHG studies. MOKE spectra for Co@sub 0.42@Cu@sub 0.58@ film are measured in the energy range of 1.2-3.6 eV. The azimuthal anisotropy of the SHG intensity observed can be attributed to the existence of a polar axis in the structure of the Co-Cu granular films, which gives rise to a bulk electrodipole susceptibility. This polar structure can be caused by a predominant regular asymmetry of the filmvacuum interface during film processing. MSHG is studied in the polar, longitudinal and transversal NOMOKE configurations. The magneto-induced rotation the second harmonic (SH) wave polarization, the magneto-induced shift of the SH wave phase (the MSHG interferometry) and magneto-induced changes in the SHG intensity are measured. For all configurations, the NOMOKE parameters exceed the MOKE parameters at least by an order of magnitude. The interference in the far-field region of the SH fields generated by the interface and bulk nonmagnetic and magneto-induced contributions to the nonlinear polarization is suggested as a mechanism of the NOMOKE enhancement.

Manufacturing Science and Technology Group
Room Hall A - Session MS-ThP

Manufacturing Science and Technology Group Poster Session

MS-ThP1 Dynamic Simulation Based Learning Tools for Manufacturing Education and Training*, G.W. Rubloff,* *A.R. Rose, Y. Sankholkar,* University of Maryland*; D.E. Eckard,* North Carolina State University

A critical issue for the semiconductor manufacturing industry is the skill of the workforce at all technical job levels. The challenge of education and training is especially difficult because it is highly labor intensive and because the reality of actual hardware is very expensive and difficult to access for training purposes. We have constructed software learning tools as an avenue to dealing with both problems. They exploit physically-based dynamic simulation, so that the learner may "operate" sophisticated equipment, even break it, without adverse consequence but with the opportunity to understand how the equipment and process work. The simulators are accompanied by integrated tutorial, guidance, and reference material to support the learner in exploring phenomena, principles, and physical behavior of the system. As self-contained learning tools, disseminated as software or across the Internet, these learning modules provide the opportunity to learn when and where the student chooses. The software platform is constructed to relate guidance materials directly to simulator objects, to support experimentation and record-keeping, to permit learner-directed exploration in depth, through examples, and through exercises and self-tests, and to facilitate authoring of tutorial material and construction of physically-motivated simulators and error handling with minimal need for manufacturing practicioners to write software. Learning modules are demonstrated which convey vacuum and gas flow, heat transfer, chemical reaction, and other concepts and realizations relevant to semiconductor manufacturing equipment and process.

MS-ThP2 Surface Cleaning on Aluminum for UHV using Supercritical Fluid CO@sub 2@ including NaCl and H@sub 2@O as Impurities*, **T. Momose**, H. Yoshida,* Miyagi National College of Technology, Japan*; Z. Sherverni, T. Ebina, Y. Ikushima,* National Industrial Research Institute of Tohoku, Japan

Ozone treatment has been applied to several metals for UHV to improve outgassing rate. The surface of the ozone treated Al and superconducting Nb cavity @footnote 1@ showed the low adsorption characteristics and low density of hydroxide in the surface. These suggest that removal of the native oxide and the treatment without water can improve vacuum characteristics of the surface. Conventional surface treatments cause inhomogeneity and need water cleaning process. Therefore, we investigated the treatment with supercritical CO@sub 2@ because supercritical CO@sub 2@ can readily dissolve nonpolar compounds. Before the removal of surface oxide and ozone treatment, supercritical CO@sub 2@ was applied to the UHV material such as Al to clean the surface. A sample was a half piece of a swagelok cylinder (10.8 mm in diameter and 8.5 mm in length) cut along the axis with hard almite coating. CO@sub 2@ was supplied from a tank and charged into a syringe pump (HPB-350) via a cooler at about -10 °C. Liquefied CO@sub 2@ was transferred into a high pressure chamber made of stainless steel 316 cylinder with inner diameter of 50 mm, inner length of 50 mm and thickness of 20 mm. The surface analysis was carried out by XPS. The cleaned level was evaluated by the density (at%) of carbon (C) determined from the ratio of convoluted area of Al2p, O1s, and C1s peaks. The C density of untreated Al was 87 %. The C density of Al treated by supercritical CO@sub 2@ at 70 °C and 94 atm for 2 hours was 65 %. Furthermore, the C density of the surface treated by the addition of H@sub 2@O of 0.5 cc and NaCl of 0.05 g to supercritical CO@sub 2@ at 100 °C and 150 atm for 2 hours decreased to 13 %. The treatment with the same fluid showed no C density (13-25 %) dependence on pressure ranging from 100 to 250 atm. The treatment also showed the black surface which was locally oxidized with the aid of the contact potential with the chamber. Similar results were observed on the almite coating of the sample. @FootnoteText@ @Footnote 1@T. Momose. et. al., Vacuum, 47, No4, 319-324.

MS-ThP3 Design of Dynamic Simulation Experiments for Assessing Manufacturing Metrics*, **R.Z. Shi**, Z. Han, K. Moores, E. Li, Z. Chen, G.W. Rubloff,* University of Maryland

Evaluation of equipment and processes commonly focuses on raw process time, with equipment overhead contributions to cycle time playing a secondary and/or separate role in decision-making. This work is directed at equipment and process design while treating on an equal footing the contributions to cycle time which arise from raw process time and the cycle time elements associated with establishing process conditions and recovering from them after process completion. Design of experiments (DOE) methodology (using commercial ECHIP@super TM@ software) and dynamic simulation (using a previously designed simulator based on VisSim@super TM@ software) are employed to optimize a rapid thermal CVD polySi process. The RTCVD simulator captures the essential physics and chemistry of mass transport, heat transfer, and chemical kinetics of the RTCVD process as embodied in a specific equipment design. Various parameters for process recipe as well as for equipment design were first selected as possible factors for the response deposition rate and cycle time. A screening design was first carried out to choose those most significant factors, followed by more extensive experiments leading to the generation of response surface models, i.e., for deposition rate and cycle time. The results reveal different regimes of process and equipment design in which cycle time is primarily determined by raw process time, as well as regimes where equipment design is critical in its influence on overhead contributions to the total cycle time, e.g., for establishing reactor pressure initially, or for wafer cooldown. This work demonstrates that the combination of DOE methodology and dynamic simulation provides a powerful tool for examination and optimization of multiple figures of merit; these include more complex but critical metrics like the full cycle time, as well as more specific process measures such as steady-state deposition rates.

MS-ThP4 Fluid Simulation of Distributed Gas Injection for Aluminum and Photoresist Etch*, **D.F. Beale**, N. Williams,* Lam Research Corporation

The differences between two gas injection designs were studied via 3D fluid simulations. The two cases considered were a typical showerhead injected reactor with side pumping and a novel distributed injection reactor. In the novel design, gas entered the reaction chamber subsonically through a hexagonal array of cells. Each cell consisted of a circular gas inlet port with a concentric annular outlet port. Simulations of both designs were performed for a typical low pressure Aluminum etch and a high pressure photoresist (PR) strip. Plasma effects were not considered because the commercial fluid simulation used predicts Al etch trends well@footnote 1@ and because the stripper plasma was distant from the wafer. Peclet number values calculated from simulation output showed more diffusive transport in the novel geometry than in the standard one. This difference was important for the transport-limited etching of Al by Cl@sub 2@, but not for the interface-limited etching of PR by O@sub 2@. Differences between the two etch chemistries were further characterized via Reynolds numbers, Knudsen numbers and sticking coefficients calculated from simulation output. Axisymmetric 2D simulations of a showerhead-injected reactor and 3D simulations of a novel injection reactor with 19 inlet/outlet cells were performed. @FootnoteText@ @footnote 1@"Trends in aluminum etch rate uniformity in a commercial inductively coupled plasma etch system", JVST B 16(3), May/Jun 1998.

MS-ThP6 Reaction Products in a-C:H Film Growth by DC Glow Discharges in the Novillo Tokamak*, **R. Valencia**,* Instituto Nacional de Investigaciones Nucleares (ININ), México*; J. de la Rosa,* Instituto Politécnico Nacional, México*; E. Camps, R. López,* ININ, México

In this work we report the reaction products generated during the growth of a-C:H films by DC glow discharges in a toroidal chamber using a calibrated mixture of 5 % methane and 95 % hydrogen and at a total pressure of 5x10@super-2@ Torr. The products were analyzed using a differentially pumped mass spectrometer. The time evolution of the partial pressure recorded after initiation of the glow discharges indicates that the reaction products are generated by the plasma-wall interaction. During the initial phase of the experiment, a continuous increase of the peak m/e=28 and a decrease of those at m/e=18, 32, and 44 was seen to occur. We suppose that the 28peak is principally due to CO because in the case of a carbonized surface, part of the initially deposited C atoms can form CO with surface oxides and the residual water vapor. The decrease of the peaks 18, 32 and 44 are due to a molecular dissociation of H@sub 2@O, O@sub 2, CO@sub 2. The films were characterized by X-ray diffraction and scanning electron microscopy. The thickness and refractive index of the films were determined from the interference fringes of the transmission spectrum.

MS-ThP7 Physically-based Dynamic Simulation of a Tungsten CVD Cluster Tool*, J.N. Kidder, Jr., **N. Gupta**, G.W. Rubloff,* University of Maryland

Dynamic, physically-based simulation has proven effective in representing the time-dependent behavior of equipment, process, sensor and control systems. Here we extend previous work to address multichamber cluster tools and to include more complex pumping systems and models. Using a Windows-based simulation program, VisSim(tm) (Visual Solutions, Inc.), we have constructed and validated a system-level dynamic simulator for the Ulvac ERA-1000 tungsten CVD cluster tool at the Laboratory for Advanced Materials Processing, U. Maryland, in order to support research on chemical sensing, control, optimization, and fault management. The simulator reflects the time-dependent behavior of: the vacuum and gas handling components of the load lock, the buffer chamber, the process reactors, multi-stage gas pumping systems (e.g., mechanical and turbo pumps), and the gas delivery and exhaust systems; the process behavior in the reactor chambers; and the dynamics associated with process recipes. This enables the evaluation of dynamic process parameters (e.g., deposition rate, film thickness) as well as manufacturing parameters (e.g., cycle time), so that manufacturing figures of merit can be evaluated as a function of process and equipment design. Synchronous measurements of process variables and equipment state parameters provide experimental validation of the dynamic simulator.

MS-ThP8 Computer Simulation of Three-Dimensional Asymmetries in Inductively Coupled Plasma Reactors*, **T. Panagopoulos**, V. Midha, D.J. Economou,* University of Houston

MPRES-3D, a three-dimensional version of the Modular Plasma Reactor Simulator, has been developed to study azimuthal asymmetries of the etch rate introduced by gas injection and pumping ports, and by non-uniform power deposition profiles. The finite element method using higher order elements allows accurate representation of complicated reactor geometries. A 3-D Maxwell solver was also implemented to self-consistently account for azimuthal variations of the power deposition in the plasma. The chlorine plasma etching polysilicon was taken as a system for study. Gas inlets were found to introduce some local azimuthal asymmetries. In general, however, they did not contribute substantially to non-uniformities at the wafer level. The effect of pumping port(s) and non-uniform power absorption were more important since significant disturbances of all essential plasma species can be introduced. The implementation of a focus ring was found to yield practically azimuthally symmetric etching profiles. Overall, 3-D simulation tools are viewed as critically important for the design and optimization of upcoming 300 mm wafer plasma processing tools.

MS-ThP9 Ion Beam Deposition Systems for Highly Uniform Defect-free Coatings for Electronic Manufacturing Applications*, **A.V. Hayes**, H. Hegde, V. Kanarov, C.C. Fang, J. Wang, D. Kania,* Veeco Instruments, Inc.

Ion beam deposition (IBD) techniques are of increasing interest for use in the manufacturing of electronic devices. The most developed application is the production of high quality Extreme Ultraviolet (EUV) reticle masks.@footnote 1@ The IBD multilayer coatings generated by this work were very uniform, precisely deposited, and were lower in defects by several orders of magnitude compared to the best sputter deposited coatings. This has directly stimulated interest in extending the technique to the coating of advanced generation optical photomasks. On another front, recent advances have been made in the production of high quality Giant Magnetoresistive sensors using IBD methods. Such sensors are used in MRAM (Magnetic RAM) devices. In this work the ion beam deposition of low defect, uniform multilayer coatings with precisely controlled thickness, and of high quality magnetic films, is reviewed. This will be followed by a discussion of modeling and preliminary experimental data regarding extension of the technique for uniform coating of 300 mm substrates. @FootnoteText@ @footnote 1@S.P. Vernon, et al, Optical Society of America Trends in Optical Photronics, 4 (1996).

MS-ThP10 Estimation of the Ion Energy Distribution Function at Sputter Coils in PVD-IMP Systems*, **R. Veerasingam**, P. Gopalraja, E Kim, J.C. Forster,* Applied Materials, Inc.

Computer simulations were used to evaluate the ion energy distribution function (iedf) at the sputter coil of PVD-IMP systems. In the simulations, Ti/Ar and Ti/N2/Ar plasmas at 20 mTorr fill pressure were used to model the systems. The simulations revealed that in TiN systems, the plasma temperature and densities are lower compared to Ti systems. The existence of the excited states of nitrogen such as N* and N2*, provide an additional channel for electron energy dissipation rather than ionization and also lead to nitridization of surfaces. A TiN surface such as a nitridized sputter coil may have lower sputter yield compared to a pure Ti coil. By modifying the ion energy distribution function it is possible to enhance sputter yields from the coils. Control of the iedf at the coil surface provides a means to improve coil sputter and hence deposition uniformity. Experimental densities will be used to calculate the iedf. Results of the calculated plasma properties and iedfs will be presented.

Nanometer-scale Science and Technology Division
Room Hall A - Session NS-ThP

Nanometer-Scale Science and Technology Division Poster Session

NS-ThP1 A Low Temperature STM System for the Study of Quantum Electronic Systems@footnote 1@*, **J.A. Stroscio**, R.J. Celotta,* National Institute of Standards and Technology

We describe a new experimental system with the goal of providing new measurement capabilities for the study of quantum electronic systems. Several experimental challenges are posed in the study of electronic systems confined to nanoscale dimensions. The physical information desired in such systems includes: the quantized electron energy distributions arising from spatial or magnetic confinement, the spatial extent of electronic wavefunctions, the role of electron-electron interactions and electron interactions with the confining boundaries, the exact physical structure of the system, the shape of the confining potentials, and finally, the physics of the electron transport. To meet these measurement challenges, we have designed a scanning tunneling microscope (STM) that will operate in the temperature range from 2-150 K with the capability of applying magnetic fields up to 10 Tesla. Equally challenging to the measurement methodology is the fabrication of quantum electronic systems. The STM is part of a facility that includes separate MBE fabrication systems for III-V semiconductor growth and thin metal film growth with in-situ transfer of samples to the STM system. In addition to these traditional fabrication techniques we are developing an autonomous atom assembler to fabricate quantum structures atom-by-atom on a large scale. In this poster we will describe the design of the overall system, its components, and performance to date. @FootnoteText@ @footnote 1@ This work is supported in part by the Office of Naval Research.

NS-ThP2 Development of Low-Temperature Ultrahigh-Vacuum Atomic Force Microscope / Scanning Tunneling Microscope (LT-UHV-AFM/STM) Using Two-Stage Coil-Spring Suspension Isolator*, **N. Suehira**, K. Sugiyama, Y. Sugawara, S. Morita,* Osaka University, Japan

Recently, true atomic resolution imaging of The Noncontact Atomic Force Microscope (NC-AFM) was demonstrated, and the NC-AFM is expected as powerful tool to investigate the surface structure including insulators and the force acting on the surface. In such measurements, low temperature (LT) is one of the best environment, because it can reduce thermal noise in the force signal measured by using AFM cantilever and thermal drift between tip and surface. However, there is a few report on NC-AFM operating under low temperature and ultrahigh vacuum (UHV) condition. Here, we describe a new LT-NC-AFM/STM design. The most serious problem in the LT Scanning Probe Microscope (SPM) design is the vibration which influences the resolution of the images and the sensitivity of the signals such as tunneling current and the force. This is due to that, in the conventional LT-SPM design, the SPM body is mechanically connected with the bottom of the helium dewar, and hence the sufficient isolation of the various vibrations such as the building vibration, the acoustic noise and bubbling of the liquid nitrogen is difficult. In our design, such problem of the vibration is solved by using two stage coil-spring suspension isolation system with eddy current damper. Using a special designed gear mechanism, the SPM body is connected with the bottom of the helium dewar during cooling down, then it is mechanically isolated from the bottom of the helium dewar and suspended by the springs during measurement. The inertial translational mechanism is used for cryogenic coarse approach between tip and surface, because its compactness, rigidity and reliability. In the AFM measurement, the cantilever is scanned by the tube scanner, and its deflection can be detected by the fiber-optic interferometer inside the tube scanner. In the STM measurement, the tunneling tip is scanned instead of the AFM cantilever. Preliminary LT-STM imaging was demonstrated on Si(111)7x7 surface with atomic resolution and the LT-AFM measurement is under way.

NS-ThP3 Characterization of Various SiO@sub2@ by Scanning Capacitance Microscopy*, **G.H. Buh**, C.J. Kang,* Seoul National University, Korea*; K. Mang,* Samsung Electronics, Korea*; S. Lee, C.K. Kim, C. Im, Y. Kuk,* Seoul National University, Korea

Although electrical charge in SiO@sub2@ system can cause an adverse effect on the device performance, little is known about its spatially resolved characteristics. By using scanning capacitance microscopy (SCM), dynamics of spatially distributed trapped charge in a SiO@sub2@ film on Si can be imaged with spatial resolution of ~20nm, which is determined by tip diameter. As in the case of macroscopic capacitance-voltage (C-V), trapped charge results in VT shift. The VT shift can be measured from C-V curves at various positions with good spatial resolution. Experiments were carried out with various kinds of SiO@sub2@ processed by thermal oxidation (wet, dry), plasma enhanced chemical vapor deposition(PECVD), and atmospheric pressure chemical vapor deposition(APCVD). The VT measured on PECVD oxide was found to be lower than that of thermal oxide. This result indicates the existence of positive fixed charges in the PECVD oxide. On the contrary to the VT shift in a thermal oxide with induced traps, the shift was not observed even after 4MV/cm stress. It is believed the traps in PECVD oxide is nearly saturated.

NS-ThP4 Automated, High Precision Measurement of Critical Dimensions using the Atomic Force Microscope*, **D.A. Chernoff**, D.L. Burkhead,* Advanced Surface Microscopy, Inc.

Atomic Force Microscopes are used in many industries for research, engineering and process control. Until now, AFM operators have usually made dimensional measurements of sub-micron features by manually placing cursors on images or cross-section plots. Time constraints and operator fatigue limit the number of measurements. This in turn limits the extent of statistical analysis. We have developed a high accuracy measurement process which overcomes these limitations. 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. We use a specific data capture protocol and automated image analysis to measure the following parameters: track pitch@footnote 1,2,3@, bump height, bump width (at various threshold levels), bump length, and four sidewall slope angles. In a single 10x10 micron image of a DVD stamper, containing about 100 bumps, we tabulate about 1000 values. It is useful to pool the data from several images. In a plot of bump width vs. bump length, we see that width at half height increases from 315 nm for the shortest bumps (420 nm long) to about 380 nm for bumps longer than 1100 nm; this matches the increase seen for corresponding optical signals produced when a finished disc is played. Where sidewall angle deviates from the norm, we are able to review the image data to identify the specific nature of the defect. @FootnoteText@ @footnote 1@D.A. Chernoff, "Nano-metrology for the data storage industry", abstract of paper presented at AVS National Meeting 10/97, p.113 @footnote 2@US Patent # 5,644,512 and other patents pending @footnote 3@see also www.a1.com/asm

NS-ThP5 Use of Phase Imaging Tapping Mode AFM to Spatially Resolve Areas of Different Doping Densities on Patterned Si Wafers*, M.W. Nelson*, *P.G. Schroeder, R. Schlaf, B.A. Parkinson,* Colorado State University

The continuously shrinking dimensions of integrated circuits demand new methods for spatially resolved characterization of doping profiles in patterned semiconductor structures. Scanning probe microscopies offer the lateral resolution required to characterize structures down to atomic dimensions. Among these methods atomic force microscopy (AFM) has the advantage that the imaging process does not depend on the conductivity of the sample surface which offers easy characterization of oxidized samples in ambient conditions. In our experiments we demonstrate the use of tapping mode AFM (TMAFM) with additionally applied bias to spatially resolve areas of different doping densities and types on Si wafers. We observed changes in the phase contrast in regions of different doping densities as a function of the applied bias. Additional measurements on metallic substrates revealed that the cantilever phase and resonance frequency are strongly influenced by the bias induced Coulomb force between cantilever and sample. This allowed the discussion of the observed phase contrast variations in terms of semiconductor surface potential changes depending on the applied bias and the doping type of the various areas.

NS-ThP6 Metallic Adhesion at the Atomic Scale*, A. Schirmeisen*, *G. Cross, P. Grütter,* McGill University, Canada*; U. Dürig,* IBM Research Division, Switzerland

A unique AFM / STM / FIM system operating in UHV has been shown to measure directly force interactions of an atomically defined tip-sample junction. A W(111) tip, terminated by only three atoms, approaching an atomically flat Au(111) surface showed structural stability even upon touching the surface. The measured force distance curves reveal adhesion peaks of 5 nN and a contact stiffness of about 40 N/m. Moreover, there are no indications of a jump to contact. The yield strength of the junction (maximum contact pressure divided by the tip radius) reaches values of up to 25 GPa. The observed metallic short range adhesion forces show substantial contributions over an unexpectedly large distance range, which can not be explained within in the standard model for metallic adhesion by Ferrante and Smith.@footnote 1@ This study is being extended to different tip materials. First results of an Ir tip approaching a Au surface will be presented. Furthermore, to complement this study, MD simulations were performed at Tampere University by J. Nieminen. @FootnoteText@ @footnote 1@ J.H.Rose, J.R.Smith, J.Ferrante, Phys.Rev.B 28, 1835 (1983)

NS-ThP7 Tribological Properties of Crystalline Surfaces*, A.J. Gellman*, *J.S. Ko,* Carnegie Mellon University

Atomic scale influences on the macroscopic tribological properties of surfaces have been explored through studies of friction between single crystalline metallic surfaces prepared and characterized under ultra-high vacuum conditions. Our experiment allows two single crystalline surfaces to be brought into contact under an applied load and then sheared at constant velocity while measuring friction forces developed at the interface. The presentation will describe observations made using Cu(111) surfaces that have been modified by adsorption of atomic and molecular species. These studies show quite clearly that in order to observe lubricating effects between Cu(111) surfaces it is necessary to adsorb at least one complete monolayer of adsorbed species. A second set of measurements have explored the frictional properties of single grain quasicrystals. Quasicrystals nominally possess low friction surfaces, however, all prior measurements have made use of surfaces contaminated by exposure to air. Under vacuum conditions the Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal surfaces have been cleaned prior to making friction measurements. While these yield coefficients of friction for perfectly clean surfaces that are significantly lower than those observed with clean metal surfaces they are much higher than those measured with quasicrystals in air. Controlled oxidation of the Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal surfaces has been shown to lower friction coefficients but not to the point observed in air. While surface contamination must be responsible, at least in part, for the low friction measurements reported in the past, oxidation alone cannot account fully for the properties of these surfaces.

NS-ThP8 Frictional Force Microscopy Study of Discrete Surface Functional Group Assembled by Langmuir-Blodgett Technique*, M. Nakamura*, *A. Shimizu, Y. Nakayama, Y. Nagasawa,* Toray Research Center, Inc., Japan

Obtaining a flat surface which contains discrete functional groups with aimed density is doubtless valuable for nanometer science and technology. The functional groups can be used as nucleation sites for vacuum deposition or as adsorption sites for biomolecules. Furthermore, such a surface can be used as a test structure for scanning probe microscopy in terms of chemical identification. For this purpose, we have studied the Langmuir-Blodgett (LB) films formed with the mixture of stearic acid (SA) and stearyl mercaptan (SM) on atomically flat silicon substrates. The length of SM is approximately same as that of SA, but SM has a -SH group instead of a hydrophilic -COOH group. We therefore expect some part of the -SH groups in the bilayer film of the mixture to protrude from the surface. It was confirmed with atomic force microscopy (AFM) that flat and tight films were obtained with the mixtures which contain less than 10% of SM. Topographic and frictional force images showed that the surfaces contained number of protrusions exhibiting higher frictional force. The diameter of the higher friction spots was more than a few nanometer and varied with the AFM tip. Their density was nearly proportional to the concentration of SM. The distribution of the topographic height of these spots clearly exhibited two peaks around 1.6 and 2.6 Å, which can be explained by the models where the -SH shifts outward for one and two -(CH@sub 2@)- units of an alkyl chain. These results imply that the expected surface was successfully obtained. An interesting point is that the distribution of the maximum friction at these spots has only single peak in contrast to the height distribution.

NS-ThP9 Quantitave Surface Force Gradient Measurements Using Atomic Force Microscopy*, L.A.W. Sanderson*, *M.A. George, J.J. Weimer,* University of Alabama, Huntsville

The accepted theory that reconciles attractive and repulsive forces has become known as the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory and may be simply stated as V@sub S@ = V@sub C@ + V@sub A@ + V@sub R@ , where V@sub S@ is the total potential, V@sub C@ is the core repulsive potential due to Pauli exclusion, V@sub A@ is the Van der Waals attractive potential and V-@sub R@ is the double layer repulsive potential. The DLVO theory is widely regarded as a cornerstone for understanding colloidal systems and forces on the molecular scale. The objective of this study is to characterize the forces between two surfaces at the molecular scale using an atomic force microscope (AFM) and to relate the results quantitatively to parameters in DLVO theory. Investigations have been made using an AFM of surface forces present between a standard Si@sub 3@N@sub 4@ AFM tip and mica substrates for water, ethanol, and carbon tetrachloride. Results agree with those previously reported in the literature. Colloidal probes over mica and silica substrates are being used in on going research to provide easier geometries for comparison to the DLVO theory. Variations in surface forces as a function of pH and salt concentrations are being examined. The goal is to obtain a means of characterizing molecular scale forces over thin films such as aminopropyltriethoxysilane and polyethyleneglycol anchored to substrates. From a fundamental side, understanding of these forces is also important in analyzing the behavior of such molecules in solution, and the results can be used to select solutions for improving image resolution with the AFM.

NS-ThP10 The Durability of Optical Fiber Probe Tips for Surface Profilometry*, J.E. Griffith*, *R. Raghunathan, L.E. Plew, J.B. Bindell,* Bell Laboratories, Lucent Technologies*; J. Carlson, A. Berghaus, J.J. Plombon, C.E. Bryson,* Surface/Interface, Inc.

The performance of a surface profiler strongly depends on the shape of the stylus or probe tip. Changes in the shape of the probe, caused by erosion or contamination during scanning, can be especially troublesome. The durability of the stylus depends on its shape, its composition, the composition of the sample, and the force sensor employed. We use cylindrical, silica glass probes etched from a specially chosen optical fiber. The glass probes are used in conjunction with a balance beam force sensor with sensitivity of approximately 10 nN. These probe tips have been used for extended periods on samples ranging from photoresist to silicon nitride with very little change in their shape from either erosion or contamination.

NS-ThP11 Force Measurement of Optical Evanescent Field using Kelvin-Null Method, ***K. Sawada***, *M. Abe, Y. Sugawara, Y. Andoh, S. Morita,* Osaka University, Japan

We have measured an optical evanescent field using a noncontact mode atomic force microscope (AFM) combined with a frequency modulation detection method.@footnote 1@ Using a semiconductor AFM tip, the surface photo voltage (@delta@@phi@) is induced by the optical evanescent field. It causes the electrostatic force acting on the tip. This force (F) can be expressed by F=(V-@phi@)(@delta@C/@delta@z)@delta@@phi@. Here, V, @phi@, C, and z are the bias voltage, the contact potential difference, the capacitance and the distance between the tip and the sample, respectively. In this method, the electrostatic force is affected not only by the potential change @delta@@phi@ due to the evanescent field but also by the contact potential difference @phi@ between tip and sample which is not uniform on the surface. In this paper, we propose a novel method to detect only the variation of the surface photo voltage due to the optical evanescent field without the influence of the contact potential difference. Applying Kelvin-Null method,@footnote 2@ bias voltage V is controlled so that V-@phi@ is kept constant. Simultaneously, the incident beam is modulated at a frequency w, and the w component of the force gradient is measured which is proportional to the optical evanescent field. @FootnoteText@ @footnote 1@M. Abe, Y. Sugawara, Y. Hara, K. Sawada and S. Morita, Jpn. J. Appl.Phys. Vol. 37 (1998) pp. L167-L169 @footnote 2@M. Nonnenmacher, M. P. O'Boyle and H. K. Wickramasinghe, Appl. Phys. Lett. Vol. 58, No. 25, (1991) pp. 2921-2923

NS-ThP12 Tunneling and Photon Emission of Colloidal Particles, ***G.S. McCarty***, *C.D. Keating, P.S. Weiss, M.J. Natan,* Pennsylvania State University

Binding of molecules of interest to colloidal particles allows the optical properties of the molecules to be studied using techniques such as surface enhanced Raman spectroscopy. By binding these colloidal particles to a conducting surface the electronic properties of the molecules can be probed using scanning tunneling microscopy. We have imaged gold and silver colloids bound to Au[111] coated with 2-mercaptoethylamine. The particles were then studied using photon emission scanning tunneling microscopy to probe the electronic and optical properties of single particles.

NS-ThP13 Temperature Dependence of the Raman Scattering Spectra in Zn/ZnO Nanoparticles, ***J. Xu***, National University of Singapore, Repubic of Singapore; *W. Ji, Z.X. Shen, S.-H. Tang,* National University of Singapore, Republic of Singapore

By using the gas evaporation technique with induction heating method, Zn nanoparticles coated with ZnO were prepared in Ar. The Raman spectra of the Zn/ZnO nanoparticles have been studied over a wide range from room temperature through liquid nitrogen temperature and up to 873 K. Heating in air, we have, for the first time, successfully observed the transformations from the surface phonon mode to bulk vibrational mode in Zn/ZnO nanoparticles.

NS-ThP14 Electromagnetic Coupling Efficiency of a Metal Coated Optical Fiber Tip, ***L. Alvarez***, CICESE, Mexico; *M. Xiao,* UNAM, Mexico

The optical coupling of a metal coated optical fiber tip is calculated by using the direct moment method. The purpose of the calculation is to study the transmission efficiency of the near field probe tips widely used in the scanning near field optical microscopy. In the scanning near field optical microscopy, the near field probe is often made of tapped optical fiber tip which is coated with a metallic thin layer to form a subwavelength aperture at the very end of the tip. It is of great importance to study the transmission efficiency of the tip as functions of the size of the aperture, the thickness of the metal coat as well as the shape and optical characters of the fiber tip. One wants to know that for a given incident light, how much light would effectively contribute to the final readout of the microscope. In the literature in near field optics, the tip transmission was studied with various two dimensional simulations and with microscopic discretional theories. In the present work, a general three dimensional electromagnetic theory is however proposed. As examples, numerical results of the coupled electromagnetic waves as functions of the aperture size, the coat thickness and the materials properties of the fiber tip are presented for the simplified case where the incident light is assumed to be a plane wave, and the results are discussed with regards to the imaging of the scanning near field optical microscope. Finally, it is pointed out that the proposed model calculation would be useful to provide guidances for the manufacture of the probe tip in the scanning near field optical microscopy.

NS-ThP15 Annealing Atmosphere and Electron Irradiation Effects on Gold Nanocrystals Buried in MgO, ***A. Ueda***, *R. Mu, M.H. Wu, D.O. Henderson,* Fisk University; *R.M. Uribe,* Kent State University; *A.F. Hepp, E.M. Gordon,* NASA Lewis Research Center; *C.W. White, J. Budai, A. Meldrum, R.A. Zuhr,* Oak Ridge National Laboratory; *P. Wang,* University of Texas, El Paso

We have reported previously annealing effects on the surface plasmon (SP) of gold nanocrystals (NCs) formed by Au ion implantation in MgO. Annealing the samples after implantation promotes the diffusion of gold atoms, nucleation and growth of the NCs. The SP absorption for the Au/MgO system annealed in an oxidizing atmosphere (OA) is observed at ~560 nm, while annealing the same sample in a reducing atmosphere (RA) shifts the SP to ~524 nm. The process is entirely reversible. We propose that the SP shift originates from the creation of F@sub n@-centers when the samples are annealed in a RA, while they are annihilated in an OA. The F@sub n@ center acts as an e@super -@donor to the Au NCs that causes a blue shift of the SP. Subsequent annealing in an OA annihilates the F@sub n@ centers and the SP shifts back to 560 nm. TEM studies on Au NCs in MgO indicate the crystals are cubic and are aligned along the direction of the MgO lattice. Maxwell-Garnet effective medium theory was used to simulate the absorption spectra of the Au NCs formed in MgO under RA and OA. A good fit was obtained for sample annealed in an OA, but the fit for the annealed sample in a RA deviated from the experimental results. This is attributed to a change in the dielectric function of the Au NC that was caused by electron transfer from the F@sub n@ center. Electron beam irradiation of the Au/MgO samples was also investigated as an alternative method to study F@sub n@center creation and their interaction with the gold NCs. The optical spectra in the SP region are presented for the electron irradiated Au/MgO samples and are compared to those annealed in a reducing atmosphere.

NS-ThP18 The Shape Evolution of Patterned Submicron Structures under Thermal and Chemical Activation, ***K.C. Lin***, University of Maryland, College Park, U.S.A; *D. Kohn, K. Thuermer, J.E. Reutt-Robey, E.D. Williams,* University of Maryland, College Park

Lithographic techniques developed extensively for microelectronics applications provide new opportunities to design experiments to explore the nanoscale realm, where traditional continuum based descriptions of morphology are likely to fail. In particular, the preparation of defined surface patterns with crystalline subfeatures, e.g. facets and steps, allows physically-based studies of mass transfer processes in response to the changes of physical and chemical environments. We utilize electron beam lithography and lift-off techniques to pattern submicron lines, squares and dots of noble metals on silicon oxide and silicon substrates, and use STM and AFM to characterize their structure and evolution. These structures are chosen to mimic the microelectronic device contact lines and model heterogeneous catalysts. We find, for example, the surfaces of submicron Au lines, as prepared, exhibit a uniform surface texture consisting of 3-D islands of ca. 50 nm size. Thermal activation for 20 hrs at 200 ° C breaks the lines into grains with ~0.2 µm size. Structures with initial size less than 0.2 µm are thermally stable and develop crystalline features. The sensitivity of these features to the carbonaceous impurities introduced during fabrication are currently being tested with the aid of an in situ plasma.@footnote 1@ @FootnoteText@ @footnote 1@work supported by UMD, NSF-MRSEC

NS-ThP19 Processing and Characterization of Nanometer Sized Copper Sulfide Particles, *S. Seal,* ***L. Bracho***, *C. Urbanik, M. Hampton,* University of Central Florida; *J. Morgiel,* Polish Academy of Science, Poland

Nanomaterials, commonly characterized by their size smaller than 100 nm, have attracted a scant attention in the modern-day technology. These materials provide unique physical, mechanical and chemical properties in the nano-crystalline state. In this paper, sulfide nanoparticles of industrial interest are formed by sol-gel process using metal chloride precursors dissolved in a mixture of silica gel and organic cellulose network followed by a reaction with hydrogen sulfide gas. Particles are then heated in a vacuum oven. Variations in the sol-gel composition are used to study the particle growth rate and fractal density resulting from the reactivity of the large surface area nano particles. While scanning and transmission electron microscopy and x-ray diffraction are used to study their morphology and structure in the nanometer scale, x-ray photoelectron spectroscopy (XPS) is employed to understand the bonding chemistry and the stoichiometry of the sulfide particles. XPS results show a change in the binding energy of the sulfide particles with various temperature treatments. Secondary ion mass spectrometry is also used to show the distribution of precursor elements with depth, i.e. the chemical reactivity from surface to bulk. Nanometer sized gold particles are also produced using this method. The results from this study are expected to show promising applications and production of other oxides, sulfides and their compounds using this modified sol-gel synthesis.

NS-ThP20 Film Formation and the Onset of Multilayer Growth in Chloromethylphenylsilane Films as Determined by Atomic Force Microscopy, ***W.J. Dressick***, Naval Research Laboratory; *J.M. Calvert,* Shipley Co.; *M.-S. Chen, S.L. Brandow,* Naval Research Laboratory

Organosilane films containing benzyl chloride functional groups are of interest for use as imaging layers in high resolution lithography due to the extreme sensitivity of the carbon-chlorine bond to cleavage by either photon or electron radiation. For applications where feature sizes are on the nanometer scale it is important to have an understanding of the surface coverage and intermolecular order of these films. We have developed protocols for the reproducible deposition of two organosilanes, p-chloromethylphenyltrichlorosilane (CMPTS) and 1-(dimethylchlorosilyl)-2-(p,m-chloromethylphenyl)ethane (CMPEMS), on native oxide silicon and fused silica substrates. Film growth was characterized using several techniques including UV absorbance, ellipsometry, and contact angle measurements. Atomic force microscopy was found to be a powerful tool for monitoring the onset of oligomer formation in the CMPTS films, ultimately allowing the macroscopic properties of the films to be correlated with their nanometer scale morphologies. Results indicate that film growth which is limited to direct chemisorption at the surface results in low coverage, disordered films. In the CMPTS system multilayer growth was found to be a predominant pathway even at sub-monolayer coverages. The significance of these observations on the design of imaging layers capable of molecular scale resolution in nanolithographic applications is discussed.

NS-ThP21 Room Temperature Fabrication of Transparent ZrO@sub 2@/Polymer Nanocomposite Thin-Films with Controlled Thickness by the Ionic Self-Assembled Monolayer (ISAM) Method, ***A. Rosidian***, *Y. Liu, R. Claus,* Virginia Polytechnic Institute and State University

Nanocomposites of transparent multilayer structures of ZrO@sub 2@/polymer thin-films have been fabricated on silicon and quartz substrates utilizing the Ionic Self-Assembled Monolayer (ISAM) method. This method is based on the alternating adsorption of anionic and cationic polyelectrolytes in the aqueous forms. The deposition process was monitored by UV/Vis spectroscopy and ellipsometry. A linear behavior of both optical absorption and film thickness as the number of bilayers increases was observed, which indicated the formation of homogeneous and uniform thin-films on both substrates. The study also showed the control of film thickness by changing the ZrO@sub 2@ concentrations. It was observed that the thickness of each bilayer of the thin-films increased with the ZrO@sub 2@ concentration. For the films with ZrO@sub 2@ concentrations of 10 and 30 mg/ml, the thickness of each adsorbed bilayer were 18 and 24 Ångstroms, respectively.

NS-ThP22 Nanowire Formation Using a Resistively-Heated Piezoresistive Cantilever, ***T. Uchihashi***, *U. Ramsperger, H. Nejoh,* National Research Institute for Metals, Japan

The main aim of our research is to fabricate atomically thin metal wires on a clean sample surface in UHV, and to investigate the electronic transport properties of such systems. For that system, it is expected that new phenomena, e.g., single electron tunneling effect, quantization of conductance, will be observed, and that relation between a structure of the wire and transport properties will be clarified. The procedures required to reach this aim would be as follows. 1) Evaporate a defined electrode pattern on a clean sample using a through-hole mask in UHV. This pattern has macroscopic electrodes, on which the four-point-probe leads is pressed, and microscopic electrodes for which a gap distance is a few micrometers. 2) Draw atomically thin metal wires in the gap between the electrodes in UHV using a scanning tunneling microscope (STM) or an atomic force microscope (AFM). 3) Measure electronic transport properties of the wire in UHV, and at low temperatures if necessary. We succeeded in fabricating a through-hole mask using a discharge cutter machine and focused ion beam (FIB) machining. The discharge cutter machine is used for building the macroscopic pattern, and FIB for the microscopic structure of the through hole mask. Further we also succeeded in drawing thin gold wires with a width of a few tens of nanometer using an AFM cantilever. A piezoresistive cantilever (provided by Park Scientific Instruments) was first coated with gold by thermal evaporation. This cantilever can be heated up resistively with a power of about 30 mW by current running through it.@footnote 1@ The gold on the cantilever tip was transferred onto the surface of both a silicon and sapphire substrate. The minimum width of gold wires fabricated thus far is around 50nm. The fabrication method using a heated AFM cantilever can be applied not only to a conductive sample but also to a insulating sample like sapphire. This fact will eliminate the difficulty in measuring conductivity of ! ! ! nano-scale wire, especially at room temperature. @FootnoteText@ @footnote 1@ H. J. Mamin, Appl. Phys. Lett. 69, 433 (1996)

NS-ThP23 Adsorbate Effect on Conductance Quantization in Metallic Nanowires, ***C.Z. Li***, *H. Sha, M. Adam, N.J. Tao,* Florida International University

We have studied conductance quantization in metallic nanowires upon adsorption of molecules with different adsorption strengths. The conductance still changes in a stepwise fashion even in the presence of strong adsorption, and the average sharpness, length and number of the conductance steps remain unchanged. However, the step positions deviate significantly from the integer values of the conductance quantum, 2e2/h. While the deviation may be attributed to the scattering of the ballistic electrons by the adsorbates, evidence shows that the adsorbates also affect the conductance by changing the atomic configurations of the nanowires. @FootnoteText@ Financial support is acknowledged through grants from AFSOR (F49620-96-1-0346) and NIH (GM-08205).

NS-ThP24 Substrate Effects on Electronic Properties of Atomic Chains, ***T. Yamada***, MRJ, NASA Ames Research Center

Atomic chains, precise structures of adatoms created on an atomically regulated surface, are candidates for constituent elements in future electronics. It was predicted that Si chains were metallic and Mg chains were semiconducting, and a doping method was also discussed.@foot 1@ The substrate was assumed to work as a noninteracting template holding the adatoms. However, this scheme requires a low-temperature environment so that the adatoms will not displace from their ideal positions due to unwanted thermal agitation. For better structural stability, we may seek a scheme to allow the adatoms to form chemical bonding with the substrate atoms and secure their positions. The chemical bonding has two major effects on the chain electronic properties. First, only the remaining s and p orbitals in an adatom not used for the chemical bonding can decide chain band structures, rather than the full set of orbitals previously assumed.@foot 1@ Second, because of a possible HOMO energy difference between adatom and substrate atom, semiconducting chains are unintentionally doped. These effects are studied with a selfconsistent tight-binding method with universal parameters. With one adatom per unit cell, adatom chains are semiconducting (1) if adatoms are of group III and form one chemical bond per adatom, or (2) if adatoms are of group IV and form two chemical bonds. The previous result@foot 1@ of realizing semiconducting chains by group II adatoms without chemical bonds is consistent with this picture. When the HOMO energy in an adatom is shallower than that in a substrate atom, the entire chain is positively polarized, unintentionally achieving p-type doping. When deeper, the chain is negatively charged, achieving n-type doping. Specific examples will be discussed. @FootnoteText@ @footnote 1@T. Yamada, Y. Yamamoto, and W. A. Harrison, J. Vac. Sci. Technol. B 14, 1243 (1996); T. Yamada, to appear in J. Vac. Sci. Technol. A 16 (1998).

NS-ThP25 Designing New Materials at the Molecular Scale - An Example in Etching and Deposition, *J.A. Gurney,* McGill University, Canada; ***E.A. Rietman***, Bell Laboratories, Lucent Technologies; *M.A. Marcus,* KLA Instruments; *M.P. Andrews,* McGill University, Canada

We desire the ability to design molecular-scale components and new materials using a heuristic programming technique such as genetic algorithms. To this end we have been investigating the possibility of designing new materials in the space of cellular automata. Molecules interact, more or less, only with their nearest neighbors. This suggests that cellular automata (arrays of nearest neighbor interacting finite state machines) may be used for modeling the dynamics of molecules. Since it is well known that structures can be "grown" in the space of the cellular automata (CA) we conjecture that by manipulation of the rule table or rule vector describing the CA dynamics we can evolve desired structures in the CA space. To support this supposition we present work on modeling the etching and deposition (dissolution and growth) of crystals. We empirically find a mapping between the automaton rule table and the surface physics of the crystal. @FootnoteText@ @footnote 1@ J.A. Gurney, E.A. Rietman, M.A. Marcus, and M.P. Andrews, "Mapping the Rule Table of a 2-D Probabilistic Cellular Automaton to the Chemical Physics of Etching and Deposition", Submitted, 1998

NS-ThP26 Spectroscopic Studies of Carbon Nanotube by Ballistic Electron Projection Microscopy*, J.-Y. Park*, *S.-H. Kim, Y.D. Suh, W.-G. Park, Y. Kuk,* Seoul National University, Korea

Geometric and electronic properties of carbon nanotubes have been studied by ballistic electron projection microscopy(BEPM). An interference pattern between the scattered and transmitted e-beam was observed using coherent electron source from an atomically sharp emitter.@footnote 1@ In this work, a microcolumn in an SAFE(STM Aligned Field Emission) microcolumn system was replaced by carbon nanotubes or self-sustaining single crystal films on TEM grid.@footnote 2@ From images of single-walled carbon nanotubes, the performances of BEPM were tested. By adding an electrostatic energy analyzer, the electron energy loss of the nanotubes was measured. When the tip is positioned at < 2 nm, the tunneling I-V could be measured using BEPM. In addition to the nanotube, the results of free-standing single crystal metal and semiconductor will be presented. It was found that the Fourier transformation of inelastic scattering pattern gives information on scattering in the sample. @FootnoteText@ @footnote 1@H. -W. Fink, W. Stocker, H. Schmid, Phys. Rev. Lett. 65, 1204(1990). @footnote 2@J. -Y. Park et al., J. Vac. Sci. Technol. A 15, 1499(1997).

NS-ThP27 Synchrotron-Radiation-Induced Deposition of Nanocrystalline Particles*, R.A. Rosenberg*, *Q. Ma, B. Lai, D.C. Mancini,* Argonne National Laboratory

The high-intensity, high-energy x-rays produced by third-generation synchrotron radiation sources have made possible many new applications, such as deep x-ray lithography, that take advantage of the long penetration lengths of the x-rays in lower-Z materials. Recently, we have initiated a program to evaluate the prospects for using x-rays for materials processing by performing Surface Photochemistry Induced by X-ray Irradiation (SPIXI). X-rays have significant advantages over more conventional sources. The high energy x-rays produced by the Advanced Photon Source have deep penetration lengths for low-Z materials. Therefore, they can be used to induce chemical reactions on surfaces of solids immersed in liquids containing low-Z molecules. The most likely mechanism by which these reactions proceed is through the production of electrons caused by core-level excitation of the substrate atoms. Therefore, the reaction rate should be both energy dependent and site specific. If the liquid contains a metal salt, then x-ray irradiation should induce deposition of metallic films or particles that can be in either polycrystalline or nanocrystalline forms. We present preliminary results which demonstrate the feasibility of the SPIXI approach for deposition of nanocrystalline particles. In particular we have deposited both gold and silver nanoparticles in liquids containing salts of the appropriate ion. In addition thin films have been formed on Mo substrates. In this paper we discuss the experiments, their results and prospects for future development. 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

Plasma Science and Technology Division
Room Hall A - Session PS-ThP

Plasma Science and Technology Division Poster Session

PS-ThP1 Improvement on Lithography Pattern Profile by Plasma Treatment*, C.P. Soo,* National University of Singapore, Singapore*; M.H. Fan,* Chartered Semiconductor Manufacturing Ltd., Singapore*; A.J. Bourdillon,* National University of Singapore, Singapore*; L.H. Chan,* Chartered Semiconductor Manufacturing Ltd, Singapore, Republic of Singapore

Chemically amplified (CA) resist is designed to have high sensitivity towards KrF excimer laser stepper. Unavoidably, this brings about substrate-specific effect as well. A few years recently, there are publications reported that during investigation of resist pattern profile by cross-sectional SEM micrographs, positive CA resist on nitride wafers revealed ?footing?.@footnote 1@ Various kinds of postulation had been made for degradation of resist pattern profile at resist/substrate interface by substrate poisoning. Sturtevant et al.@footnote 2@ reported that the chemical contaminants of substrate degraded the resist patterns on nitride and other substrate. A. Usujima et al.@footnote 1@ reported that substrate treatment using oxygen plasma is extremely effective in improvement on resist footing problem. However, down-stream oxygen plasma treatment needed to be optimized as excessive plasma treatment gave adverse performance because of surface damage. In this study, further optimization on oxygen plasma treatment was done. Besides using oxygen plasma, N@sub 2@O plasma treatment, was experimented to obtain repeatable straight resist profile. Besides , the substrate-specific effect was discussed from the standpoint of chemical interference from nitride substrate. The contaminants on the nitride substrate was studied by XPS and GC mass-spectrometry. XPS and GC mass-spectrometry were also used to investigate the effect of various surface treatments. The performance of each kind of surface treatment was evaluated by looking at cross-sectional profiles. @FootnoteText@ @footnote 1@ A. Usujima, K. Tago, A. Oikawa, K. Nakagawa, "Effects of substrate treatment in positive chemically-amplified resist", Proc. SPIE, vol 2438, pp529-39, 1995 @footnote 2@ J. Sturtevant, S. Holmes, S. Knight, D. Poley, P. Rabidoux, L. Somerville, T. McDevitt, E. Valentine, W. Conley, A. Katnani, J. Fahey, "Substrate contamination effects in the processing of chemically amplified DUV photoresists", Proc. SPIE, vol 2197, pp770, 1994.

PS-ThP2 Tantalum Film for X-ray Lithography Mask Deposited by Electron Cyclotron Resonance Plasma Source Coupled with Divided Microwaves*, H. Nishimura*, *T. Ono, M. Oda, S. Matsuo,* NTT System Electronics Laboratories, Japan

An advanced ECR plasma source by which a conductive film can be stably formed has been developed and applied to Ta film formation.@footnote 1@ We investigate the applicability of ECR-Ta as absorbers of x-ray masks. It is found from TEM observation that an ECR-Ta film is a polycrystal film that has a large grain size of (>0.5 µm) and a dense microstructure. The x-ray absorber material must satisfy several conditions, such as low, uniform, and stable stress. The stress change of ECR-Ta film is rarely observed not only in the air but also under the SR irradiation condition. In order to control film stress, we have investigated the stress-depth distribution. The stress is analyzed to be a sum of an interfacial stress (retained near the film-substrate interface) and a bulk stress (retained in the film bulk). These individual stresses can be independently controlled. The interfacial stress depends on the substrate temperature, working-gas pressure, and deposition rate. The bulk stress varies toward compressive by adding Ar to the sputtering gas (Xe). A low stress film with no stress-depth distribution (15 MPa at 200-400 nm) is obtained by optimizing deposition parameters. A highly accurate x ray mask is achieved by using an ECR-Ta film. These results show that the dense microstructure including the grain boundary rather than the film structure (polycrystal or amorphous) is important for a highly accurate x-ray mask. The ECR sputter method is suitable for depositing dense microstructure film because of the enhancement of film formation reaction on the surface by low energy (10-30 eV) ion irradiation. @FootnoteText@ @footnote 1@ H. Nishimura, et al., J. Vac. Sci. Technol. A15 (19 97) 707.

PS-ThP3 Control of Ion Energy Distribution at Substrates During Plasma Processing*, S.B. Wang*, *A.E. Wendt,* University of Wisconsin, Madison

It is well-known that ion bombardment of the substrate is one factor that makes plasma processing indispensable in semiconductor fabrication. In an effort to understanding the factors governing selectivity in oxide etch processes, we examine the energy of ion bombarding the substrate. We start with a design study for an experimental system producing a narrow distribution of ion energies at the substrate. With fine control over the energy of the nearly monoenergetic ions, we can elucidate the effect of ion energy on selectivity. The ion energy distribution reaching the substrate has been investigated by a self-consistent spherical shell plasma model. The results show that the broadening of ion energy distribution depends on the area ratio of substrate to grounded wall which is varied by changing the radii of the two spherical shell electrodes. As the area ratio increases, the plasma potential is more strongly modulated by the rf potential on the powered electrode. Therefore, the ion energy, which is proportional to the difference between plasma potential and substrate potential, becomes narrower with increasing area ratio. This result suggests differences in processing performance between tools with similar plasma conditions but different effective grounded wall areas, such as ECR and inductively coupled plasmas. In addition, we show that the ion energy distribution can be controlled by modulation of the voltage waveform applied to the substrate electrode. In the simulation, the broadening shrinks as low as ~2T@sub e@(T@sub e@ is electron temperature in Volts) as compared to 20T@sub e@ or greater for a sinusoidal voltage waveform. In addition, the shape of the energy distribution is single peak rather than a saddle. This is a good tool for threshold energy studies. Based on these results, we have designed a system for experimental study of ion energy thresholds for selective etching. Experiments in ion energy control and selectivity improvement in experiment are currently underway. This work supported by NSF Grant #EEC8721545

PS-ThP4 Simulations of Electronegative Discharge Sheaths@footnote 1@*,* *S.K. Kanakasabapathy*, *J.L. Kleber, L.J. Overzet,* University of Texas, Dallas

Measuring negative ion concentrations in discharges continues to be difficult. Negative ions do not easily escape the glow center and as a consequence are more difficult to probe than electrons or positive ions. When the negative ion concentration becomes a large enough fraction of the total negative charge, however, the plasma kinetics can become dominated by the ions, and the electrons can become relatively insignificant. This kind of plasma is sometimes referred to as an "ion-ion plasma." We have developed a one-dimensional, time dependent, fluid model (SHEATHSIM) to simulate the behavior of ions and electrons near RF biased electrodes, double probes and a novel four point probe in just such electronegative plasmas. In each sheath, the ion momentum conservation and continuity equations, closed by Poisson's equation are solved for a given set of bulk densities, temperatures and mean free path lengths. The set of equations for two such sheaths are closed by a common bulk potential and current continuity. Such modeling helps us to understand the measurements we are making of highly electronegative "ion-ion" discharges. In this poster, we will present the results from our simulation as compared to measurements made in SF@sub 6@ and Cl@sub 2@ discharges. @FootnoteText@ @footnote 1@ This material is based upon work supported by the National Science Foundation under Grant No. CTS-9713262 and by the State of Texas Advanced Research Program under Grant No. 009741-043.

PS-ThP5 Negative Ions in Inductively Coupled Plasmas@footnote 1@*, J.L. Kleber*, *L.J. Overzet,* University of Texas, Dallas

The effects of negative ions on continuous wave and pulsed low pressure inductively coupled plasmas (ICP's) are being investigated using a Langmuir probe and a microwave interferometer. The sheath resistance (R@sub sh@) can cause the plasma potential to rise when a Langmuir probe in the plasma is biased above floating potential.@footnote 2@ This can lead to errors in calculating plasma parameters such as electron density (n@sub e@), electron temperature, and the electron energy probability function (EEPF). We have measured R@sub sh@ for continuous wave ICP's in the Gaseous Electronics Conference (GEC) reactor in argon and nitrogen and will measure it in a mixture of argon and chlorine all at or under 50 mTorr. We found that R@sub sh@ had a power law dependence on n@sub e@ and will demonstrate how this arises. We have also investigated the spatial and temporal behavior of plasma parameters in pulsed pure argon ICP's and will investigate them in a mixture of argon and chlorine. We focus on the afterglow when it is possible for the negative ions to influence more the chemistry of the plasma as the electron density decays. @FootnoteText@ @footnote 1@This material is based upon work supported by a National Science Foundation under a Graduate Research Fellowship and Grant No. CTS-9713262 and by the State of Texas Advanced Research Program under Grant No. 009741-043. @footnote 2@M. B. Hopkins, J. Res. NIST 100, 415-425 (1995)

PS-ThP6 Time Resolved Electrostatic Probe Measurements of Electron Temperature and Plasma Density Radial Profiles in a Pulsed ICP Plasma*, X.M. Tang*, *D.M. Manos,* College of William and Mary

This paper reports results of a study of a pulsed 13.6 MHz ICP plasma which has been configured for multiple purposes, including etch, cleaning, and deposition. The pulse-packet frequency can be varied over a wide range. For these studies it was varied from 50Hz to 10kHz to create plasmas in a variety of gas mixtures including oxygen, carbon tetrafluoride, and argon. The plasma is characterized using a variety of methods, including electrostatic probes and optical emission. Probe data were analyzed using nonlinear regression methods and equivalent resistance methods. The comparative advantages of each will be discussed. The agreement between the methods is good. Spatially resolved measurements of the time-dependent electron density and temperature, taken on the time scale of the power modulation, are presented as a function of rf power, frequency, duty cycle, and gas composition. These results confirm, among other things, that the modulated plasma density is higher than the plasma density resulting from CW operation at the same average power. High-temperature transients at the pulse onset do not appear at high frequencies. Comparisons with similar prior studies and with simulated plasma models will also be presented.

PS-ThP7 Electron and Negative Ion Density in BCl@sub 3@ / Cl@sub 2@ / Ar Gas Mixtures*, G.A. Hebner*, *M.G. Blain,* Sandia National Laboratories*; T.W. Hamilton,* Sandia National Laboratories, U. S. A*; C.A. Nichols, R.L. Jarecki,* Sandia National Laboratories

Electron and negative ion density have been measured in a modified Applied Materials DPS chamber using gas mixtures of BCl@sub 3@, Cl@sub 2@ and Ar. Measurements were performed for four different substrate types to examine the influence of surface material on the bulk plasma properties; aluminum, alumina, photoresist and Aluminum / PR. The plasma conditions of source power, bias power, pressure, Cl@sub 2@ / BCl@sub 3@ ratio, total flow rate and argon addition were varied over a wide operational parameter space. Electron densities in the Cl@sub 2@ / BCl@sub 3@ mixtures varied between 0.5 and 8.0 x 10@super 12@ cm@super -2@ or approximately 0.25 to 4 x 10@super 11@ cm@super -3@. Photodetachment measurements of the negative ion density indicate that the negative ion density is smaller than the electron density. In general, we noted that photoresist had a major influence on the electron and negative ion density. In most cases, the electron density above wafers with PR was a factor of two lower while the negative ion density was a factor of two higher than the aluminum or alumina surfaces. The trends observed in the DPS chamber were similar to trends observed in the previous measurements in the GEC rf reference cells at Sandia. The only exception was the pressure dependence of the electron and negative ion density. This difference in the two systems is likely related to the different coil configuration and geometry of the two chambers. This work was performed at Sandia National Laboratories and supported by SEMATECH, Applied Materials, and the United States Department of Energy (DE-AC04-94AL85000).

PS-ThP8 Rare Gas Dilution of Fluorocarbon Plasmas: Te Measurements using TRG-OES and Processing Implications*, H.L. Maynard*, Bell Laboratories, Lucent Technologies*; M.V. Malyshev,* Bell Laboratories (Also at Princeton University)*; W.W. Tai, V.M. Donnelly,* Bell Laboratories, Lucent Technologies

In the etching of sub-250 nm oxide contacts and vias with high-densityplasmas, rare gas dilution of the fluorocarbon etchant gas has several benefits, including the suppression of etch stop. The addition of a small amount of Ar to a C@sub 2@F@sub 6@ plasma in an Applied Materials' High Density Plasma etcher increases the oxide etching rate (as measured in features > 350 nm). Further addition of Ar does not decrease the oxide etching rate until the diluent concentration exceeds ~80%. For Ar dilution between 20-80%, sufficient fluoropolymer deposits on the oxide surface to provide reactant, and the energy required to drive the etching reaction can apparently be provided equally well by either an Ar or a CF@sub x@ ion. For [Ar] > 80%, insufficient fluoropolymer is deposited to provide sufficient reactant for the oxide etching or to protect the photoresist. For relatively dilute mixtures (50 < [Ar]

PS-ThP9 Molecular Dynamics Simulation of Cu and Ar Ion Sputtering of Cu Surfaces@footnote 1@*, J.D. Kress*, *D.E. Hanson, A.F. Voter,* Los Alamos National Laboratory*; C.-L. Liu, D.G. Coronell,* Motorola

In ionized physical vapor deposition (PVD) used in Cu interconnect technology, the interaction of energetic ions with the growing Cu substrate is not well characterized by a constant sticking probability independent of ion impact angle or energy. Such detailed information, not known experimentally, is necessary input for realistic feature scale modeling of step coverage in the metallization of vias and trenches in integrated circuits. Here we describe the results of molecular dynamics (MD) simulations of sputtering of Cu (111) and (100) surfaces by Cu and Ar ions suitable for incorporation into feature scale simulations. For the interatomic potentials, the many-body embedded atom method for Cu-Cu and a Ziegler-Biersack-Littmark pair potential for Ar-Cu were used. For each impact angle and energy (10 to 100 eV for Cu ion and 50 to 175 eV for Ar ion), a series of 150 impact events were run with an initial surface temperature of 300 K. At the end of each series, the average sputter yield (number of Cu atoms sputtered per impact), sticking probability, reflection angle and energy, and sputtered angle and energy were calculated as a function of impact energy and angle. For Cu and Ar ion impact energies below 50 eV or angles of incidence of 70 degrees or greater, the sputter yield is essentially zero. For Cu ion impact angles of 20 degrees or less, the sticking probability is essentially unity for all impact energies studied.

@FootnoteText@ @footnote 1@Supported in part by US Department of Energy Cooperative Research and Development Agreements (CRADAs).

PS-ThP10 Monte-Carlo Simulation of Atomic Scale InP Surface Etching, *L. Houlet, **A. Rhallabi**, G. Turban,* Institut des Materiaux de Nantes, France

Monte-Carlo method has been applied to simulate CH@sub 4@-H@sub 2@ Reactive Ion Etching (RIE) process for an atomic scale InP Surface. Two neutral precursor types and one ion type have been considered in the surface etching process.CH@sub 3@ and H adsorbed precursors are assumed to be bonded to the surface substrate leading to the desorption of the indium and phosphorous sites respectively, while the energetic ions allow the sputtering of the In(CH@sub 3@)@sub x@ and P(H)@sub x@ (0@<=@x@<=@3). XPS analyses show that the ion bombardment gives rise to an amorphous surface. Consequently, the initial InP material was represented by the stoichiometric indium and hydrogen sites which were randomly placed in the 3D discrete network. The model takes account of precursor and site identities, ion preferential sputtering, isotropic transport of neutrals to the surface, adsorption, migration, reaction or desorption of neutrals as well as the independent choice of binding energies between each neutral and site type. The surface migration process is based on the empirical bond-breaking model which is used to determine the amount of energy which must be supplied for a physisorbed precursor to move from one site to another. This process depends on the substrate temperature and the bonded energies for each site type. By setting the available experimental data, the simulation results confirm the surface phosphorous depletion which was observed by XPS analyses. The increase in RMS roughness, the etching rate and neutral surface coverage is obtained when the atomic hydrogen ion flux ratio increases.

PS-ThP11 Analysis of Fast Neutrals in Plasma Monitoring, ***J. Wei**, R.E. Pedder,* ABB Extrel

Fast neutrals are generated in plasma and high energy ion sputtering processes. The kinetic energy of the fast moving molecules can be as high as a few hundred electron volts. The analysis of these fast neutrals with a regular residual gas analyzer has been shown to be very difficult in many cases. The first problem in the analysis is the decrease in the number of ions from the ionizer as the kinetic energy of the fast neutrals increases. The second problem is the loss of ion transmission through the quadrupole mass filter with the high energy ions from the fast neutrals. The combination of these problems often translates into distorted peak shapes in the mass spectrum and very low sensitivity for the fast neutrals. We will present the results on the analysis of fast moving neutrals with a quadrupole mass spectrometer. This quadrupole mass spectrometer is equipped with a biasable quadrupole mass filter assembly and an ion energy analyzer. With this setup, we can either slow down all the ions through a bias potential on the mass filter assembly or select only the ions at a given kinetic energy range and then slow them down to an optimum kinetic energy when they travel into the quadrupole mass filter. This bias potential on the quadrupole mass filter assembly minimizes the ion transmission loss through the quadrupole and restores the sensitivity for the detection of the fast neutrals. Furthermore, when the kinetic energy of the fast neutrals are a couple of electron volts or higher, we can use the energy analyzer to distinguish the fast neutrals from the same gas components or components with identical mass in the residual gas background.

PS-ThP12 The Application of Helicon Antennas as a Secondary Plasma Source for Ionized PVD, ***D.B. Hayden**, D.N. Ruzic, D.R. Juliano, M.M.C. Allain,* University of Illinois, Urbana

Ionized PVD may extend the usefulness of PVD for several generations by allowing the directional fill of higher aspect-ratio features. Previous work typically has used an inductively coupled plasma (ICP) coil of various designs to drive a high-density plasma in between the sputter target and substrate. A different approach using a helicon antenna to drive the high-density plasma instead is discussed. Helicon-produced plasmas are renowned for their high coupling efficiency given modest input powers. This remotely located source (external to the sputter chamber) has distinct advantages over an immersed ICP coil by eliminating shadowing and flaking problems. Helicon plasmas also have higher maximum achievable densities, thus yielding a higher ionization fraction than ICP coil-driven plasmas. Data for one external source (with various antennas including the helical and Nagoya type III) are shown. The surrounding electromagnets needed for igniting and sustaining the helicon plasma are variable up to 1.5 kG. Pressures investigated are 5-50 mTorr. The effects of multiple antennas surrounding the chamber, which would improve uniformity and density considerably, are discussed.

PS-ThP13 CF@sub 2@, CF Radical Behaviors in a Magnetized Inductively Coupled Plasma and the Correlation with Oxide Etch Characteristics, ***J.H. Kim**, H.J. Lee, K.W. Whang,* Seoul National University, South Korea*; J.H. Joo,* Kunsan National University, South Korea

Fluorine-based plasma has been used to etch SiO@sub 2@ layer in LSI circuit fabrications, and the low-pressure high-density plasma sources are being studied for ultra-fine structure fabrication. It has been known that the high density plasma has low etch selectivity over Si, but recent studies show that the highly selective SiO@sub 2@ etching is possible in the restricted area. However, the etching mechanism was not revealed clearly until now. A key parameter governing the selectivity is believed to be the ratio of (CF@sub x@) density to fluorine atom density and of radical density to ion density. Here, we report the CF@sub 2@ and CF radical behaviors based on appearance mass spectrometry(AMS), actinometry and laser induced fluorescence(LIF), along with the correlation between other species and the etch characteristics in the magnetized inductively coupled plasma which was reported for the highly selective SiO@sub 2@ etching. A 13.56MHz RF power up to 2.5kW was coupled to the 4 turn antenna and generated a CF@sub 4@ or C@sub 4@F@sub 8@ plasma at the operating pressure of 1-10mTorr. The CF@sub 2@ radical increased with the operating pressure and decreased with the main RF power, which were well coincident with the global model simulation. But the rates of increase were somewhat different according to the diagnostics tools. The increase rate measured with AMS was about 1.5 times greater than those measured with LIF or actinometry. This was caused by the plasma perturbation in using the AMS technique, the quartz contamination while LIF or actinometry and so on. We will discuss the CF@sub 2@ and CF radical behaviors with the various plasma process parameters and their correlation between other species and etch characteristics. Especially, we will present the effect of bias power on the plasma chemistry near the substrate.

PS-ThP14 Determination of Gas Phase Species Concentrations in High Density Plasmas for Dielectric Deposition, ***M.L. Jezl**, R.C. Woods,* University of Wisconsin, Madison

Simultaneous application of various gas-phase spectroscopic techniques are used in order to determine the species present in a 2.45 GHz electron cyclotron resonance (ECR) reactor. The plasmas investigated are primarily silicon dioxide and fluorinated silicon dioxide deposition plasmas (SiH@sub 4@/SiF@sub 4@/TEOS + O@sub 2@). For these plasmas we are able to determine absolute concentrations of many of the important species present, while relative concentrations can be determined for many more. Among the techniques utilized are microwave spectroscopy (which can detect species densities as low as 10@super 9@ cm@super -3@), Fourier transform infrared (FTIR) spectroscopy, and silicon atomic absorption spectroscopy. Microwave and FTIR spectroscopy have demonstrated their ability to detect highly complimentary subsets of detectable molecular species. This has greatly expanded the range of species that can be monitored concurrently. In addition to determining absolute and relative concentrations of gas-phase species, we attempt to correlate the observed trends of their concentrations with the resulting film properties such as thickness, refractive index, infrared absorption, and wet etch rate. Molecules monitored include CO, CO@sub 2@, H@sub 2@O, HF, SiH@sub 4@, SiF@sub 4@, SiF@sub 2@, TEOS, H@sub2@CO, C@sub 2@H@sub 5@OH, and other TEOS decomposition products. @FootnoteText@ This work was supported by the NSF under Grant no. EEC-8721545.

PS-ThP15 Characterization of the Reactive Species in a Helium/Oxygen Atmospheric-Pressure Plasma Jet, ***J.Y. Jeong**, S.E. Babayan, A. Schuetze,* University of California, Los Angeles*; J. Park, I. Henins,* Los Alamos National Laboratory*; R.F. Hicks,* University of California, Los Angeles*; G.S. Selwyn,* Los Alamos National Laboratory

An atmospheric-pressure plasma jet has been developed. The jet etches organic polymer films with an He/O@sub 2@ gas feed. In addition, silicon, silicon dioxide, and metal films have been etched with an He/CF@sub 4@/O@sub 2@ gas mixture. The reactive species in the plasma jet effluent and their chemistry have been investigated by optical and infrared emission spectroscopy, chemical titration, and numerical modeling. An ozone density of 10@super 14@-10@super 16@ was measured by UV absorption and the oxygen atom concentration is believed to be of same order of magnitude. The charged particle flux, monitored with a Langmuir probe, has been found to be around 10@super 14@ cm@super -2@ s@super -1@ in the effluent. With regard to kapton etching, it appears that oxygen atoms and possibly metastable oxygen molecules are the key reactive intermediates in this process. At the meeting, the chemistry of the plasma jet will be compared to conventional low-pressure plasma discharges.

Surface Science Division
Room Hall A - Session SS-ThP
Surface Science Division Poster Session

SS-ThP1 Photon-Induced Localization and Correlation Effects in Optically Absorbing Materials*, **D.E. Aspnes**,* North Carolina State University*; L. Mantese,* University of Texas, Austin*; K.A. Bell,* North Carolina State University*; U. Rossow,* Technical University of Ilmenau, Germany

Surface-optical data that contain structures related to energy derivatives of bulk critical points show that photons themselves modify the optical properties of the material being measured, and therefore, that the standard picture of optical absorption must be revised. Using a simple model that retains correlations discarded in the random phase approximation yet can be solved analytically to first order in time-dependent perturbation theory, we show that (1) the final electron and hole states are localized near the surface by the finite penetration depth of the photons but (2) these final-state packets also evolve by propagation with their respective group velocities. More important, since the energy of a wave function is the expectation value of the Hamiltonian, for finite packets the surface contribution to the energy and lifetime is also finite, thereby providing a natural explanation to derivative structures and to apparent differences in nominally bulk critical point energies and broadening parameters with surface preparation. Further, we show that (3) broadening must be described by a sinc function as in standard filter theory, instead of the traditional phenomenological broadening parameter. The implications are extensive. For example, these results show that (4) slab calculations of surface electronic properties, where limited spatial extent is an unwelcome consequence of limited computing power, may actually provide a more accurate representation of surface optical spectra than hypothetical calculations that take the entire bulk into account.

SS-ThP2 Study of Aluminum Deposition on GaN (0001)@footnote 1@*, **H. Cruguel**, Y. Yang, S.H. Xu, G.J. Lapeyre,* Montana State University*; J.F. Schetzina,* North Carolina State University

GaN has attracted much attention because of its great importance in fabricating light emitting diodes (LED), detectors and laser devices which operate in the green, blue and ultraviolet range. The vapor (in situ) deposition of Al on wurzite n-GaN(0001) clean surface is investigated with high-resolution photoemission. The samples grown at North Carolina State University were successfully clean by several techniques and measured at the Wisconsin Synchrotron Radiation Center (SRC).We have measured both Al 2p and Ga 3d photoemission level for different coverage of Al on GaN. With the Voigt line fitting of Al 2p we found two components, in addition to the metallic component, for all the deposition. The behavior is attributed to the formation of both AlGa@sub x@N@sub 1-x@ and AlN compounds on the GaN surface. The explanation is in agreement with the line fitting of Ga 3d level which also shows three components (bulk GaN, AlGa@sub x@N@sub 1-x@ and metallic). When we anneal the sample after the Al deposition the metallic peak disappears but the intensity of the two other components of the Al line and the components in the Ga line associate with AlGa@sub x@N@sub 1-x@ are still increasing. This means that the reaction still occurs and that the thickness of the two compounds increases. In addition we have deposited Mg on the sample to determine which compound is nearest the surface. We found that a metallic peak is only observed in Al 2p spectra. The results suggest that the sequence of materials is AlN on top, following by AlGa@sub x@N@sub 1-x@ and then GaN. The interpretation of the data will be presented. @FootnoteText@ @Footnote 1@ Research supported by ONR/DEPSCOR grant, SRC supported by NSF.

SS-ThP3 Adsorption Site of Mg on GaN(0001) from Photoelectron Holography Imaging*, S.H. Xu, H. Cruguel, Y. Yang,* Montana State University*; J.F. Scheitzina,* North Carolina State University*; **G.J. Lapeyre**,* Montana State University

The adsorption sites of Mg on GaN(0001) with and without predosed atomic hydrogen have been determined by the small-cone photoelectron holographic imaging(PHI) technique.@footnote 1@ The experiments were performed at the Iowa/Montana State University beamline at Synchrotron Radiation Center(SRC) in Madison. The diffraction data is directly inverted without the need for models to observe the local site of the Mg emitter. The GaN samples were grown with the MOCVD method. In the analysis chamber the samples were cleaned by several heatings at about 850 °C, and the sample showed a good 1x1 LEED net. After dosing with atomic hydrogen followed by deposition of 0.5 ML Mg, the 1x1 LEED net is still observed but with a higher background. A set of 82 emission spectra by photon energy scans at the constant initial energy(CIS) of the Mg 2p level were measured. The angles for the set of CIS span a grid over one-sixth of the emission hemisphere(the surface irreducible symmetry element). The PHI images show that the adsorption sites in each case is different. With H interlayer, Mg adsorbs in a three fold site with an atom directly below the Mg emitter, usually called the T4 site. The adsorption height is about 1.4 Å above the Ga adlayer. Without the H interlayer, Mg likes to replace the Ga atoms in adlayer. The observations suggested that the H interlayer plays a key role in preventing Mg from diffusion into GaN bulk by not interchanging with the Ga atoms. This work is supported by ONR/DEPSCOR grant, SRC supported by NSF. @FootnoteText@ @footnote 1@Huasheng Wu and G. J. Lapeyre, Phys. Rev. B 51, 14549(1995)

SS-ThP4 Time-Resolved RHEED Studies of Ge(111)-c(2x8) <-> (1x1) Phase Transition*, **X.L. Zeng**, B. Lin, H. Elsayed-Ali,* Old Dominion University

The dynamic behavior of Ge(111)-c(2x8) <-> (1x1) phase transition was investigated by time-resolved reflection high-energy electron diffraction which employs a 100 ps electron pulse as a RHEED probe synchronized with 100 ps 1.06 µm laser pulse to produce a transient surface temperature rise. By recording the RHEED intensities of (0,1/2) and (0,1) spots, the transient process of the reconstruction phase transition was monitored. First, our static RHEED study shows that Ge(111)-c(2x8) reconstruction state starts to disorder at the vicinity of 500K and are converted to a highly disordered adatom arrangement at 573K. Second, the time-resolved RHEED measurements are carried out by biasing the Ge(111) sample at 500K and using IR laser to produce a transient surface temperature jump as high as 130K. Under these conditions the Ge(111)-c(2x8) reconstructed adatom arrangement remains ordered up to 630K for a time duration of 400 ps, which is well above the characteristic temperature of 573K for the Ge(111)-c(2x8) <-> (1x1) phase transition.

SS-ThP5 Correlation Effects and Origin of the Phase Transition in Pb/Ge(111)*, **A. Mascaraque**,* Universidad Autonoma Madrid, Spain*; J. Avila, M.C. Asensio,* LURE and CSIC, France*; E.G. Michel,* Universidad Autonoma Madrid, Spain

The @sr@3 x @sr@3-Pb/Ge(111) structure undergoes a phase transition to a @sr@3 x @sr@3 phase at low temperature (LT),@footnote 1@ which has been interpreted as the stabilization of a charge-density-wave.@footnote 1@ The role of correlation effects and Fermi surface (FS) nesting as driving forces of the transition has been considered.@footnote 1,2@ We report an investigation on the electronic structure and Fermi surface of Pb/Ge(111) along the phase transition using angle-resolved photoemission. Pb/Ge(111) exhibits a prominent Pb p@sub z@ dispersing surface state at RT, that splits in two dispersing bands at LT. We monitored in detail the intensity at the Fermi energy, both at room temperature (RT) and LT, in different points of the surface Brillouin zone. While there is an overall intensity decrease at LT, the effect is more pronounced at 1/2@GAMMA@K, suggesting that the LT phase is indeed metallic. The role of correlation effects and FS nesting was also tested by measuring the dispersion of the surface features both at LT and RT. The evidences found support that nesting is not the driving force of the transition. However, the modifications observed in the LT electronic structure indicate a significant gain in electronic energy along the phase transition. These findings will be discussed in view of existing theoretical models. @FootnoteText@ @footnote 1@J.M. Carpinelli et al., Nature 381, 398 (1996). @footnote 2@A. Goldoni et al, Phys.Rev. B 55, 4109 (1997).

SS-ThP6 Adatom Pairing or Dimer Formation for Si on Ge(001)?*, **H.J.W. Zandvliet**, E. Zoethout,* University of Twente, The Netherlands*; W. Wulfhekel,* University of Twente, The Netherlands, Netherlands*; G. Rosenfeld, B. Poelsema,* University of Twente, The Netherlands

The early stages of room temperature growth of Si on Ge(001) have been studied with Scanning Tunneling Microscopy. The smallest observed entity is a cluster containing two Si atoms. The two atom clusters residing on top of the substrate dimer rows are dimers. These on top dimers exhibit a rotational mode and diffuse preferential along the substrate rows with activation barriers of 0.7 eV and 0.86 eV, respectively. Using dual bias imaging we show that the two-atom clusters that are positioned in trough positions are ordinary dimers too rather than adatom paired units. These "trough" dimers occasionally hop to an on top position and vice versa providing a pathway for diffusion across the substrate dimer rows.

SS-ThP7 Step Fluctuations on Vicinal Si(113)*, **K. Sudoh**, T. Yoshinobu, H. Iwasaki,* Osaka University, Japan*; E.D. Williams,* University of Maryland

The properties of steps play an important role in the description of dynamics of processes such as faceting and crystal growth. The vicinal surfaces of Si(113) are a model system for studying the evolution of steps into stable facets involving step-step attractions.@footnote 1@ In this paper, we investigate quantitatively the fluctuation properties of steps relevant to step coalescence using scanning tunneling microscopy (STM) on a Si(113) surface miscut along a low symmetry azimuth. In local thermal equilibrium at 710 °C, which is near the faceting transition temperature, coexistence of single, double, triple, and quadruple steps has been observed. To determine the dependence of the step stiffness on step height, we have measured the step-correlation function@footnote 2@ for the steps with different heights from STM images. This result shows that the step stiffness is proportional to the step height. This behavior can be qualitatively understood in terms of a terrace-step-kink (TSK) model which includes a short range step-step attraction. Performing Monte Carlo calculations, we have found that the linear dependence of the step stiffness on step height is expected only near the faceting temperature where unbinding of steps becomes facile. The high resolution STM images of the edge of triple and quadruple-steps evidently reveal significant unbinding of steps, in agreement with the prediction. @FootnoteText@ @footnote 1@S. Song and S. G. J. Mochrie, Phys. Rev. B51, 10068 (1995) @footnote 2@N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surf. Sci. 273, 308 (1992)

SS-ThP8 Control of Atomic Step Arrangements on a Patterned Si(111) Substrate Through Molecular-Beam Epitaxy*, **H. Omi**, T. Ogino,* NTT, Basic Research Labs, Japan

Atomic steps on a surface have great potential to act as templates for nanostructure formation. Therefore, control of step arrangement is critical for positioning these nanostructures on a wafer-scale. In our previous study,@footnote 1@ we have focussed on step motions on a patterned Si(111) surface during high temperature annealing and found that regular atomic step bands are formed on the surface. In this presentation, we show that atomic step arrangement can also be designed by step-flow growth on a patterned Si(111) surface using molecular-beam epitaxy. We used a Si(111) wafer, miscut by 1.5 ° to the direction, 7 ° rotated from the [1 1 -2] direction, on which periodic mesa and trench patterns were fabricated by standard Si process. These patterns are aligned along the direction, 7 ° rotated from the [1 1 -2]. The pattern sizes are 1 - 10 µm wide and 1 µm deep. By the introduction of such boundaries on the Si(111) surface, step-flow speed can be changed. This is because, concentration of adsorbed atoms on the restricted surface will be modulated by the presence of boundaries. In fact, we obtained particular step patterns related to the step-flow speed modulation. On a surface of 1 µm wide mesa, for instance, steps become curved and projected towards the [-1 -1 2] direction by high temperature annealing before the Si deposition. These steps evolve into arrowhead-like shape with increasing Si layer thickness. These step arrowheads point towards the [1 1 -2] direction at an arrow angle of 60 °, and therefore suggest that they are composed of [-1 -1 2] type steps. The above results demonstrate that the orientation of steps on a Si(111) surface can be regulated by introducing boundary conditions into the step-flow growth. The step-flow growth on a patterned substrate offers the possibility to design step arrangements on a wafer scale. @FootnoteText@ @footnote 1@ T. Ogino, H. Hibino, and Y. Homma, Appl. Surf. Sci. 117/118, 642 (1997).

SS-ThP9 The Atomistics of Silicide Formation on Si(111) and Si(113) Studied with High Temperature STM*, **V. Dorna**, P. Kohstall, U.K. Koehler,* Ruhr-Universitaet Bochum, Germany

Basic steps of the nucleation of iron silicide on Si(111) and Si(113) during gas phase deposition (CVD) were investigated by high temperature STM directly during growth up to 650°C. The formation of ordered silicides above 300°C is directly observed in form of STM-"movies". When solely iron is deposited via Fe(CO)@sub 5@ as a gaseous source, silicon from the substrate reacts to form the silicide. On Si(111) always three different types of islands nucleate even in the very first stage. The dominating @gamma@-silicide type is surrounded by holes in the silicon substrate. In a quantitative analysis the stochiometry of the silicide nuclei was found to be temperature dependent, whereas the sticking behavior of the precursor gas is not activated. At higher temperatures the fraction of a second island-type increases, which shows an only weakly ordered surface periodicity pointing to an @alpha@-silicide. A reversible transition between both phases can be forced by a surplus of Si or Fe. The third island type is implanted into the substrate surface. When Fe and Si using Si@sub 2@H@sub 6@ are co-deposited, a gas composition for a stochiometric silicide growth is found which is in agreement with separately determined sticking coefficients on the substrate. With increasing coverage all different phases transform into @gamma@-silicide, but no layer by layer growth could be archived on Si(111). On Si(113), on the other hand, the 3D-growth seems to be suppressed in the case of the co-depostion, which may be a chance to achieve layer by layer growth.

SS-ThP10 Reconstructions of Ag on High-Index Silicon Surfaces*, **S.R. Blankenship**, H.H. Song, A.A. Baski, J.A. Carlisle,* Virginia Commonwealth University

Si(5 5 12), a recently discovered, stable high-index surface of silicon, may offer a superior template for the growth of 1D metallic structures. This surface predominately consists of long pi-bonded Si rows. We are using Reflection High-Energy Electron Diffraction (RHEED) to determine the surface phase diagram of Ag on this surface, and the related surface of Si(337). Each of these surfaces exhibit a very sharp (2x1) reconstruction after flashing to ~1250°C. The growth of Ag on these surfaces is split into two distinct regimes. For growth at low coverages (@THETA@0.4 ML) and temperatures (450°C

SS-ThP11 Structure Determination of Si(111)/Sb-(@sr@3x@sr@3)R30@degree@ using Photoelectron Diffraction Direct Methods*, M. Martin,* LURE, Centre Universitaire Paris Sud and ICMM, France*; H. Ascolani,* Centro Atomico Bariloche, Argentina, Argentine*; N. Franco, J. Avila, **M.C. Asensio**,* LURE, Centre Universitaire Paris Sud and ICMM, France

The determination of the local adsorption structure of absorbed atoms and molecules on single-crystal substrates is a key prerequisite for understanding the electronic and chemical properties of surfaces. Most of the fragments or molecular adsorbates generally present a well defined local order, although, do not form the long-range ordered structures required for conventional LEED studies. One technique applicable to such problems is Photoelectron Diffraction, where the intensity of a core level peak is recorded as a function of the kinetic energy or the emission angle. The spectra measured in this way show intensity modulations which can be strictly correlated with the local structural environment of the atomic emitter. Recently, new direct methods based on energy scan mode have been developed relying on the high scattering factor for 180° backscattering, at low energies. This "backscattering searching" approach requires the measurement of scanned energy spectra at several angles along the high symmetry direction. In the present communication, we report the results of different direct methods for the Si(111)-Sb (@sr@3x@sr@3) structure. The limitations and advantages of each method are analized and the results are contrasted with the final structure obtained by a full multiple scattering trial-and-error analysis.

SS-ThP12 Photoelectron Diffraction Intensity Calculation by Using Tensor LEED Theory*, **S. Omori**, Y. Nihei,* University of Tokyo, Japan

Low-energy photoelectron diffraction (PED) by using synchrotron radiation (SR) has become more and more important for determining surface structures. In particular, PED has the advantage that surfaces having no two-dimensional translation symmetry such as initial-stage adsorption systems can be analyzed provided that the atomic arrangements around photoelectron emitters are symmetric. Since low-energy PED is extremely sensitive to surface structures, multiple structural parameters are usually to be determined by fitting experiment and theory. However, since multiple-scattering effects are important at low photoelectron energies, the structural analysis might be very time-consuming. In this study, we tried to incorporate the tensor LEED (TLEED) theory, a powerful perturbative approach to LEED intensity calculation,@footnote 1@ into the PED formalism and to develop a high-speed trial-and-error method for the structure determination with PED. Since scattering processes that occur in solid surfaces are almost the same for PED and LEED, the formulation of tensor PED is straight-forward. The change in the transition matrix of an atom brought about by its displacement can be calculated by the same method as in TLEED. Once the quantities related to the reference structure, namely the amplitudes of spherical waves incoming to and outgoing from the displaced atom are calculated in the process of multiple-scattering cluster (MSC) calculation for the reference structure and are stored in a hard disk, it is easy to evaluate the changes in the diffraction wave field for many trial structures. We demonstrate the efficiency and accuracy of this method. @FootnoteText@ @footnote 1@P. J. Rous et al., Phys. Rev. Lett. 57 (1986) 2951.

SS-ThP13 The Surface Structure Determination of @alpha@-Fe@sub 2@O@sub 3@(0001) by Low-Energy X-Ray Photoelectron Diffraction*, **S. Thevuthasan**, Y.J. Kim, S.A. Chambers,* Pacific Northwest National Laboratory*; J. Morais, R. Denecke, C.S. Fadley,* Lawrence Berkeley National Laboratory*; P. Liu, T. Kendelewicz, D.E. Brown Jr.,* Stanford University

The structure and composition of oxide surfaces strongly influence the chemical and mechanical properities of these materials. As such, there is a growing interest of determining surface termination, reconstruction and relaxation on these surfaces. Recent theoretical work by Wasserman et. al [1] have shown that hematite(@alpha@-Fe@sub 2@O@sub 3@(0001)) surface has a single Fe layer termination with relaxations in the first four planes of -49%, -3%, -41%, and 21% of the bulk values respectively. We recently performed x-ray photoelectron diffraction measurements at Advanced Light Source on a clean, epitaxially grown Fe@sub 2@O@sub 3@(0001)/Al@sub 2@O@sub 3@(0001). A photon energy of 400 eV (Fe 3p E@sub kin@ = 344 eV) was used to collect several Fe 3p azimuthal scans at different take off angles. The experimental data were compared to the theoretical simulations using single and multiple scattering calculations with trial geometries. R-factors were calculated and minimized to obtain the optimum geometry. The surface appears to be Fe-terminated and the first four layer spacing are -41%, +18%, -8%, and 47% of the associated bulk values, respectively. @FootnoteText@ Work supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences and Biological and Environmental Research Environmental Management ScienceProgram

SS-ThP15 Barrier-Height Imaging of Defects on the Si(001) 2x1 Surface*, **S. Kurokawa**, A. Sakai,* Kyoto University, Japan

The C-type defect on the Si(001) 2x1 surface is known to be an active site in Fermi level pinning and also in the initial oxidation of Si(001). In spite of its practical importance, the atomic structure of this defect has not completely understood yet. Controversies also exist on the tunneling barrier height at the C defect. Hamers and Köhler@footnote 1@ found that the barrier height decreases around the defect but increases just above the defect site. On the other hand, Ukraintsev et al.@footnote 2@ reported no such changes in the barrier height at and around the C defect. We have performed the STM barrier-height imaging on clean and oxygen-adsorbed Si(001) 2x1 surfaces and investigated the barrier height at various surface defects. We find that the apparent barrier height at the C defect closely follows the STM corrugation profile: the barrier height increases at the defect site under positive sample bias, but shows no depression around the defect. Our finding is consistent with the relation between barrier-height and STM images but not in agreement with Hamers and Köhler.@footnote 1@ Upon exposure to 1L of oxygen, preliminary barrier-height measurements show that the apparent barrier height at the C defect site appears to be reduced. The effects of oxygen adsorption on other surface defects will also be presented. @FootnoteText@ @footnote 1@R. J. Hamers and U. K. Köhler, J.Vac.Sci.Technol. A7, 2854 (1989). @footnote 2@V. A. Ukraintsev, Z. Dohnalek, and J. T. Yates. Jr., Surf. Sci. 388, 132 (1997).

SS-ThP16 Disappearance of Element-Specific Kikuchi Bands from Fluoride Surfaces*, S. Omori, **Y. Nihei**,* University of Tokyo, Japan

We will discuss X-ray photoelectron diffraction (XPED) from fluoride surfaces with different crystal structures, namely SrF@sub 2@ (fluorite structure) and MgF@sub 2@ (rutile structure). Scanned-angle XPED patterns of substrate emission over a large solid angle consist of strong forward-scattering peaks along high-density crystal axes, surrounded by first-order interference fringes, and Kikuchi bands along the projections of low-index crystal planes. In contrast to Kikuchi electron diffraction, Kikuchi bands in XPED patterns originate from a specific element in a sample. It has been shown that such element-specific Kikuchi bands have the following characteristics;@footnote 1@ (1) There is a site-specific extinction rule, in addition to the ordinary one that the Fourier coefficients of the crystal potential are zero. (2) The intensity of Kikuchi bands strongly depend both on those coefficients and on photoelectron-emitter sites. (3) Dark Kikuchi bands of depressed int! ! ! ensity can occur if photoelectron emitters satisfy a certain condition. In this presentation, we mainly concentrate on such element-specific Kikuchi-band effects. It was found that a set of (111) bands disappear in the Mg 2s pattern for MgF@sub 2@ and in the F1s pattern for SrF@sub 2@, although they were clearly observed in the pattern for the other element of each sample. We show that these element-specific effects on the extinction of Kikuchi bands occur by different mechanisms and that such apparently complex intensity properties can be well understood on the basis of three principles described above and can be well reproduced by multiple-scattering cluster (MSC) calculations. @FootnoteText@ @footnote 1@ S. Omori et al., Jpn. J. Appl. Phys. 36 (1997) L1689.

SS-ThP17 Anisotropic Electron Scattering from Point Defects on Graphite at Low Temperature*, **K.F. Kelly**,* Rice University*; J.G. Kushmerick, H.P. Rust,* The Pennsylvania State University*; N.J. Halas,* Rice University*; P.S. Weiss,* The Pennsylvania State University

A low temperature ultrahigh vacuum scanning tunneling microscope was used to image threefold symmetric electron scattering from point defects in the graphite surface. Such defects were theoretically predicted,@footnote 1@ but had only previously been observed with C@sub 60@-functionalized tips at room temperature.@footnote 2@ Cryogenic temperatures sharpen the Fermi distribution enabling the observation of electron scattering. The energy dependence of the scattering was mapped by spectroscopic imaging and acquiring complete current-voltage curves at specific positions with respect to the scattering center. @FootnoteText@ @footnote 1@H. A. Mizes and J. S. Foster, Science 244, 559 (1989). @footnote 2@K. F. Kelly, D. Sarkar, G. D. Hale, N. J. Halas, Science 273, 1371 (1996).

SS-ThP18 Vacancy Creation as the Rate Limiting Step in Halogen Etching of Si(100)-2x1*, **K. Nakayama**,* University of Minnesota*; C.M. Aldao,* Universidad Nacional de Mar del Plata-CONICET, Argentina*; J.H. Weaver,* University of Minnesota

We have studied the etching on Si(100)-2x1 using scanning tunneling microscopy. Surfaces exposed to Cl@sub 2@ or Br@sub 2@ are etched at elevated temperature via the thermal activation reaction 2SiX(a) <--> SiX@sub 2@(a) + Si(a), where SiX@sub 2@(a) is a volatile molecule, Si(a) is a bystander Si atom, and X = Cl or Br. Formation of SiX@sub 2@(a) breaks the dimer @sigma@-bond and leaves the destabilized bystander with two dangling bonds. Conventional wisdom would indicate that SiX@sub 2@ desorption is the rate-limiting step. Instead, we show that the rate limiting step occurs when the bystander breaks away and moves onto the terrace. Thus, the de-excitation pathway to 2SiX(a) is eliminated. This increases the overall probability for SiX@sub 2@ desorption. We show that the rate of etching increases with halogen concentration until ~0.8 ML. It is reduced at higher coverage as the adsorbates block the escape of the bystander onto the terrace. We discuss the consequences and examine the post-etch surface morphology.

SS-ThP19 Growth of Ultrathin Mn Films on W(110)*, M. Bode, **M. Hennefarth**, M. Getzlaff, R. Wiesendanger,* University of Hamburg, Germany

At room temperature bulk Manganese (Mn) exhibits complicated cubic structures with large unit cells. Simple crystallographic structures like fcc @gamma@- and the bcc @delta@-Mn are high temperature phases. However, it is well known that thin solid films can be stabilized on appropriate substrates in crystalline symmetries and lattice constants that are far from those of the corresponding bulk material. We have studied the growth of Mn on W(110)-substrates by means of STM and LEED. With our home-build MBE-STM@footnote 1@ we obtained growth sequences of particular microscopic locations. Up to a coverage of 0.5ML the nucleation of first monolayer islands which are elongated along the [110]-direction could be observed. The nucleation of second monolayer patches occurs before the completion of the first ML. We found that up to a total coverage of 2 monolayers Mn grows pseudomorphically on W(110), i.e. in the bcc @delta@-phase and strained by approximately 10%, as indicated by the absence of satellite spots in the LEED-pattern. If the total amount of deposited material exceeds 2ML we observed the evolution of rectangular islands with a minimum height of 5ML. This coincides with an increasing diffuse background in the LEED-pattern. Further deposition leads to a very rough surface morphology. @FootnoteText@ @footnote 1@ Ch. Witt, U. Mick, M. Bode, and R. Wiesendanger, Rev. Sci. Instrum. 68, 1455 (1997).

SS-ThP20 Electronic States and Structural Characterization in Single-Crystal Fe-Ni-O Alloy Thin Films Grown by Molecular Beam Epitaxy*, **C.L. Chang**,* Tamkang University, Taiwan*; G. Chern,* Chung-Cheng University, Taiwan*; C.L. Chen, H.H. Hsieh, W.F. Pong,* Tamkang University, Taiwan*; T.C. Leung,* Chung-Cheng University, Taiwan

Stimulated by the recent success of the research on epitaxial Fe@sub 3@O@sub 4@ and NiO thin films on MgO(001), we extend our study to the growth of a series of alloy Fe-Ni-O thin films with various Fe/Ni concentration ratio by molecular beam epitaxy. Total of 9 samples, around 500 Å thick, are fabricated including Fe@sub 3@O@sub 4@, NiO and Fe@sub x@Ni@sub 1-x@O@sub y@ (x=0.15, 0.3, 0.35, 0.5, 0.56, 0.65, 0.71). These films are expected to show a structural crossover from spinel to rocksalt structure and to show an associated change on valance states of Fe and Ni ions while x varies from 0 to 1. After analyzed by in-situ reflection high energy electron diffraction (RHEED), ex-situ x-ray diffraction, and x-ray absorption spectroscopy (XAS). It is observed that the crystal structure of all the alloy Fe@sub x@Ni@sub 1-x@O@sub y@ films resembles that of the spinel Fe@sub 3@O@sub 4@. The lattice spacing along the perpendicular direction as a function of x shows a minimum at x=0.5 instead of a linear variation indicating that the structures are different from a bulk ferrite Fe@sub 2@NiO@sub 4@-like phase. The distribution of the cations in Fe@sub x@Ni@sub 1-x@O@sub y@ system was studied by Fe and Ni L@sub 2,3@ XAS edge shapes, which are sensitive to the structural symmetry of the sites of the absorbing atoms. The results are qualitatively consistent with the x-ray observations. For x0.5 the excessive Ni ions occupy the Fe@super 3+@ sites of tetrahedral and octahedral symmetry up to the x value 0.71. The mechanism of forming the metastable phase and its implication on the magnetic properties of these Fe-Ni-O films will also be discussed. This work is supported by National Science Council of R. O. C. under grands NSC87-2613-M-032-001 and NSC87-2112-M-194-009

SS-ThP21 Field Desorption of Gallium from Liquid Metal Ion Source Studied by Back Scattered Electron Scanning Electron Microscopy*, H. Kimata*, *Y. Kondo,* ERATO, Japan Science and Tech. Corp., Japan*; K. Takayanagi,* Tokyo Institute of Technology, Japan

Field desorption of gallium metal from a home-made liquid metal ion source (LMIS) was studied in a scanning electron microscope (SEM). The LMIS has a needle and a reservoir filled with the liquid gallium and a filament. The needle apex is electrochemically sharpened, and the temperature of the LMIS was controlled. We found that the back scattered electron scanning electron microscopy (BSE-SEM) can give images of the needle apex during operation, the emission current being monitored simultaneously. The Taylor-cone and the change of the cone angle depending on the extraction voltage was observed by BSE-SEM. In case that the needle was grooved enough to supply liquid gallium towards the apex,@footnote 1@ the emission current vs. extraction voltage relations were found to fit well with the previous experimental results and theoretical predictions qualitatively. Rarely, the emission did not occur at the apex but the side of the needle, when the supply was limited by poor grooving on the needle. The critical voltage Vc was found to decrease linearly as the temperature T of the ion source increased from 200 to 450(°C). The Vc vs. T relations were analyzed to estimate temperature dependence of the surface tension of the liquid gallium, using the tip radius measured in SEM. The surface tension change like (0.8) - (3x10@super -4@)T, in accordance with the value given in a literature, (0.721) - (1.0x10@super -4@)T. Thus, BSE-SEM is useful to study the dynamics of LMIS. The present techniques are applied for testing a commercial LMIS because of large sample space in a SEM. @FootnoteText@ @footnote 1@A. Wagner and T. M. Hall, J. Vac. Sci. Technol. 16, 1871 (1980).

SS-ThP22 Stoichiometric Phase Transition and Facetting of Low Index Fe@sub 3@Si Surfaces*, J. Schardt*, *W. Weiss, W. Meier,* University of Erlangen-Nuernberg, Germany*; C. Polop, P.L. de Andres,* Universidad Autonoma de Madrid, Spain*; U. Starke, K. Heinz,* University of Erlangen-Nuernberg, Germany

In binary compounds segregation of one of the constituents is a freqently observed phenomenon. The respective changes of the stoichiometry are often not restricted to the topmost surface region. In this line, two phases of different stoichiometry can be stabilized on the (100), (110) and (111) surfaces of Fe@sub 3@Si bulk samples. On each surface the two phases can be reversibly transformed into each other by extended annealing cycles. The stability regions of each phase and the phase transition temperatures were determined using the stoichiometric information obtained from Auger electron spectroscopy (AES) and structural fingerprints gained from spot intensity spectra, I(E)-curves, of the low-energy electron diffraction (LEED) pattern. These I(E)-curves were used for quantitative LEED structure analyses of each phase. In the low temperature regime (400° C) for all surfaces a D0@sub 3@ crystal structure can be confirmed. However, for preparation temperatures of around 600° C a restructuring of the surface region is observed. Segregation leads to a Si enrichment of the surface. This is accompanied by a structural transition to a CsCl crystal structure within the region accessible to the low-energy electrons. In addition, using LEED facetting of the (100) and (111) surfaces is observed with facets in (110) orientation which obviously is the energetically most stable plane of Fe@sub 3@Si.

SS-ThP23 Local Composition and Electronic and Optical Properties of Cr Oxide-Based Thin Films*, J. Smith*, *D.A. Bonnell,* The University of Pennsylvania, US*; P. Carcia, R.H. French,* E.I. Dupont de Nemours*; X.F. Lin,* The University of Pennsylvania

Oxynitride thin films are increasingly used to optimize resolution in optical lithography. Recently, a series of complex Cr-O-C-N films have been developed that allow simultaneous precise control over optical transmission, reflection, and phase shift. Subtle variations in optical properties appear to be related to small differences in O:C:N bond ratios across 100 nm films. To understand the mechanisms by which variations in anion coordination affect properties, the electronic structure near the Fermi level and local electrical conductivity measured by tunneling spectroscopy was related to optical properties in the end member compositions. Results from CrOx, CrCx, and CrNx this films, where x varies from 0.1 to 0.7, will be discussed in terms of the relationship between electronic and optical density and the consequence to optical properties.

SS-ThP24 Formation of a Bilayer Ordered Surface Alloy of Mn Thin Films*, W. Kim*, Seoul National University, Republic of Korea*; J. Seo,* Chodang University, Republic of Korea*; J.-S. Kim,* Sook-Myung Women's University, Republic of Korea*; S.-J. Oh,* Seoul National University, Republic of Korea

We report a new type of surface alloy,the formation of a bilayer ordered surface alloy of Mn thin films deposited on some transition metal (100) surfaces, from the results of Low-energy electron diffraction(LEED) I/V analyses. For Mn on Ag(100), very sharp and bright c(2x2) LEED pattern is observed with norminal 1 monolayer Mn deposited, and the experimental I/V curve is well fitted only by a model, a bilayer ordered surface alloy structure with little corrugation of Mn atom. Sudden disappearance of c(2x2) pattern is, however, observed on light annealing at 400K. By analyses on atomic compositions of each layer using averaged t-matrix approximation(ATA), we find out that vanishment of LEED superstructure is due to the segregation of Ag atoms. For the case of Mn on Pd(100), we achieve more improved fitting of the experimental I/V curves by employing a bilayer ordered surface alloy instead of the single layer ordered alloy model which was tried in the previous study of Tian et. al.@footnote 1@ However, unlike the Mn atoms deposited on Ag(100) surface, the topmost Mn atoms in this system are severely buckled out from the surface and its amount of corrugation is comparable to that of Mn/Cu(100) system. Thermodynamic property is also different:More clear c(2x2) LEED pattern is obtained after annealing. Mn 3s core level spectra of both systems show exchange splittings similar with that of bulk Mn, so magnetic effect on surface alloying is important in common with two cases. The distinctive characteristics of these two systems belonging to the same class of surface alloy, can be understood qualitatively, considering the differences in surface free energy and atomic size effect between Ag and Pd. @FootnoteText@ @footnote 1@ D. Tian, R.F. Lin, F. Jona, P.M. Marcus, Solid State Commun. Vol. 74, 1017(1990)

SS-ThP25 Surface Reconstruction and Charge Density Wave on ß-(BEDT-TTF)@sub 2@PF@sub 6@ Studied by Scanning Tunneling Microscopy*, M. Ishida*, *K. Miyake, K. Hata,* University of Tsukuba, Japan*; T. Mori,* Tokyo Institute of Technology, Japan*; H. Shigekawa,* University of Tsukuba, Japan

ß-(BEDT-TTF)@sub 2@PF@sub 6@ is one of the quasi-one-dimensional organic conductors and is known to show metal-insulator transition at ~297 K with Charge Density Wave(CDW). STM/AFM study on this crystal revealed the characteristic properties of the molecular crystal surface for the first time. On the PF@sub 6@ surface, superstructure was formed by missing alternate molecular rows of PF@sub 6@. This is the first observation of the surface reconstruction of molecular crystal including a dractic change in the molecular arrangement.@footnote 1@ On the other hand, BEDT-TTF terminated surface induced molecular rearrangement with charge redistribution resulting in the symmetry breaking; formation of the two-fold periodicity in the direction perpendicular to the one-dimensional conductive axis. The origin of these structures could be explained comprehensively by the compensation mechanism of the incomplete charge transfer on the polar surface.@footnote 2@ Furthermore, STM measurement was performed from 80K to room temperature to observe the CDW phase directly. In the low temperature range up to 280 K, it was difficult to observe detailed surface structure because of low conductivity owing to the CDW gap. In the temperature range from 280 K, however, long range modulations were observed and we concluded that the modulations reflect the CDW phase. @FootnoteText@ @footnote 1@M. Ishida, K. Hata, T. Mori, and H. Shigekawa, Phys. Rev. B 55, 6773 (1997). @footnote 2@M. Tsukada and T. Hoshino, J. Phys. Soc. Jpn. 51, 2562 (1982).

SS-ThP26 Structure of the Five-Fold Surface of Al@sub 70@Pd@sub 21@Mn@sub 9@, *J. Ledieu, A. Munz, T. Parker, R. McGrath,* University of Liverpool, United Kingdom*; **R.D. Diehl,*** Pennsylvania State University*; D.W. Delaney, T.A. Lograsso,* Iowa State University

Quasicrystals are bi- or tri-metallic alloys with long range orientational order and no short range translational order. Coatings of quasicrystals have low coefficients of friction and high resistance to wear,@footnote 1@ and hence the surface structure is of obvious interest. We have investigated the five-fold surface of the Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal using STM, LEED and AES. Surfaces annealed to 875 K showed excellent five-fold symmetric LEED patterns, and STM revealed disordered clumps of cluster-like protrusions 25±2 Å in diameter, similar to those observed for surfaces cleaved in vacuum.@footnote 2@ Higher resolution images showed these clusters were themselves composed of 2.5 Å diameter protrusions. Surfaces annealed to 1100 K showed sharp LEED patterns and atomically flat surfaces, in agreement with previous work.@footnote 3@ The data quality have allowed us to go beyond the previous analysis@footnote 3@ to examine structural features of the surface in detail. The most striking features are groups of protrusions forming five-fold star-shaped patterns. Threshold and pattern analysis of the images shows that the surface can be generated by tiling with pentagons using parallelograms to take up frustration. The parallelograms contain defects in the form of large protrusions, and gradients of the defect peaks were found to match angles present in the stereographic projection of the icosahedral group m35. Ratios of distances between the defect peaks and ratios of sequential step heights were found to equal the golden mean @tau@. Further analysis and adsorption experiments are being undertaken. @FootnoteText@ @footnote 1@S. L. Chang, W. B. Chin, C. M. Zhang, C. J. Jenks and P. A. Thiel, Surf. Sci. 337 (1995) 135; S. S. Kang, J. M. Dubois and V. J. Stebut, J. Mater. Res. 8 (1993) 2471. @footnote 2@Ph. Ebert, M. Feuerbacher, N. Tamura, M. Wollgarten, K. Urban, Phys. Rev. Lett. 77 (1996) 3827. @footnote 3@T. M. Schaub, D. E. Buergler, H. -J. Guentherodt, J. -B. Suck, Phys. Rev. Lett. 73 (1994) 1255.

SS-ThP27 Quantum-Size Effects on the Pattern Formation of Monatomic-Layer-High Metal Islands at Surfaces*, **K. Jin,*** University of Tennessee, Knoxville*; G.D. Mahan,* Univ. of Tennessee, Knoxville & Oak Ridge National Lab*; H. Metiu,* University of California, Santa Barbara*; Z. Zhang,* Oak Ridge National Laboratory

The quantum-size effects are shown to play a crucial role in defining pattern formation of metal island on surface.@footnote 1@ The energy in elongated needle-like growth is found to oscillate with the width of the needle, clearly demonstrating the existence of preferred needle widths. The energy of the square or rectangular islands varies periodically with the side length, predicting stability variations of the islands with different sizes. This work is supported by University of Tennessee, by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464 @FootnoteText@ @footnote 1@ K.-J. Jin, G. D. Mahan, H. Metiu, and Z. Y. Zhang, Phys. Rev. Lett. 80, 1026 (1998).

SS-ThP28 Finite-size Scaling Behavior of the Tracer Surface Diffusion Coefficient near a Second-order Phase Transition*, F. Nieto,* Universidad Nacional de San Luis, Argentina*; A.A. Tarasenko,* National Academy of Science of Ukraine, Ukraine*; **C. Uebing,*** Max-Planck-Institut fuer Eisenforschung, Germany

We investigate the finite-size scaling behavior of the tracer surface diffusion coefficient in the vicinity of a second order phase transition. For this purpose, we use a lattice gas model of repulsively interacting particles on a square lattice. For all lattice sizes L studied, the measured tracer surface diffusion coefficient, D@sub t@, is a smooth function, having an inflexion point at critical temperature. Its derivative, dD@sub t@/d(1/k@sub B@T), exhibits a cusp-like maximum which is (a) sharply pronounced and (b) converged to T@sub c@ for large lattice sizes. We have analyzed the finite-size behavior of D@sub t@ and obtained its critical exponent @sigma@=0.665±0.003.

SS-ThP29 Computer Simulation of the Au(111) @sr@3 x 22 Surface Reconstruction*, **T.M. Trimble,*** University of Maryland*; R.C. Cammarata,* Johns Hopkins University*; E.D. Williams,* University of Maryland*; K. Sieradzki,* Arizona State University

A computer simulation study of the Au(111) @sq@3 x 22 surface reconstruction will be discussed. This reconstruction can be described as involving a uniaxial in-plane contraction of the top monolayer corresponding to a surface strain of about 4%, and has been observed to be the stable surface structure at low temperatures. The driving force for this reconstruction has been identified as the difference in the surface stress f and the surface free energy @gamma@ of the 1x1 surface, while the opposing force is owing to the free energy cost associated with the top monolayer losing atomic registry with underlying lattice. A simple continuum analysis gave the following stability criterion: a (111) fcc metal surface will undergo a reconstruction involving contraction of the top monolayer if the ratio (f - @gamma@)/µb exceeds a certain critical value of order 0.1, where µ is the shear modulus and b is the nearest neighbor distance. This criterion was tested with computer simulations that were conducted using the Johnson analytical embedded atom method (EAM) potential. Since the standard Johnson potential for Au leads to the result that the 1x1 surface is stable to reconstruction, modifications were made in values of some Johnson EAM input paramters in order to stabilize the reconstruction. It was found that although the resulting values of f and @gamma@ were somewhat lower than those obtained from first principles calculations, the driving force (f - @gamma@) obtained by the simulation and the first principle calculations were very close. Furthermore, the critical value of the stability parameter (f - @gamma@)/µb, inferred from results obtained from simulations of reconstructions with different surface strains, was found to be very close to that predicted by the continuum analysis. This work was supported by NSF through the University of Maryland MRSEC.

SS-ThP30 LEED Study of the Relaxation of Cu(211)*, **Th. Seyller**, R.D. Diehl,* Pennsylvania State University*; F. Jona,* State University of New York, Stony Brook

A low-energy electron diffraction study of the vicinal Cu(211) surface has been carried out at 300 K. The experiments were carried out at normal incidence to the (211) planes and the calculations were carried out using the CHANGE program@footnote 1@ which is capable of calculating intensities for surface structures which have small interlayer spacings. The results indicate a large (15 percent) contraction of the top layer Cu atoms and essentially bulk spacings for deeper layers. The large contraction of the top layer agrees very well with a first principles calculation for Cu(211).@footnote 2@ However, the first-principles calculation as well as earlier embedded-atom model calculations@footnote 3@ predict large relaxations of the deeper layers as well. These discrepancies will be discussed in light of structure determinations for other vicinal surfaces. @FootnoteText@ @footnote 1@D. Jepsen, in "Determination of Surface Structure by LEED" edited by P.M. Marcus and F. Jona, Plenum Press 1984, p.17. @footnote 2@C.Y. Wei, Steven P. Lewis, E.J. Mele and Andrew M. Rappe, Phys. Rev. B 57 (1998) 10062. @footnote 3@S. Durukanoglu, A. Kara and T. S. Rahman, Phys. Rev. B 55 (1997) 13894.

SS-ThP31 Interlayer Diffusion Near Ledge Contacts: Comparison of Systems with Positive and Negative Schwoebel-Ehrlich Barriers*, V. Shah, **L. Yang,*** Iowa State University*; T.L. Einstein,* University of Maryland

We present molecular statics studies on the diffusion mechanisms near steps on fcc (111) surfaces. We use the Molecular Dynamics/Monte Carlo-Corrected Effective Medium (MD/MC-CEM) interatomic potential, which has been applied to the study of the Schwoebel-Ehrlich (SE) barriers for single atom diffusion towards a single descending step on Ag, Cu, Au, Pd, Ni, and Pt [Y. Li and A. E. DePristo, Surf. Sci. 351, 189 (1996)]. Among these six transition metals, the MD/MC-CEM potential predicts that Cu and Pd, respectively, have the highest (137 meV) and lowest (-4 meV) SE barriers for interlayer diffusion, via the exchange mechanism at the B-type step. In the present study, we focus on the change in the SE barrier for single- and multi-atom diffusion at descending step edge contacts for two model systems that have positive (Cu) and slightly negative (Pd) SE barriers for atomic diffusion at a single step. We also track the potential surface as an atom approaches corners while diffusing along island edges and as it diffuses away from the step edge on an island plateau. Our results on the behavior of mass transport near ledge contacts will be discussed in the light of recent experimental observations [M. Giesen et al., Phys. Rev. Lett. 80, 552 (1998)]. Two of us (VS and LY) would like to thank members of the Department of Chemistry and the surface physics group at the University of Maryland for their hospitality during our visit there. TLE was supported by NSF-MRSEC at U. of Md.

SS-ThP32 Scanning Tunneling Spectroscopy and X-ray Photoemission Spectroscopy Studies of Thin Films of WO3 and In2O3*, **S. Santucci**, L. Lozzi, L. Odorisio, M. Passacantando, C. Cantalini,* Università dell'Aquila, Italy

p-n junction between p-Si and n-type semiconductor oxides like WO3 and In2O3 have been fabricated by thermal evaporation in high vacuum of pure powders onto p-doped Si(100) and submitted to anneal at different temperatures up to 450°C at different times. The rectifying properties of the films have been studied by using the Scanning Tunneling Spectroscopy (STS) technique in air and using Cr-Au contacts on the etched surface of silicon and on the deposited films respectively. I-V characteristics have been measured for the films in the presence of NOx gas carried in a flux of dry air. The surface morphology of the deposited films with different annealing temperatures have been studied by Atomic Force Microscopy (AFM) where we have observed a regular rearrangement of the surface with a globular aspect for the In2O3 deposits whereas for WO3 films it showed a more flat and regular surface. X-ray Photoelectron spectroscopy (XPS) has been employed to study the composition of the deposited films and an ion beam depth profile technique to study the interface formation with the silicon substrate. n-type behavior of the films which is due to the oxygen deficiency has been observed by studying the valence band spectra of the films. A comparison with the Density Of States obtained by calculating the (dI/dV)/(I/V) of the I(V) curves detected by the STS technique has been also performed.

SS-ThP33 Atomic Force Microscopy Examination of the Evolution of the Surface Morphology of Bi@sub 4@Ti@sub 3@O@sub 12@ Grown by Molecular Beam Epitaxy*, **G.W. Brown**, M.E. Hawley,* Los Alamos National Laboratory*; C.D. Theis, J. Yeh, D.G. Schlom,* Pennsylvania State University

Bi@sub 4@Ti@sub 3@O@sub 12@ is a candidate material for use in electro-optic devices and non-volatile ferroelectric-based memories. In these applications, obtaining the desired electronic or optical properties depends on the ability to deposit very smooth films. We have examined the molecular beam epitaxial nucleation and growth of these films on SrTiO@sub 3@ with ex-situ atomic force microscopy (AFM) to observe the thickness dependence of the surface morphology. From the AFM data we obtain the direct, real space surface morphology, the RMS surface roughness as a function of thickness, the amount of material present in the growing layers, and the height difference correlation function of the surface. Bi@sub 4@Ti@sub 3@O@sub 12@ growth begins with the nucleation of a layer that is 1/4 unit cell thick followed by growth of 1/2 unit cell thick layers. A transition to multilayer island (3-dimensional) growth occurs somewhere between deposition of 25 % of the second layer and the completion of the third layer. This implies that the film grows in a Stranski-Krastonov mode with a critical thickness between 0.325 and 1.250 monolayers. After 3-dimensional growth begins, the surface morphology can be described with the dynamic scaling hypothesis (DSH).@footnote 1,2@ The DSH scaling exponents, extracted from the AFM images, are compared to other thin film growth systems and should provide checks for future models or simulations of Bi@sub 4@Ti@sub 3@O@sub 12@ growth. We observe an interesting thickness dependence of one of the scaling exponents which may be related to the stress relief involved in the S-K growth mode. Possible models for the stress relief will be discussed. Finally, results of deposition on substrates providing different lattice mismatches will be shown and implications for the growth of thicker, smooth films will be discussed. @FootnoteText@ @footnote 1@F. Family and T. Viscek, J. Phys. A: Math. Gen. 18, L75 (1985). @footnote 2@J. Lapujoulade, Surf. Sci. Rep. 20, 191 (1994).

SS-ThP34 AES-LEED Study of the Growth Mode of Ag on Au (111),(311) and (554) Single Crystal Surfaces*, V.F.S. Rooryck, C. Buess-Herman,* Universite Libre de Bruxelles, Belgium*; G.A. Attard,* University of Wales, United Kingdom*; **F.A.B. Reniers**,* Universite Libre de Bruxelles, Belgium

The growth mode of silver onto gold substrates has been the subject of many controversies. The energetics and lattice misfit between gold and silver seems to favor a layer-by-layer mode, confirmed by some studies, while others reported a Stransky-Krastanov mode. The deposition method (electrodeposition, UHV deposition), the analysis technique and the surface structure could be responsible for these different results. We have undertaken a LEED-AES study of the deposition of thermally evaporated silver onto gold single crystal surfaces. The Au (111), (311) and (554), with different atomic roughness were investigated. The deposition mode was determined from the intensity versus time evolution of the Auger lines of gold (69 eV) and silver (351-356 eV). The Gallon model was used to fit the experimental data to theoretical simulations. The most recent values of IMFP and AL were introduced in the model. Following the results, the Stransky-Krastanov growth occurs, but 2 or 3 layers are deposited before the island growth begins. The evolution of the surface structure during silver deposition was simultaneously followed by LEED. We showed that the reconstruction of thermodynamically equilibrated pure gold surfaces was progressively removed by silver adsorption, apparently starting at half a monolayer coverage. The possibility of the formation of an interfacial alloy is investigated, and a comparison is made with the results that we obtained for the electrodeposition of silver on the same gold surfaces.

Friday Morning, November 6, 1998

Applied Surface Science Division
Room 307 - Session AS+VT-FrM

Application of Surface Analysis Techniques to Semiconductor Technology

Moderator: F.A. Stevie, Cirent Semiconductor

8:20am **AS+VT-FrM1 An Overview of the Applications of Surface Analysis Techniques in Semiconductor Technology***, **B.R. Rogers**, R. Gregory, G. Harris, D. Werho, W. Chen,* Motorola, Inc. **INVITED**

Over the years the role of surfaces and interfaces has become increasingly important in determining the performance of semiconductor based microelectronic circuits. Consequently, the use of both new and traditional surface analysis techniques in the development of materials and processes as well as in manufacturing metrology and trouble shooting has become more and more popular. This presentation will review the strengths and weaknesses of the more common surface analysis techniques, such as Auger electron spectroscopy, Rutherford backscattering spectrometry, secondary ion mass spectrometry, total reflection x-ray fluorescence, and atomic force microscopy. Some of the newer scanning probe based techniques, such as scanning thermal microscopy and scanning capacitance microscopy, will be introduced. Several application examples will be presented to highlight the strengths and complimentary nature of these techniques. These examples will include: analysis of barrier metal composition as a function of depth into device features, two dimensional dopant profiling, measurement of ion implantation damage in SiC, analysis of fluorinated silicon dioxide film stability, development of wafer cleaning techniques, and the optimization of chemical mechanical polishing processes.

9:00am **AS+VT-FrM3 An Evaluation of SIMS Analytical Capabilities For Sub-0.25 Micron Implant Technology***, **V.K.F. Chia**,* Charles Evans & Associates

The applications of SIMS (secondary ion mass spectrometry) to the microelectronics industry are very diverse. In the ion implantation sector SIMS is perhaps the most widely used analytical technique. This is not too surprising because SIMS can detect all elements, produce high precision profiles, and provide elemental surface and bulk information with excellent detection sensitivity. As the design rule continues to shrink the question that arises is, "Can SIMS still be a valuable tool?". This paper addresses this question and reviews advances made in protocol development. For example, SIMS can perform high precision implant characterization (HPIC) to match the dose delivered by two different implanters to within <1% (67% confidence interval) during process replication or transfer, and for initial implanter qualification during fab start-ups. A better understanding of near-surface profiling phenomena has led to more accurate depth profiling of ultra-low energy ion implants (e.g. <1 keV B). SurfaceSIMS was developed to monitor and accurately quantify unintentional contamination that occurs during ion implantation, for example dopant cross-contamination in multi-purpose implanters, and to monitor inadvertent contamination related to sputter erosion or outgassing of implanter construction materials. As device dimensions shrink in size the need to perform ion implant characterization in small areas with high sensitivity becomes increasingly important. One solution is to interleave reactive primary ion species with high current density probes. This procedure enables 12 µm x 12 µm areas to be depth profiled with a sensitivity similar to analyzing a 180 µm x 180 µm area using Cs primary ions alone. In view of these advancements, SIMS appears to be well positioned to continue its primary role in ion implant characterization beyond the year 2000.

9:20am **AS+VT-FrM4 Accurate Dynamic Secondary Ion Mass Spectrometry (SIMS) and Auger Electron Spectroscopy (AES) Characterization of SiGe Stoichiometry and Hetero-Junction Bipolar Transistor (HBT) Dopant Levels***, **T.H. Büyüklimanli**, J.T. Mayer, M.S. Denker, R.L. Moore, C.W. Magee,* Evans East

The recent growth of the consumer microwave electronics market has spurred the development of SiGe HBTs. There are several physical and chemical properties of the device that affect performance and most importantly bandwidth. This has prompted us to take a fresh look at the acquisition and quantification of the SIMS and AES data. This paper investigates the characterization of two parameters of device fabrication: first the stoichiometry of the Ge-doped base layer, second the dopant (typically B) and impurity (typically O) concentration and distribution in the base layer. SIMS and AES were used to characterize a sample set ranging from 5-45 atomic percent Ge. Each sample was ion implanted with B, P, C and O. Differences in sputter rates, recommended analytical protocols (SIMS), data post-processing and changes in relative sensitivity factors will be addressed.

9:40am **AS+VT-FrM5 A Comparison Auger and TOF-SIMS Depth Profiling of Silicon Oxide Nitride Multilayers Using Low Incident Ion Energy***, **S.E. Molis**, R.E. Davis,* IBM Corporation, East Fishkill Facility*; D.W. Kisker,* IBM Research Division*; D. Paul,* Physical Electronics

The ever-shrinking dimensions of semiconductor devices have placed steadily more difficult challenges in front of analytical instruments and methods as well as fabrication tools and processing. In the future, this shrinkage will have a proportionally greater impact on the vertical dimensions. The SIA Technology Roadmap lists for example a gate oxide thickness equivalent of 2-3 nm by the year 2001, and a phasing out of SiO2 in favor of alternative dielectric materials. The difficulty of this analytical challenge makes it likely that no single technique will be able to tackle any type of complex process problem alone. Rather, a synergistic approach involving the strengths of each will be called for. New techniques are needed, and the current limits of current techniques must be extended. This paper describes one approach, teaming TOF-SIMS and Auger electron spectroscopy, with sputter ion gun designs which can provide adequate sputter rates at impact energies of less than 500 eV, to improve depth resolution. A Ni-Cr multilayer standard of thicker dimensions was used to measure and optimize experimental conditions. A set of various thin oxide and nitride single films and multilayers wa examined by both techniques, to mutual advantage. The TOF-SIMS approach generally gave superior depth resolution compared to Auger, although not as good as the structural view of X-TEM. The SIMS matrix effect was interpreted by comparison to the Auger profiles. TOF-SIMS was able to give some insight into the question of hydrogen content of the films. The propensity for thermal damage was also studied.

10:00am **AS+VT-FrM6 A New High Performance TOF-SIMS Instrument for 300 mm Wafer Inspection***, **E. Niehuis**, C. Bendel, D. Rading,* ION-TOF GmbH, Germany

We have developed a high performance TOF-SIMS instrument for the analysis of wafers up to 300 mm diameter. It includes a new sample stage with 5 axis and interferometric x,y position control for ultimate navigation accuracy. The instrument is equipped with a Ga liquid metal ion gun for surface analysis and imaging, and a flexible dual source gun with electron impact and Cs source for dual beam depth profiling. In a production environment high sample throughput, high reproducibility and ease of use are most important. To meet these requirements, we implemented complete instrument automation to setup the instrument for a specific task, to find a specific area on a wafer and to acquire and analyze the data. The navigation part includes the import of coordinates from other inspection tools, an auto-heigth-adjustment and optical pattern recognition. For the interpretation of the spectra we make use of a high mass resolution SIMS database for automated compound identification. In this paper we will describe the instrument performance and discuss the various applications of this tool in IC production. TOF-SIMS can be used for the screening of various surface contaminants like trace metals (alkali, transition metals), small inorganic molecules (e.g. sulfates) as well as organic contaminants (e.g. photoresist residues, cleaning agents, plasticizers from storage containers). The technique also offers depth profiling with excellent depth resolution for the characterization of gate oxides and ultra-shallow implants. In defect review TOF-SIMS provides high lateral resolution and detailed chemical information on sub-micron particles.

10:20am **AS+VT-FrM7 Automated Process Monitoring Using ESCA and Numerical Methods***, **D.J. Hook**, J.F. Moulder, J.S. Hammond,* Physical Electronics, Inc.

There currently exists a need in the electronics industry for automated process control to increase product yield and reliability. An example of this is the hard disk industries' push to higher media storage density that has placed increasingly stringent requirements on the lubrication media needed for disk surfaces. Similarly, uniformity of oxide thickness on silicon wafers is an important property that can affect the finished device and in turn overall production capability of a semi-conductor facility. The ability to obtain quantitative ESCA results over large areas and present information in an easy to understand visual format can provide feedback for the production environment. The combination of totally automated process monitoring with Graphical User Interface (GUI) driven film thickness calculations and large area mapping software is a new development in ESCA which can address this need. Examples of automatically collected lube thickness measurements on new and used hard disks and oxide thickness maps on cleaned 200 mm silicon wafers will be presented.

10:40am **AS+VT-FrM8 Measurement of Carrier Concentration and Lattice Absorption in Bulk and Epitaxial Silicon Carbide Using Infrared Ellipsometry***, **T.E. Tiwald,*** University of Nebraska, Lincoln*; S. Zollner,* Motorola Semiconductor Products Sector*; J.A. Woollam,* University of Nebraska, Lincoln*; J. Christiansen,* Motorola Semiconductor Products Sector*; P.G. Snyder,* University of Nebraska, Lincoln

We have measured the dielectric function of bulk nitrogen-doped 4H and 6H SiC substrates from 700 to 4000 cm@super -1@ using Fourier-transform infrared spectroscopic ellipsometry. We observe a strong reststrahlen band between 800 and 1000 cm@super -1@ due to photon absorption by transverse optical phonons. The shape of this band is influenced by plasma oscillations of free electrons, which can be described with the Drude model. A detailed analysis of the data allows the determination of the free electron concentration, which is between 10@super 18@ and 10@super 19@ cm@super -3@, in good agreement with electrical measurements. We were also able to determine the surface layer thickness for epitaxial 4H SiC (with an electron concentration of 10@super 16@ cm@super -3@) on heavily-doped bulk 4H SiC. Finally, we observe Berreman peaks near the longitudinal optical phonon energy in all samples. These interference effects are the result of carrier depletion and accumulation near the surface. The effect is strongest in the epitaxial sample and the more lightly doped substrates.

11:00am **AS+VT-FrM9 Si Dopant Site Within Ion Implanted GaN Lattice***, **H. Kobayashi**, W.M. Gibson,* State University of New York, Albany

There has been considerable interest in GaN for the fabrication of blue light emitting devices. In addition, this material is attractive for use in high temperature or high power electronic devices. Therefore, ion implantation for selective area doping is becoming more important for future GaN device technology. It has been demonstrated that Si and Mg ion implantation and post-implant annealing are useful to obtain n-type and p-type GaN, respectively. However, there is still little information on actual lattice location of impurities. We have investigated the Si dopant site in the GaN lattice using ion channeling technique in combination with Rutherford backscattering spectrometry (RBS), particle induced X-ray emission (PIXE) and nuclear reaction analysis (NRA). Metalorganic chemical vapor deposition (MOCVD) grown GaN on a c-plane sapphire substrate implanted with @super 28@Si at a dose of 7x10@super 14@cm@super -2@ with post-implant annealing was investigated. Channeling measurements were performed by taking angular scans around the and axes and recording RBS, PIXE and NRA yields for Ga, Si and N, respectively. The channeling results indicate that almost 100 % of Si goes into the Ga site when the samples are annealed at 1100°C for 30 minutes while for annealing at 1050°C and below, Si is distributed almost randomly. This suggests that a drastic change of Si substitutionality takes place in a narrow temperature region near 1100°C. Our results directly indicate that the electrical activation of Si implanted GaN with post-implant annealing is due to the formation of substitutional Si at this temperature.

11:20am **AS+VT-FrM10 Laser Assisted Etching of InP Studied with XPS***, **D.M. Wieliczka**, J.M. Wrobel, C.E. Moffitt,* University of Missouri, Kansas City*; J.J. Dubowski,* National Research Council of Canada, Canada

X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) have been used to study the surface chemistry and morphology of InP wafers after photo-chemical etching of the surface. The etching process employed 308 nm illumination from a XeCl excimer laser in conjunction with a low pressure atmosphere of 10%/90% Cl@sub 2@/ He mixture. The samples were exposed to laser radiation with fluences ranging from 73 mJ/cm@super 2@ to 210 mJ/cm@super 2@. The lower fluence is well below the ablation threshold for InP under vacuum conditions. The use of a Kratos AXIS-HS photoelectron spectrometer allowed for mapping the surface chemical composition within the illuminated region and in the vicinity with a 60 µm spot size. Photoelecron spectral lines from In, P, Cl, C, and O were monitored for determining the surface chemical composition and for creating surface maps of the illuminated regions. The results showed a distinct correlation between surface chemical composition and laser fluence. At high fluence levels, the surface composition changed dramatically between the illuminated region and the exterior. Evidence for In-Cl compounds was found within the crater with thermal processes occurring in the region near the crater. At low laser fluence, the etching process showed no thermal effects in the near crater region and produced a crater with minimal Cl incorporation. In addition to the chemical changes with fluence, the surface morphology is dramatically altered. At high fluence levels, SEM images indicate the etched surface was rough and deposits of ablated material were left in the vicinity of the crater. At low fluence the images indicate a better surface morphology. This work was supported by the University of Missouri Research Board.

Electronic Materials and Processing Division
Room 316 - Session EM-FrM

Fabrication and Characterization of Semiconductor Device Layers

Moderator: A. Bensaoula, University of Houston

8:20am **EM-FrM1 Optical, Structural, and Morphological Properties of Epitaxial Al@sub x@Ga@sub (1-x)@N(0001) Films Grown by Gas-Source Molecular Beam Epitaxy***, **J.E. Van Nostrand**,* Air Force Research Laboratory*; R.L. Hengehold,* Air Force Institute of Technology*; K.D. Leedy, M.L. Seaford, D.H. Tomich, C.E. Stutz, Q.-H. Xie,* Air Force Research Laboratory

Al@sub x@Ga@sub (1-x)@N/GaN(0001) is a material system of great interest due to its potential for optoelectronic and high temperature electronic applications. However, published studies on the growth and characterization of Al@sub x@Ga@sub (1-x)@N films are limited, and the structural and optical properties of Al@sub x@Ga@sub (1-x)@N films are not well understood. We present optical, microstructural, and morphological results for 0.5 µm thick Al@sub x@Ga@sub (1-x)@N thin solid films on 2.0 µm thick GaN on Al@sub 2@O@sub 3@(0001) grown by gas source molecular beam epitaxy. Films are deposited at 800°C with a 0.5 µm hr@super -1@ growth rate, and ammonia is used for the nitrogen source. High-resolution X-ray diffraction results show deformation of the unit cell in the Al containing layers for x<0.15 due to tensile biaxial strain. Measurement of the evolution of surface morphology as a function of Al mole fraction using atomic force microscopy shows a large increase in surface roughness with increasing Al mole fraction for x<0.15, followed by an order of magnitude decrease in roughness for relaxed films. Microstructural properties such as dislocation type and density as a function of Al mole fraction are systematically evaluated using cross-sectional transmission electron microscopy. Finally, low temperature (6K) cathodoluminescence is used to evaluate the location of the donor-bound exiton in the Al@sub x@Ga@sub (1-x)@N bandgap as a function of Al mole fraction. An approximately linear dependence on x is observed, suggesting the Al@sub x@Ga@sub (1-x)@N bandgap also exhibits a linear dependence on x.

8:40am **EM-FrM2 Investigation of High Temperature Characteristics of Metal-Insulator-Semiconductor Diode Structures Fabricated Using BN Layers Grown on GaN and SiC***, **D. Starikov**, N. Badi, I. Berichev, N. Medelci, A. Tempez, V. Zomorrodian, A. Bensaoula,* University of Houston

Dielectric materials commonly used for fabrication of silicon-based semiconductor devices did not prove their viability when applied on wide band gap materials for high temperature applications, such as GaN and SiC. Boron nitride layers grown by physical vapor deposition have several advantages over conventional dielectrics due to their high thermal and chemical stability, mechanical and radiation strength, and excellent surface morphology. In this work we will describe the basic technological processes for fabrication of Metal-Insulator-Semiconductor (MIS) structures on GaN and SiC using insulating BN layers. I-V curves measured in a temperature range up to 700 °C will be presented for MIS-structures based on GaN grown on sapphire, epitaxial 3-C SiC films grown on silicon, and 6H-SiC single crystal wafers. These data will be compared with results obtained from MIS-structures fabricated using similar technology on silicon wafers. The potential barrier height for all structures will be calculated using C-V and I-V measurements at different temperatures. Preliminary results show that GaN-based MIS structures rectify up to 600 °C, while those based on silicon lose their rectification characteristics only at 250 °C. The dependence of the potential barrier height on the thickness of the dielectric (BN) layer and its stability under high temperature vacuum annealing will be discussed and presented. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061

9:00am **EM-FrM3 Chemical Beam Epitaxy of GaAsN on GaAs (100)***, **J.W. Rogers, Jr.**, C.L. Aardahl, H.K. Yun, T.P. Pearsall,* University of Washington

Chemical beam epitaxy (CBE) has been used to deposit GaAsN on GaAs (100) at a growth pressure of order 5e-5 mbar and a substrate temperature of order 500C. Triethyl gallium, arsenic dimers, and an electron cyclotron resonance (ECR) nitrogen plasma were used as the Ga, As, and N sources, respectively. Secondary-ion mass spectrometry (SIMS) showed a maximum nitrogen content of 15% in the films grown in this study. Thermodynamic arguments predict that GaAs and GaN are immiscible due to the large discrepancy in atomic radii between As and N which leads to a positive heat of mixing for GaN and GaAs alloys. X-ray diffraction measurements show that higher nitrogen content does indeed result in phase segregation to a mixture of zinc-blende GaAs, zinc-blende GaN, and wurzite GaN depending on the growth conditions. However, unstrained alloys were deposited with a nitrogen content of up to 3%. Transmission electron micrographs and selected area diffraction patterns are used to discuss the orientation of segregated phases and ordering in the films. The effect of these morphological features on the band gap bowing parameter of the GaAsN system is discussed.

9:20am **EM-FrM4 InP Photocathode Surface Preparation by Atomic Hydrogen Cleaning***, **K.A. Elamrawi**, M.A. Hafez, H. Elsayed-Ali,* Old Dominion University

III-V semiconductors are efficient photocathodes. They provide a high quantum efficiency (QE), defined as the number of emitted electrons per incident photon. The QE is strongly reduced if the surface is contaminated with oxides and carbon compounds. For InP, the cleaning temperature is about 530 °C. At this temperature, incongruent evaporation occurs, and phosphorous evaporates preferentially leaving indium droplets on the surface. This heat cleaning process produces a surface that cannot be activated to Negative Electron Affinity (NEA). We use a low temperature cleaning process at 360 °C under atomic hydrogen irradiation. This process produces a phosphorous stabilized surface free of contaminants that can be activated to NEA. RHEED patterns acquired before the atomic hydrogen cleaning process show a halo indicating a thick oxide layer on the surface. However, the patterns acquired after cleaning show clear (2x4) reconstruction features. QE more than 6.5% is obtained after atomic hydrogen cleaning for InP photocathodes activated with cesium and oxygen. InP photocathodes revived by heating with atomic hydrogen irradiation produce higher QE than photocathodes revived by heating only.

9:40am **EM-FrM5 Deposition and Electroluminescent Properties of Sputter Deposited Zn(x)Mg(1-x)S:Mn***, M.R. Davidson, **K.E. Waldrip**, J.S. Lewis, D. Moorehead, B. Speck,* University of Florida, Gainesville, U.S.*; P.H. Holloway,* University of Florida, Gainesville*; S.S. Sun,* Planar Systems, Inc.

Alternating current thin film electroluminescent devices (ACTFELD) have been prepared using a ZnxMg(1-x)S:Mn phosphor. The phosphor films were deposited by RF magnetron sputter deposition. The composition of the films was varied by adjusting the substrate temperature causing the relative sticking coefficient of the ZnS and MnS to vary. It was found that the Mg gives a green shift of the peak emission of up to 17 nm. This shift is due to the increased crystal field on the Mn due to the smaller Mg ion substituting on a Zn site. The effects of the Mg on the crystal structure and emission have been characterized using XRD, TEM, and UV-Visible band-edge absorption spectroscopy. The effects of post-deposition anneal and fluxes on the ZnMgS:Mn ACTFELDs will be discussed.

10:00am **EM-FrM6 Small Area XPS Analysis of Silicon Wafers Employing Cu Line Technology***, **E. Principe**, R. Brigham, T.J. Schuerlein,* Charles Evans & Associates

Shrinking device sizes are requiring semiconductor manufacturers to change the materials they use in their processes. The semiconductor industry is becoming aware that the future generations of devices will no longer be able to utilize aluminum as a conductor. As a fundamentally new technology, the development of copper metallization using Damascene processes have undergone a great deal of investigation. It is understood that the chemical and physical states of the copper and surrounding silicon can alter device performance, and therefore these states must be controlled. X-Ray Photoelectron Spectroscopy (XPS, also know as Electron Spectroscopy for Chemical Analysis, ESCA) can provide information that is difficult, if not impossible, to obtain by other methods. XPS will be shown to provide chemical state identification of copper, as well as measure the copper oxide thickness. Residual copper concentrations on the silicon surface at various process steps will be reported.

10:20am **EM-FrM7 Epitaxial Ferroelectric Ba@sub (1-x)@Sr@sub x@TiO@sub 3@ Thin Films for Tunable Microwave Devices***, **C.L. Chen**,* University of Houston, U. S. A.*; F.F. Feng,* University of Houston*; Z.H. Zhang,* University of Houston, U. S. A.*; A. Brazdeikis,* University of Houston*; F.A. Miranda,* Lewis Research Center*; Y. Liou,* University of Houston*; W.K. Chu,* University of Houston, U. S. A.*; C.W. Chu,* University of Houston

Perovskite Ba@sub (1-x)@Sr@sub x@TiO@sub 3@ thin films have been synthesized on (001) LaAlO@sub 3@ substrates by pulsed laser ablation. Extensive X-ray diffraction, rocking curve, and pole-figure studies suggest that the films are (001) oriented and exhibit good in-plane relationship of SBTO//LAO. RBS studies indicate that the epitaxial films have excellent crystalline quality with an ion beam minimum yield of only 2.6 %. Atomic force microscopy studies indicate that the as-epitaxial films are atomic smooth under the selected growth conditions. The dielectric property measurements by the interdigital technique at frequency up to 1.0 GHz show room temperature values of the relative dielectric constant and loss tangent of 1000 and 0.007 with no bias, and 500 and 0.001 with 35 V bias, respectively. The obtained data suggest that the as-grown BSTO films can be used for development of room temperature high frequency tunable elements and DRAM applications.

10:40am **EM-FrM8 Reaction Pathways/Energetics for Chemical Attack of Amorphous Si-O-F and C-F-(H,OH) Low-k Dielectric Thin Films by Water Molecules***, **H. Yang**, G. Lucovsky,* North Carolina State University

Amorphous films of Si-O-F and C-F-(H,OH) are being considered for low-k inter-metal dielectrics in advanced CMOS devices. The relative stabilities of these different types of dielectrics with respect to chemical attack by water molecules are discussed. FTIR studies have provided the basis for a pseudobinary alloy model for Si-O-F with F-atoms incorporated solely in Si-F bonds. Network bonding statistics have been used to calculate the probability for F-atoms being i) isolated[1] on Si-atoms separated by one or more O-Si-O groups, ii) paired[1] on Si-atoms connected through at most one O-atom, and iii) more strongly clustered. Ab intio calculations are used to study reaction pathways for attack of Si-F bonds by water. For isolated Si-F bonds, the energy of attachment, E@sub a@, of a water molecule through one H-bond is Si-OH + HF, is exothermic by ~0.1 eV, whereas the reaction between a pair of Si-F bonds and a water molecule, HOH + 2Si-F --> 2HF + Si-O-Si, is exothermic by 0.7 eV. Based on the alloy model statistics, the ab initio calculations predict good stability against attack by water extending to ~10 at.% F, corresponding to a dielectric constant of 3.2 to 3.4. The situation is quantitatively different for the C-F materials. Reaction pathways for attack of C-F bonds by water have also been studied by the same ab initio approach. The attachment energies of water for isolated, and near-neighbor C-F bonds are each significantly lower, ~0.1 eV, and reaction pathways are endothermic: e.g., HOH + 2C-F --> 2HF + C-O-C is endothermic by 1.6 eV. This suggests that initial attack of C-F low-k materials by water must be through other bonding groups such as C-H or C-OH. Ab initio calculations are being extended to C-F-(H,OH) materials to study reaction pathways and reaction energetics. Supported by ONR, NSF and INTEL Corporation.

11:00am **EM-FrM9 Carbon Incorporation in SiGeC Alloys Grown by UHV/CVD***, **A.C. Mocuta**, D.W. Greve,* Carnegie Mellon University

We report on growth and carbon incorporation in Si@sub1-x-y@Ge@sub x@C@sub y@ alloys with up to 2% carbon concentration grown by Ultrahigh Vacuum Chemical Vapor Deposition using silane, germane and methylsilane as Si, Ge and C precursors. Alloy growths have been performed at temperatures ranging from 550 °C to 650 °C. Carbon incorporation has been studied for alloys with Ge content of about 5%, 10% and 20%. The Si@sub1-x-y@Ge@sub x@C@sub y@ layers grown on Si(100) substrates have been analyzed by High Resolution X-ray Diffraction (HRXRD) and Secondary Ion Mass Spectrometry (SIMS). For low methylsilane flow and growth temperature of less than 600 °C carbon is incorporated on substitutional positions in levels of up to 0.3%. With increasing methylsilane flow carbon begins to occupy interstitial positions as well but also, the germanium fraction in the layer begins to increase. For carbon concentrations of 1% or higher the crystal quality of the alloy is degraded. Thermal stability and critical thickness for layers with about 10% Ge and low carbon levels (0.2%) has also been studied. Addition of small amounts of carbon to SiGe layers greatly improves the thermal stability of the layer. Upon annealing for 1 hour at 900 °C no significant strain relaxation occurs in Si@sub1-x-y@Ge@sub x@C@sub y@ single layers or multiple quantum well structures while in similar SiGe structures with comparable strain and thickness strain relaxation is observed.

11:20am **EM-FrM10 XPS Study of the Role of Ti and TiN Caps on the Cobalt / SiO@sub 2@ Interface***, **T. Conard**,* IMEC, MAPFCA, Belgium*; E. Kondoh, W. Vandervorst,* IMEC, Belgium

Continuous downscaling of devices features and increases in operation frequency of ICs requires a low electric resistance of interconnects to transistors. Due to its low resistivity, high thermal stability and small lattice mismatch with Si, the integration of CoSi@sub 2@ into ultra large scale ICs is becoming the main stream. The role of metal caps layer (Ti, TiN) on the Si/Co interface chemistry has already been described but its effect on insulation dielectric such as SiO2 has not yet been widely studied. In this study, a 20 nm Co film was grown on a 150 nm LPCVD SiO@sub 2@ and Ti or TiN top layers were deposited on the Co layer without breaking the vacuum. The samples were annealed for 90 sec at 850 C in N@sub 2@ ambient and the specimens were analyzed by X-ray Photoelectron Spectroscopy (XPS) in depth profile mode using Ar@super +@ sputtering. Significantly different depth profiles were obtained depending on the nature of the cap layer. The multilayer with a top TiN layer presents a profile corresponding to sharp interfaces with only a limited diffusion of Ti inside the Co layer and no differences in chemistry of the interfaces due to the annealing procedure. The Co depth profile has a very symmetric shape. On the contrary, the presence of a Ti cap layer induces very strong modification of the interface reactions. First, an important diffusion of the Ti is observed through the Co layer is observed and an accumulation of Ti occurs at the Co/SiO@sub 2@ interface. At the interface, Ti is observed in an oxidized form and reduces the SiO@sub 2@ top layer. The effect of the annealing temperature will also be presented.

Magnetic Interfaces and Nanostructures Technical Group
Room 324/325 - Session MI-FrM
Magnetization Dynamics and Magneto-Optics

Moderator: J. Unguris, National Institute of Standards and Technology

8:20am **MI-FrM1 Magnetization Dynamics: A Study of the Ferromagnet/Antiferromagnet Interface and Exchange Biasing***, **R.E. Camley**,* University of Colorado, Colorado Springs **INVITED**

We use a method which employs a dynamic calculation of magnetization motion to find both the static configuration and the spin wave excitations in a ferromagnet/antiferromagnet layered structure. Our results for the static structure are similar to those found in Koon's model; i.e. in zero applied field the ferromagnet points perpendicularly to the easy axis of the antiferromagnet, and the surface spins of the antiferromagnet are in a surface spin flop configuration. The calculated hysteresis curve for this structure shows a small exchange bias, in agreement with typical experimental results. We explore how this bias depends on the parameters of the antiferromagnet and on the nature of the interface coupling. The spin wave modes are developed using the same simple model. The frequency of the lowest spin wave in the ferromagnet shows a dramatic dip when the ferromagnet spins begin to rotate - where the hysteresis curve drops as the field is reduced from the saturated state. The spin wave modes in the ferromagnet should be easily observed by Brillouin Light Scattering. The spin waves in the antiferromagnet also show dramatic changes as the antiferromagnet structure is changed.

9:00am **MI-FrM3 Switching Field Measurements of Longitudinal Magnetic Recording Media***, **A. Moser**, D. Weller, M.E. Best,* IBM Almaden Research Center **INVITED**

Media stability is one of the key issues in the development of future high density magnetic recording media, as it determines the lifetime of a disk. At short time scales the coercivity strongly increases and recording information requires high write fields. Both, media stability and enhanced coercivity at short time scales can be examined using switching field measurements H@sub CR@ as a function of the magnetic field pulse width t. The data can be analyzed within the framework of the Arrhenius-Neel law using the equation H@sub CR@ = H@sub 0@ (1 - [C log(t f@sub 0@)]@super n@).@footnote 1@ Here, the constant C describes the stability of the media and is related to the viscosity parameter. H@sub 0@ is an intrinsic switching field related to the anisotropy field H@sub K@, f@sub 0@ is an attempt frequency (of the order of 10@super 9@ Hz) and n is an exponent which takes values between 1/2 and 1. By measuring H@sub CR@ over more than 9 decades in time using a novel experimental method, we can determine both the stability parameter C and the switching field H@sub 0@ for a series of CoPtCr media of different thicknesses.@footnote 2@ These samples have varying areal moment densities Mrt between 0.17 and 0.39 memu/cm@super 2@ and remanence coercivities H@sub CR@ between 500 and 2500 Oe at a pulse width of 1 s. It will be shown that H@sub CR@ can vary by more than a factor of 3 over the observed range of pulse widths. The results are compared to conventional signal decay measurements and to experimental and theoretical results found in literature.@footnote 3@ @FootnoteText@ @footnote 1@M.P. Sharrock, IEEE Trans. Magn. 26, (1990) 193. @footnote 2@Samples provided by M. Doerner, IBM Storage Systems Division, 5600 Cottle Rd., San Jose, CA 95193 @footnote 3@M.Yu, M.F. Doerner, D.J. Sellmyer, MMM-Intermag ?98, San Francisco, Jan. 6-8, 1998

9:40am **MI-FrM5 Magnetic Properties of Submicron Magnetic Wires Fabricated by e-beam Lithography Investigated by using GMR Effect***, **T. Ono**, H. Miyajima,* Keio University, Japan*; K. Shigeto, K. Mibu, N. Hosoito, T. Shinjo,* Kyoto University, Japan

The magnetization reversal study of a single submicron magnetic wire is presented. The magnetization reversal in a single submicron magnetic wires can be very sensitively observed by utilizing the giant magnetoresistance (GMR) effect.@footnote 1@ GMR is the electrical resistance change accompanied with the change of magnetic structure. This means, in turn, the magnetic structure of the system can be determined from the resistivity measurements. In a wire case, the magnetic shape anisotropy restricts the direction of the magnetization to be parallel or antiparallel along the wire axis. The GMR change is directly proportional to the magnitude of the switching layer magnetization. A single NiFe(40nm)/Cu(20nm)/NiFe(5nm) trilayer wire 500 nm in width was prepared. An artificial neck was introduced in the wire. The temperature dependences of the nucleation field and the propagation velocity of the magnetic domain wall in the wire were studied by using the GMR effect. The result clearly shows that the artificial neck works as a pinning center for the magnetic domain wall. The temperature dependence of the nucleation field in a single submicron magnetic wire was investigated by measuring the coercive field at which the electrical resistance abruptly changes by the GMR effect. The nucleation field shows a thermal excitation behavior down to 5 K. The study at lower temperatures, down to 50 mK, is now in progress. By measuring the time dependence of the resistance during the magnetization reversal, the propagation velocity of the magnetic domain wall was estimated. Under the external magnetic field of 90 Oe, the velocity in the NiFe layer (40 nm in thickness and 500 nm in width) is about 5 cm/s at 77 K, the velocity of which is much smaller than that reported by Sixtus and Tonks for bulk NiFe wire in 1931.@footnote 2@ @FootnoteText@ @footnote 1@T. Ono, H. Miyajima, K. Shigeto and T. Shinjo, Appl. Phys. Lett. 72, 1116 (1998). @footnote 2@K.J. Sixtus and L. Tonks, Phys. Rev. 37, 930 (1931).

10:00am **MI-FrM6 Magnetic Reversal on Vicinal Surfaces***, R.A. Hyman,* Georgia Institute of Technology*; **M.D. Stiles**,* National Institute of Standards and Technology*; A. Zangwill,* Georgia Institute of Technology

Ultrathin films of magnetic material on non-magnetic vicinal substrates may be the simplest systems that exhibit non-uniform magnetization reversal. These systems can be modeled by equally spaced and infinitely long step edges separating flat terraces. The intrinsic four-fold anisotropy of the terraces is augmented by uniaxial anisotropy localized at the step edges. For in-plane magnetization, the zero temperature behavior of these systems depends on two dimensionless parameters: the ratio of the step anisotropy energy to the domain wall energy on the flat terraces, and the ratio of the terrace length to the domain wall width. Numerical results give a rich phase diagram for the hysteresis loop structure as a function of these two parameters. In some cases, simple analytic formula for the domain wall depinning field can be derived that agree well with numerical work. For some values of the system parameters, the calculated hysteresis curves exhibit the shifted loop structure found in experiments. The reversal processes are a combination of domain nucleation at step edges, depinning due to domain wall interactions, and coherent rotation in the center of flat terraces. No sharp transition separates the limit of reversal by coherent rotation from that of reversal by domain wall depinning from steps. Instead, there is a smooth crossover from coherent rotation dominated reversal to domain wall depinning dominated reversal and most major loop structures are obtained in both limits.

10:20am **MI-FrM7 Magneto-optics: Science and Technology***, **M. Mansuripur**,* University of Arizona **INVITED**

The current trend in rewritable optical data storage is toward the use of novel techniques to achieve densities and data rates that are superior to those achievable in hard disk magnetic recording. After a brief review of the magneto-optical properties of amorphous rare earth-transition metal alloys, we describe the methodology and potential advantages/disadvantages of solid immersion lens (SIL), front-surface recording, magnetic super resolution (MSR), land & groove recording, and partial-response-maximum-likelihood (PRML) detection schemes. We point out the differences between magneto-optical and phase-change media, which are the contenders for the rapidly developing market in Rewritable Digital Versatile Disk (DVD) products.

11:00am **MI-FrM9 Magnetism of Oxide NiO/@alpha@Fe@sub 2@O@sub 3@ Multilayers Studied by Magneto-Optical Faraday Effect***, **N. Keller**, M. Guyot, R. Krishnan,* Université de Versailles - CNRS, France

Magneto-optical Faraday measurements were performed on magnetic oxide NiO/@alpha@Fe@sub 2@O@sub 3@ multilayers. These samples have been prepared by pulsed laser deposition technique. The magnetic particularity of this model system is given by the antiferromagnetism of both base oxides NiO and @alpha@Fe@sub 2@O@sub 3@, which can only form the ferrimagnetic nickelferrite, NiFe@sub 2@O@sub 4@, by interdiffusion at the interfaces. The magnetism of this interlayer compound can be used as a local probe for the study of interdiffusion. Increasing the number of interfaces and hence the number of ferrimagnetic layers should lead to a regular increase of the total magnetic moment. Surprisingly, we observed a pronounced oscillation of the total magnetic moment with the number of interface layers.@footnote 1@ This oscillation can only be accounted for by assuming an antiparallel alignment of the moments of each interlayer with respect to the neighboring interlayers. The magneto-optical Faraday rotation was measured in the range from 1.5 eV to 3 eV on samples with a different number of interfaces. The ellipticity of the Faraday rotation shows a similar energy dependence when compared to Kerr spectra (rotation and ellipticity) of bulk NiFe@sub 2@O@sub 4@ taken from the literature. Especially two crystal field excitations at 2.3 eV at 2.8 eV appear in both spectra. However, normalization of the ellipticity by the number of interfaces doesn't show in the entire spectral range a unique dependence. At energies higher then ~2.1 eV a non - negligible difference can be observed in the normalized ellipticity for samples with different numbers of interface. @FootnoteText@ @footnote 1@N.Keller, M. Guyot, A. Das, M. Porte, R. Krishnan, Solid State Comm. 105 (1998) 333-337

11:20am **MI-FrM10 Magnetooptical Characterization of Layered Structures using Variable Angle of Incidence Generalized Magnetooptical Ellipsometry (VA-GME)***, **A. Berger**, M.R. Pufall,* University of California, San Diego

Recently, we have developed the technique of Generalized Magnetooptical Ellipsometry (GME) which allows a complete optical and magnetooptical characterization of a ferromagnetic bulk material.@footnote 1@ The technique combines the advantages of a generalized ellipsometric approach, enabling us to retrieve the maximum amount of information from a reflection experiment, with a high sensitivity measurement which allows for a precise determination of the relatively small magnetooptical material constants. In the present study, we have extended the concept of GME to multiple measurements with variable angle of incidence (VA). This not only allows for a consistency check of the previously performed magnetooptical bulk measurements, but in addition it enables us to characterize more complex layered structures by a simultaneous analysis of the VA-GME data sets. The experiments are performed with an experimental setup almost identical to the previously reported one, using a HeNe-Laser as a light source and 2 linear polarizers as the polarization sensitive elements.@footnote 1@ The sample orientation and the position of the detector arm of the ellipsometer are rotatable to allow for a variable angle of incidence. As a first test structure we have used a thick permalloy film with a SiO@sub 2@ overcoating. The magnetooptical structure analysis was then performed by a least square-fit procedure of the entire VA-GME data set. The consistency of the results was checked by a conventional ellipsometric measurement and by a self-consistent comparison of independently measured VA-GME data sets for different in-plane orientations of the magnetization. Our results clearly demonstrate the successful extension of GME to a variable angle of incidence measurement technique, which allows a complete optical and magnetooptical characterization of layered magnetic materials. This work has been supported by the ONR-N000-1495-10541, NSF-DMR-94-00439, and the CMRR at UCSD. @FootnoteText@ @footnote 1@A. Berger and M. R. Pufall, Appl. Phys. Lett. 71, 965 (1997)

11:40am **MI-FrM11 Magnetization Induced Optical Second Harmonic Generation as a Readout of Thin Film Magnetic Memories***, **T.V. Murzina**, A.A. Fedyanin, A.V. Melnikov, T.V. Misuryaev, O.A. Aktsipetrov,* Moscow State University, Russia

The search for new materials for the magnetic memory devices gives rise to the search for new nondestructive readout techniques. In the present paper magnetization induced second harmonic generation (MSHG) is suggested as a readout for thin magnetic film-based memories. The advantage of the MSHG probe is a high sensitivity of quadratic nonlinear-optical response to the magnetic properties of nanostructures and low-dimensional systems. The fundamental wavelength can be chosen far from electronic resonance. That makes the MSHG probe nondestructive, while the MSHG wavelength can be resonant and thus provide an effective MSHG output sensitive to the magnetic state of the memory. In this paper, the results of systematic MSHG studies in thin magnetic films are presented which demonstrate the potential of this probe as a readout for thin film-based magnetic memories. Three systems are studied: Gd-containing Langmuir-Blodgett (LB) films, rare-earth iron garnet films, and magnetic Co-Cu nanogranular films. The output of a Q-switched YAG:Nd@super +3@ laser at 1064 nm, a pulse duration of 15 ns and an intensity of about 1 MW/cm@super 2@ is used as a fundamental radiation. DC-magnetic field up to 1.5 kOe is applied to the films in a longitudinal NOMOKE configuration. The MSHG readout is shown to be based either on the magneto-induced rotation of the polarization of the second harmonic (SH) wave polarization or on the magnetoinduced changes in the SHG intensity and magnetoinduced changes of the SH wave phase. It is shown that in nonresonant conditions, i.e. as both the fundamental and SH wavelength is far from electronic resonance of a magnetic film, the probability of the misreading (readout error) is rather small. Apart from three magnetic systems studied, the MSHG readout can be potentially used for a wide variety of magnetic storages based on thin film structures.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+AS-FrM

Innovative Nanoscale Measurements

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am **NS+AS-FrM1 Nanoscale Variations in Surface Potentials at Interfaces***, **B.D. Huey**, D.A. Bonnell,* University of Pennsylvania, US

Nanoscale variations in the electronic properties of individual oxide grain boundaries have been directly measured. In-situ application of atomic force microscopy used as a Kelvin probe maps local field variations in the presence of lateral applied bias and current flow within an oxide grain boundary device, providing measurements while the device is in operation. The in-situ experiment involves: 1) applying a lateral bias across microfabricated contacts on varistor and SrTiO@sub 3@ bicrystals, and 2) simultaneously mapping the surface potential in the vicinity of grain boundaries. Voltage dependent properties of both multiple boundaries as well as carefully characterized individual interfaces are thus measured. The non-linear voltage dependence of potential barriers at the grain boundaries is additionally obtained at the nanoscale as a function of local orientation, chemical content, and position.

8:40am **NS+AS-FrM2 Noncontact Measurement of Electrical Dissipation using Ultrasensitive Cantilevers***, **T.D. Stowe**,* Stanford University*; D. Rugar,* IBM Almaden Research Center*; D.J. Thomson,* University of Manitoba, Canada*; T.W. Kenny,* Stanford University

We have used ultralow loss 0.17 µmm thick silicon cantilevers to measure electrical dissipation in insulators and doped silicon samples using a technique similar to the one originally developed by Denk and Pohl.@footnote 1@ Images were taken by recording the mechanical Q of a self-oscillating cantilever as it was scanned 10-100 nm above the sample surface in a perpendicular orientation. All experiments were performed at room temperature in vacuum with cantilevers having 10@super -4@-10@super-3@ N/m spring constants and 10-100 kHz resonant frequencies. Electrical dissipation was measured as function of applied voltage, tip-sample distance, and resistivity. We were able to measure electrical dissipation as small as 10@super -14@ N-s/m and ohmic losses as small as 10@super -18@ Watts. Using tips with 50 nm radii, we were able to simultaneously image permanent charge in the surface oxide and doping levels between 10@super 15@-10@super 19@ /cm@super 3@ in silicon with 200 nm spatial resolution. Possibilities for improving the spatial resolution and doping sensitivity of this technique will be discussed.

@FootnoteText@ @footnote 1@W. Denk and D. W. Pohl, Appl. Phys. Lett. 59, 2171 (1991).

9:00am **NS+AS-FrM3 Nanocalorimetry for Thermodynamic Measurements of Nanostructures***, **L.H. Allen,*** University of Illinois, Urbana-Champaign **INVITED**

This talk will focus on a novel calorimetry technique@footnote 1,2,3@ for measuring the thermodynamic properties of nanometer size material. The thermodynamic properties of material having small nanometer dimensions can be considerably different as compared to material in bulk form (e.g., the reduction of melting point). This occurs because of the tremendous influence of the surface energy. Conventional differential scanning calorimetry (DSC) techniques are extremely difficult to apply to the study of small structures because the total amount of heat generated during the transformation is too small as compared with the background heat capacity of the calorimeter. The new nanocalorimeter is fabricated using standard MEMS thin film techniques and it has the capability of measuring the dynamics of the energy exchange at the level of 0.2 nanojoule. This technique is so sensitive that it can easily measure the melting process of 1 Angstrom of Sn, which has been deposited on a Si-N surface. Results of specific materials studies will be discussed including the size-dependent melting point depression of small particles of Sn and Al and preliminary work on the coalescence of small clusters. @FootnoteText@ @footnote 1@S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath and L.H. Allen, "Size-Dependent Melting Properties of Small Tin Particles: Nanocalorimetric Measurements", Phys. Rev. Lett. 77, 99-103 (1996) @footnote 2@S.-L. Lai, P. Infante and L. H. Allen, "Heat capacity of Sn nanostructures via Thin Film Differential Scanning Calorimetry," Appl. Phys. Lett., 70, 43-46(1997). @footnote 3@S. L. Lai, J. Carlsson and L. H. Allen, "Melting Point Depression of Al Clusters Generated During the Early Stages of Film Growth: Nanocalorimetry Measurements," Appl. Phys. Lett., Appl. Phys. Lett. 72, 1098 (1998)

9:40am **NS+AS-FrM5 Recent Advances in Scanning Capacitance Microscopy***, **C.C. Williams,** J.S. McMurray, V.V. Zavyalov, J. Kim,* University of Utah **INVITED**

Scanning Capacitance Microscopy is a rapidly developing technique for the characterization of the electronic properties of semiconductor materials on a 10 nanometer scale. Oxide, semiconductor interface and near surface "bulk" properties can be studied by this technique. Recently, new capabilities have been developed to extract quantitative dopant/carrier profiles near electrical junctions in cross-sectioned devices. Built-in internal electric fields have been measured and compared with electrical models. Random distributions of nanometer scale "defects" have been observed at the surface of uniformly doped and oxidized silicon samples. Two-dimensional diffusion of dopant impurities has been measured by SCM and directly compared with predictions of TSUPREM4. These new developments and capabilities of the Scanning Capacitance Microscope will be described and presented.

10:20am **NS+AS-FrM7 Nanometer-scale Electrical Characterization of Semiconductor with a Scanning Capacitance Microscope***, **H. Tomiye**, Y. Takafumi,* Tohoku University, Japan

Recently, nanometer-scale material characterization has become a necessity in Si technology. The scanning probe microscope is one of the most powerful characterization techniques at this scale. A variety of information can be obtained by this technique which is of importance in the assessment of material and device aspects of silicon. Scanning capacitance microscope (SCaM) can clearly show local variation of capacitance, which reflects the electrical properties of a Si substrate, SiO@sub 2@/Si interface and SiO@sub 2@ layer. We have developed a SCaM/AFM consisting of a W wire cantilever and a capacitance sensor. The unique features of our microscope are as follows: (1) Our SCaM can directly detect a sample capacitance with / without using lock-in amplifier. It means we can measure capacitance (C) of the sample in addition to the capacitance derivative (dC/dV). (2) We can simultaneously obtain a SCaM image and C-V characteristics. It means we can achieve quantitative measurements of the capacitance at a nanometer-scale. (3) The spatial resolution for the capacitance measurements is estimated to be less than 20 nm. It is demonstrated that the local impurity concentration profiling of lateral p-n junction is achieved by the C-V measurements. We have injected electrical charge into a SiO2 layer and investigated the nature of charge storage at the SiO@sub 2@/Si system by the SCaM and C-V characterization. A shift of the flat-band voltage due to the trapped charges is observed, which enables one to estimate the density of trapped charge. This paper will report on the development of a SCaM and its applications to the characterization of SiO@sub 2@/Si and fabrication of a charge storage device.

10:40am **NS+AS-FrM8 A Study on the Post-stress Charges in SiO@sub2@ Films on Si by Scanning Capacitance Microscope***, **K. Mang**,* Samsung Electronics, Korea*; C.J. Kang, G.H. Buh, C.K. Kim, S. Lee, C. Im, Y. Kuk,* Seoul National University, Korea

Using scanning capacitance microscope, The induced traps on SiO@sub2@ were imaged with @<=@20nm spatial resolution. The static and dynamic behaviors of the electronic charges were evaluated. After a voltage stress, an anomalous post-stress charge generation and relaxation effect were found. Depending on the polarity of stress voltage, post-stress tip voltage and stressed time, different relaxation trend exists at the stressed area. The induced charge density in the stressed SiO@sub2@ film was higher with the stressed time The trap dynamics is also a function of initial stress field. With the high field applied to the SiO@sub2@ film, the larger and faster generation(or relaxtion) was observed. After the trapped charges are formed, the amount and polarity of the charge vary dynamically. It is believed that thermal excitation or tunneling of one or two electrons, can cause the turn around effect, which has been poorly understood so far.

11:00am **NS+AS-FrM9 Imaging Buried Interfacial Lattices with Quantized Electrons***, **I.B. Altfeder**, D.M. Chen,* The Rowland Institute for Science

We demonstrate that interfacial lattices buried under as much as 100 Å of a metal can be directly imaged by low temperature scanning tunneling microscopy with an unexpectedly high lateral resolution.@footnote 1@ To achive such a remarkable resolving power we expolite the presence of the quantum-size sigularities in the electron energy spectrum in the metal as well as its high sensitivity to the defects at the boundaries. Our theoretical model shows that this unique phenomena can be atrributed to the nondifractive scattering of the quantized electron waves at the interface as a result of their highly anisotropic motions in a two dimensional nano-structure. @FootnoteText@ @footnote 1@I. B. Altfeder, D. M. Chen, K. A. Matveev, Phys. Rev. Lett. (in press). @footnote 2@I. B. Altfeder, K. A. Matveev, D. M. Chen, Phys. Rev. Lett. 78, 2815 (1997).

11:20am **NS+AS-FrM10 Nanoparticle Near-Field Spectroscopy by a Microscopically Narrow (Subnanometer) Electron-Beam***, **H. Cohen**,* Weizmann Institute of Science, Israel*; T. Maniv,* Technion, Israel*; Y. Rosenfeld Hacohen, R. Tenne,* Weizmann Institute of Science, Israel*; O. Stephan, C. Colliex,* University of Paris-Sud, France

Single nanoparticle near-field spectroscopy is performed in a scanning transmission electron microscope at non-intersecting beam-particle configuration. Separating the surface collective modes from the entire excitations spectrum, the energy loss signal is quantitatively accounted for, using a relatively simple theoretical model. Advantaged by the sub nanometer size of the e-probe, the highly controlled beam-surface distance introduces an effective window in momentum space, exposed to a long wavelength relativistic dispersion, which provides an enhanced sensitivity to beam and particle size effects. The spatial dispersion of the particle dielectric function, associated with the electronic band structure, is practically filtered out. "Particle spectroscopy", namely the selective excitation of modes which characterize the particle geometry and size, is available at selected beam-particle distances.

Partial Pressure Measurements and Process Control Topical Conference

Room 317 - Session PC-FrM

Process Monitoring and Control

Moderator: M.L. Passow, IBM Corporation

8:20am **PC-FrM1 Challenges for Real-Time Control in Reactive Semiconductor Manufacturing Process Environments***, **G.W. Rubloff**,* University of Maryland **INVITED**

The potential of mass spectrometry and other chemical sensing approaches to determine dynamic chemical constituency through a reactive semiconductor process cycle holds substantial promise for process control and attendant manufacturing benefits. Applications to mainline VLSI processes have already demonstrated value in supplying metrology information (rates, deposition thickness, etch endpointing) and in revealing process mechanisms and equipment subtleties, information which significantly complements the existing raison-d'etre for RGA's in manufacturing, namely, equipment qualification and debugging. However, the benefits of advanced process control will require other elements. Use of sensor signals for metrology depends on having good sensor models, which in turn often means good models for the sensor IN the tool. Real-time or run-to-run control necessitates either good models or robust algorithms which are less sensitive to model or data error. Fault management - i.e., fault classification and prognosis as well as detection - requires multi-sensor integration including equipment state signals for decision support to minimize down-time, along with dynamic models for interpreting system behavior. This talk will provide examples for mass spec based metrology and process insight, along with an outline of how sensor information might lead to beneficial control and fault management responses.

9:00am **PC-FrM3 Reaction Analysis and Rate Metrology of Selective Area Silicon PECVD using In-Situ Real-time Mass Spectroscopic Sensing and Mass Balance Modeling***, **A.I. Chowdhury**, T.M. Klein, G.N. Parsons,* North Carolina State University

Thin film processes in microelectronics fabrication often have intermediate steps that need to be quantified for optimization purposes. These intermediate steps, including concurrent etching and deposition cannot be quantified using only final state analysis. Additional real-time process state data is required. Mass spectroscopy is a useful process state sensor for SiH@sub 4@ processes because it is particularly sensitive to changes in silane concentrations in the sampled gas. We use real-time in-situ mass spectroscopy and mass balance modeling to quantify deposition and etching reaction rates in a cyclic deposition/etch process that leads to selective area microcrystalline silicon PECVD. The procedure involves repeated cycles of a SiH@sub 4@/He/H@sub 2@ plasma followed by a He/H@sub 2@ plasma. In order to monitor reactant concentrations in real time, process trace data were collected at 30 amu corresponding to SiH@sub 2@@super +@, the principal SiH@sub 4@ related signal generated in the ionization region of the mass spectrometer. We have developed a mass balance model that can be used in conjunction with real-time sensor data, such as mass spectroscopy, to quantify deposition and etching rates in selective deposition. During SiH@sub 4@/He/H@sub 2@ flow, when the plasma is initiated, we observe a decrease in the silane signal that is correlated to film deposition. During the He/H@sub 2@ plasma the silane signal is larger when the plasma is on, and the change is a quantitative indicator of silane produced by etching. OES data does not show comparable sensitivity to silane concentration changes for our process. The transition from selective to non-selective conditions can be detected in real-time. A sharp change in slope of the silane signal is observed during etching, which is consistent with complete removal of stray nuclei from the non-receptive surfaces. Fitting the real-time mass spectroscopic data to the mass balance model we calculated the etch rate to be ~2.1 nm/min on receptive surfaces such as c-Si and ~4.5 nm/min on non receptive surfaces such as SiO@sub 2@. The values are consistent with other results. This demonstrates rate sensitivity for intermediate process steps. The mass balance analysis also reveals that these rates are obtainable only if real-time process sensor data is available.

9:20am **PC-FrM4 Sensor Integration on a W-CVD Cluster Tool for Real-Time Process Monitoring and Control***, **J.N. Kidder, Jr.**, Y. Xu, N. Gupta, T. Gougousi, G.W. Rubloff,* University of Maryland

Research in in-situ chemical process sensing and sensor integration is motivated by the potential value of real-time and in-line sensing for metrology, control, and optimization. In this work, the chemical composition of a W-CVD process flow downstream of the reactor was analyzed using a differentially-pumped closed ion source mass spectrometry system. LabView software and data acquisition hardware were employed to integrate equipment state signals (total pressure, valve status, temperature, etc.) with mass spectrometer measurements so that time-synchronized system behavior was obtained and the relation between the equipment and process variables was established. The sensor integration allowed us to monitor the reaction process via the chemical composition of the gas-phase reaction products while capturing the dynamics of the reactant delivery and pump behavior through the process cycle. Generation of product species from the W nucleation and growth stages as well as other time-dependent variations in the downstream process flow composition were detected with rapid response time (~2 s), which provided insight to the reaction dynamics at critical stages in the process. In addition, this sensor fusion facilitates identification of subtleties like flow rate fluctuation and run to run effects which are important for process design and fault management.

10:00am **PC-FrM6 In situ Measurement of Moisture Contamination in Reactive Process Atmospheres***, **J.J.F. McAndrew**, R.S. Inman, D. Znamensky,* Air Liquide*; J.-M. Girard,* Air Liquide, France*; G. Goltz,* France Telecom, France*; J.-M. Flan,* SGS-Thomson, France

In situ measurement of molecular contamination in semiconductor processing is important for (i) early detection of contamination events to avoid accidental misprocessing (ii) real-time control of purging procedures to improve tool utilization, and (iii) understanding of actual contamination levels in process atmospheres. In the present work the primary goal is to simplify chamber qualification and process more wafers between maintenance. Semiconductor processing applications use reactive atmospheres with which in situ monitoring equipment must be compatible. Achieving real benefits in a manufacturing environment requires a sensor which is user-friendly and reliable, even under demanding conditions. Absence of drift and reliability of calibration are also important. In order to simplify implementation, it is desirable to monitor as few species as necessary to obtain the desired information. Water vapor may be used as a general diagnostic of ambient contamination, because it is present in relatively high concentration in air and is often the most difficult species to eliminate from the process atmosphere. The implementation of Tunable Diode Laser Absorption Spectroscopy (TDLAS) for in situ monitoring of water vapor in a Rapid Thermal Processor (RTP) has been described previously.@footnote 1@ That work did not address compatibility with reactive atmospheres, as the RTP uses only nitrogen as process gas. Here, we will describe the implementation of TDLAS in aggressive environments, including application to silicon nitride CVD and other processes. Implementation of the TDLAS system in a CVD process poses significant challenges, as deposition of reaction products on the sensor optics must be carefully limited. In silicon nitride CVD, appropriate heating of the optics has been found to be critical. Water vapor levels measured during processing and their impact on process parameters will also be described, as will the use of real-time contamination measurement to improve tool-utilization by simplifying chamber qualification. @FootnoteText@ @footnote 1@J.J.F. McAndrew R. S. Inman, A. Haider and J. Brookshire, 44th International Symposium of the AVS (1997) Abstract Number: 1159: Program Number: MS+VT-ThA7 (submitted to JVST A)

10:20am **PC-FrM7 RGA Process Monitoring in Semiconductor Manufacturing***, **J.M. Baker**,* IBM T.J. Watson Research Center **INVITED**

Although RGA's have been a mainstay in vacuum technology for decades, the semiconductor industry has been slow in realizing their potential for tasks other than leak checking and vacuum troubleshooting. This is in large part because the pace and culture of the manufacturing environment provides neither the time nor the skill to deal with the combined complexities of a process tool plus an RGA system. To succeed in this environment, it is necessary to extend the basic sensor technology and build the infrastructure so that the sensor is tightly integrated with the process tool and can adapt to the process and product types. I will show how we have addressed some of these obstacles in IBM fabs through a combination of distributed hardware and software. By incorporating tool signals with the data collection software, we have been able to detect and stop contaminated wafers at a degas station in the presence of interfering pressure bursts. Through links to factory/tool control software, we have been able to obtain recipe information and adjust our monitoring methods to different process chemistries. With this capability, we have been able to collect extensive data and observe a variety of interesting and often unexpected behavior, examples of which will be presented. In concluding, I will discuss some of the implications of our experience for utilizing versatile sensors such as RGA's as part of an advanced fault detection or process control system and the importance of having the information infrastructure necessary to closely integrate with the tool, the process, and ultimately the product.

11:00am **PC-FrM9 Process Monitoring of Chemical Vapor Deposition Systems by In-situ Gas Analysis***, **B. Lu**, E. Baker,* Novellus Systems, Inc. **INVITED**

Chemical vapor deposition (CVD) is a key technology for both interconnection and front-end wafer processing in advanced IC fabrication. CVD systems present a challenge for process state monitoring due to the inherent complexity of the process chemistry involved. When combined with other process knowledge, in-situ gas analysis using mass spectrometry (typically referred to as RGA) can provide real-time information representing the process chemical composition, process sequence, and equipment status. Consequently, such process monitoring tools can aid significantly in the continuous improvement and new product development of semiconductor processes and process equipment. Several applications will be presented to illustrate the use of a properly configured mass spectrometer on CVD process systems for (1) rapid learning of process chemistry and process state, (2) verification of system design improvement, and (3) optimization of loadlock operation to eliminate residual air contamination. We will also discuss some of the current obstacles that must be overcome in the use of mass spectrometer as a "full-time" process state sensor.

Plasma Science and Technology Division
Room 318/319/320 - Session PS-FrM
Plasma-Surface Interactions - II

Moderator: J.E. Johannes, Sandia National Laboratories

8:20am **PS-FrM1 Large Enhancement of Silicon Etch Rate by Metal Contamination***, P.G.M. Sebel*[1]*, L.J.F. Hermans, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

Given the ever decreasing dimensions of I.C.'s, it is essential to understand the various influences which affect the etching behaviour. We found a remarkably large enhancement of silicon etch rates by even small contamination with Ni and W. Our experiments indicate that the contamination migrates into the silicon due to vacancy production by ions. The experiments were performed in a molecular beam setup, where silicon is etched by XeF@sub 2@ and Ar@super +@ ions. The etch behaviour is monitored by a mass spectrometer using the SiF@sub 4@ signal. The effect of contamination appears very pronounced when the ion beam is switched off. With contamination, a temporary enhancement of the spontaneous etch rate is measured. With traces of contamination in the order of 0.01 ML the etch rate may be enhanced by a factor of 2 for W and somewhat less for Ni. It is concluded that the contamination moves into the silicon by diffusion to vacancies created by the Ar@super +@ ions, as proposed by Hart et. al. for Cu contamination.@footnote 1@ For 1 keV Ar@super +@ ions the contamination moves to a depth of 30 Å, equal to the penetration depth of the ions. As the effect of contamination disappears after etching of 170 Å, it is concluded that contamination has a catalytic effect on the silicon etch rate. Simulations, which describe the measured effect of contamination very well, indicate that only 3% of the contamination is removed after etching a monolayer silicon. Besides this catalytic effect, there are indications that the etch rate can be lowered under certain conditions, because of the formation of silicides. @FootnoteText@ @footnote 1@R.R. Hart, H.L. Dunlap and O.J. Marsh, J. Appl. Phys. 46, 1947 (1975).

8:40am **PS-FrM2 Laser Detection of Chlorinated Neutral Etch Products During Cl@sub 2@ / Ar@super +@ Etching of Si(100)***, N. Materer, R.S. Goodman, S.R. Leone,* JILA, NIST, and University of Colorado, Boulder

Pulsed laser single-photon ionization time-of-flight mass spectrometry is used to investigate neutral etch products formed during ion enhanced etching of Si(100). Single-photon ionization is accomplished using the ninth harmonic of a Nd:YAG laser at 118 nm to ionize neutral species. This approach eliminates dissociative ionization difficulties found in conventional electron impact ionization. Ions are first ejected from the region in frunt of the wafer by pulse field extraction prior to the laser pulse. The Ar@super +@ ion bombardment energy is varied from 275 to 1000 eV, and the flux of molecular chlorine is varied from 10@super 1@@super 4@ to 10@super 1@@super 5@ molecules per cm@super 2@. Under all conditions examined, SiCl is the major product. Neutral Si atoms are also detected during etching and there is some evidence for SiCl@sub 2@. The Si and SiCl products decay within 20µsec after a 500µsec ion pulse. This fast decay supports a mechanism in which these etch products are formed in a direct collisional process. In addition, the influence of the molecular chlorine flux is examined in detail. The introduction of molecular chlorine is found to first rapidly increase the yield of neutral Si and, at higher fluxes, to slowly decrease the yield. This subsequent decrease is attributed to the generation of an increasingly chlorinated surface. As in the case of Si, the yield of SiCl as a function of molecular chlorine flux increase rapidly at first. However unlike the Si yield, this fast increase is followed by a gradual increase at fluxes higher than 10@super 1@@super 5@ molecules per cm@super 2@. The direct detection of etch products results mechanistic details that can be compared to recent molecular dynamic simulations.

9:00am **PS-FrM3 Recombination of Halogen Atoms on Surfaces***, **J.W. Coburn**, G.P. Kota, D.B. Graves,* University of California, Berkeley **INVITED**

The recombination of halogen atoms [F, Cl, Br] has been measured as a function of temperature on a variety of surfaces [Si(111), poly-Si, WSi, W, quartz, photoresist, stainless steel, anodized Al]. Beams of halogen atoms were directed onto the surface under study in an ultrahigh vacuum system and the species evolved and reflected from the surface were detected with a differentially pumped modulated beam mass spectrometer. Since the halogen atoms undergo only a single collision with the surface, low recombination coefficients [less than a few percent] cannot be measured. In all cases studied, the recombination coefficient decreased with increasing surface temperature. The magnitude of the recombination coefficient for the various gas-surface combinations studied varied from as large as 0.8 to below the limit of our measurement [a few percent]. The recombination of Cl atoms on poly-Si was substantially larger than on Si(111). In general, the recombination coefficient for F atoms was much less than for Cl and Br atoms. The data is interpreted in terms of an incident atom or a moving physisorbed atom recombining with an immobile weakly chemisorbed atom.

9:40am **PS-FrM5 Removal of Si-O, Si-C and Si-F by Hydrogen Bake after Reactive Ion Etching on the Silicon Surface***, **Y.-B. Kim**, M. Caymax, H. Bender, S. Vanhaelemeersch,* IMEC, Belgium

In order to remove the damage/contamination left by Reactive Ion Etching (RIE) in a fluorocarbon chemistry on Si surface, a cleaning process consisting of an oxygen plasma/HF/H@SUB 2@ bake has been developed. ARXPS found Si-F, Si-C, Si-O and C-C/H bonds under the CF@sub x@ residues after RIE. Oxygen plasma formed a 2 nm thick film of fluorinated oxide on the RIE samples, removing the CF@sub x@ and C-C/H. A 2 % diluted HF dip for times between 10 and 200 s of the samples treated in RIE/oxygen plasma could not remove the Si-C, Si-F and Si-O. Next, the samples processed in RIE/O-plasma/HF were baked for 10 min at different temperatures (500 - 900 °C) in 1 bar of molecular hydrogen followed by quantitative XPS measurements. Up to 600 °C, no significant change in Si-C and Si-F was detected. Si-F and Si-C bonds decreased from 700 °C on and disappeared completely at 800 °C (Si-F) resp. 900 °C (Si-C). Si-O, which is abundantly present, is stable up to 800 °C, and abruptly decreases at 900 °C. AFM and MIR spectra respectively showed that the surface roughness decreases abruptly and the surface was reconstructed to a (2x1) dimer structure after a 900 °C anneal. A possible mechanism explaining these observations will be presented. Si-F and Si-C are formed by dissociation of the fluorocarbon radicals on the top surface and by insertion of the F and C into the upper atomic layers of the Si lattice by reactive ion mixing during the RIE. The observation that Si-O is removed very slowly by HF dipping indicates that O probably also gets buried into the Si matrix during the RIE. F is removed during hydrogen annealing by formation of the volatile HF at rather low temperature. The oxygen bonds are removed at 900 °C due to the consumption of the silicon surface atom on the Si-O sites by the well known reaction between Si and SiO@sub x@ resulting in volatile SiO. C is also removed at this temperature by its reaction with O into the volatile CO or CO@sub 2@.

10:00am **PS-FrM6 Characterisation of Self-aligned Contact Etch Processes using X-ray Photoelectron Spectroscopy, Time-Of-Flight SIMS, and Optical Emission Spectroscopy***, **F.H. Bell**,* Siemens AG, Germany*; T. Lill,* Applied Materials*; A. Cuthbertson,* Siemens Microelectronics Ltd, England*; U. Scheithauer, R. Treichler,* Siemens AG, Germany

The self-aligned contact process (SAC) is one of the key technologies for 64M DRAM fabrication and beyond. The oxide etch process relies on C@sub 4@F@sub 8@/CO/O@sub 2@ gas mixtures to provide high selectivity between oxide and the nitride barrier layer. Critical manufacturing issues are etch stop caused by fluorocarbon polymer deposition and shorts between bitline conatcts and gate due to insufficient oxide to nitride selectivity. The robustness of the process is strongly influenced by the ratio of the C@sub 4@F@sub 8@, CO, and O@sub 2@ gases. In order to understand the mechanism of the selective oxide to nitride etch, we analysed the oxide and nitride surfaces after etching using x-ray photoelectron spectroscopy (XPS) and time-of-flight SIMS. XPS results show that the composition of the fluorocarbon polymer film on nitride is only slightly influenced by the CO and O@sub 2@ gas flows whereas the thickness of the polymer film strongly decreases with oxygen addition. TOF SIMS analyses show that the higher the CO flow the more carbon is implanted into the nitride barrier layer. Since the nitride etch rates decrease as a function of CO flow and increase with oxygen addition, the selectivity between oxide and nitride is found to depend on two mechanisms: the passivation of the nitride barrier layer by formation of a

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

fluorocarbon polymer film and the implantation of carbon in the nitride caused by the CO gas in the SAC etch chemistry. Due to the small open area of the SAC process, optical emission spectroscopy studies were performed to improve end point detection and thus establish a robust production process.

10:20am **PS-FrM7 Experimental Investigation of the Respective Roles of Oxygen Atoms and Electrons in the PECVD Deposition of SiO@sub 2@ in O@sub 2@/TEOS Helicon Plasmas***, **A. Granier**, C. Vallée, A. Goullet, K. Aumaille, G. Turban,* Institut des Materiaux de Nantes, France

The respective roles of electrons and oxygen atoms in the plasma enhanced chemical vapor deposition of SiO@sub 2@-like films are investigated in a rf helicon oxygen/tetraethoxysilane (TEOS) plasma. The O atom density (a few 10@super 13@ cm@super -3@) and flux are monitored by actinometry and the electron density (a few 10@super 10@ cm@super -3@) by combination of optical emission spectroscopy (OES) and Langmuir probe analyses. The variations of the electron and atomic oxygen densities are studied as a function of the rf power (up to 500 W), the pressure (1-25 mTorr) and the organosilicon fraction in the O@sub 2@/TEOS plasma, simultaneously to the measurement of the deposition rate (using in situ ellipsometry) and analysis of the deposited films. The incorporation of ethoxy and silanol groups is determined from infrared spectroscopy. The refractive index and density of the films are deduced from UV-visible spectroscopic ellipsometry and gravimetric measurements respectively. It is shown that the TEOS fragmentation and the deposition rate are strongly related to the electron density while the main role of oxygen atoms is the etching of the organic part of the growing film, and not to dissociate the organosilicon molecules. In order to gain insight into the etching of the growing film by oxygen atoms, organosilicon films freshly deposited in a TEOS rich plasma are exposed to a pure oxygen plasma. During this post-exposure to an oxygen plasma, the film and the plasma are analyzed by ellipsometry and OES respectively : the film etching is clearly evidenced by the significant decrease in film thickness and the emission from CO, OH and H excited species which are related to the CO, CO@sub 2@ and H@sub 2@O etching products. It is furthermore shown that the film undergoes structural modifications over several ten nanometers.

10:40am **PS-FrM8 Surface Chemistry Mechanism of Oxide Etching by High Density C@sub 2@F@sub 6@ Plasma***, J. Feldsien, T. Panagopoulos, **D.J. Economou**,* University of Houston

Fluorocarbon plasmas have been studied extensively because of their use in selectively etching oxide over silicon. It is widely known that these plasmas produce unsaturated fluorocarbon radicals that may polymerize on surfaces in contact with the plasma. Oxide surfaces exposed to intense ion bombardment, on the other hand, are etching. More work remains to be done to understand the mechanisms that produce the observed behavior. In this work, a comprehensive surface chemistry model was developed to understand the mechanism of etching or deposition on oxide surfaces exposed to a high density C@sub 2@F@sub 6@ plasma. The surface chemistry model in combination with a gas phase plasma chemistry model developed by E. Meeks and J. Johannes of Sandia National Labs was implemented in the Modular Plasma Reactor Simulator (MPRES) to study oxide etching and uniformity under typical processing conditions. Simulation results on etch rate and uniformity as a function of source power, bias power, and pressure were consistent with experimental data. The transition from polymerization to etching as the ion bombardment energy (bias power) was increased was also captured by the simulation. Under low pressure conditions (several mtorr) the ion flux peaked at the wafer center while the neutral flux peaked at the wafer edge. Under such conditions, the oxide etch rate was edge fast. This supports the important conclusion that oxide etching is ion driven but neutral dominated. Surface coverages by important species and their interrelation to etch or deposition rate will also be discussed. This work was supported by Sandia National Laboratories/SEMATECH.

11:00am **PS-FrM9 Large Positive Silicon Ion Clusters in a Remote Silane Plasma***, **W.M.M. Kessels**,* C.M. Leewis, M.C.M. van de Sanden, D.C. Schram, Eindhoven University of Technology, The Netherlands

We report on the production of hydrogen poor cationic silicon clusters Si@sub n@H@sub m@@super +@ with up to ten silicon atoms in an expanding argon-hydrogen-silane plasma having implications for hydrogenated amorphous silicon films deposited by remote deposition techniques. It is shown that these cationic clusters are inevitably created by silane ions initiating chain reactions with silane when the product of silane density and geometrical path length is large. The initial silane ions are, in the plasma under consideration, produced by dissociative charge exchange between argon and hydrogen ions, emanating from the thermal plasma source, and silane. The deposition itself is dominated by SiH@sub 3@-radicals created by hydrogen abstraction from silane by atomic hydrogen emanating from the source and this has been determined by appearance potential mass spectrometry. The small hydrogen content (the clusters contain dominantly one hydrogen atom) in comparison with, e.g., ions in conventional rf silane plasmas is attributed to the high gas temperature due to the thermal plasma source used. The observation proves furthermore that the often quoted rates for the chain reactions of Mandich and Reents@footnote 1@ are not appropriate in this type of plasmas as even ions with more than six silicon atoms have been observed to a large extent. Moreover, a simple computer code showed that the rates for the chain reactions are not heavily depending on the number of silicon and hydrogen atoms present in the ion in contrast to their results. The contribution of the ions to film growth as determined from a combination of mass spectrometry and Langmuir probe measurements will be presented for various conditions and the influence of the ion clusters on the hydrogenated amorphous silicon film quality will be discussed. @FootnoteText@ @footnote 1@ See, e.g., W.D. Reents, Jr. and M.L. Mandich, Plasma Sources Sci. Technol. 3, 373 (1994).

11:20am **PS-FrM10 Surface Chemistry of NF@sub 3@ Plasma and Si Surface Interaction***, **T.W. Little**,* University of Washington*; A. Endou, A. Miyamoto,* Tohoku University, Japan*; M. Kitajima,* National Research Institute for Metals, Japan*; F.S. Ohuchi,* University of Washington

As an etchant gas, nitrogen trifluoride (NF@sub 3@) has become a viable contender to such mainstays in the semiconductor industry as carbon tetrafluoride (CF@sub 4@) and other perfluorocarbon compounds (PFCs) for certain plasma etching applications involving silicon (Si). Despite the technological importance of NF@sub 3@, there have been almost no studies on the interaction of NF@sub 3@ with Si from a surface science point of view. We have used x-ray photoelectron spectroscopy (XPS) and other diagnostics to determine the chemistry of interaction of NF@sub 3@ and Si surfaces. Although XPS results for the Si 2p core level are similar to those found for other etchants, we have seen unusual behavior in the F 1s core level and F 2s quasi-core level spectra. In addition to a F peak resulting from Si-F bonds, there are significant high-binding energy components which indicate that F is assuming a more positive or even neutral charge. The appearance of these peaks is closely related to both the type and amount of diluent gas. Upon heating, the high binding energy components are seen to disappear. These results lead to the supposition that F may be incorporated into the Si lattice as a result of an ion bombardment damage mechanism. While XPS is sensitive to changes in local chemistry, we have also applied a novel, in-situ Raman scattering technique which is sensitive to plasma surface interactions before they have progressed to the state in which chemical changes can be measured by XPS. The results of these measurements are described and compared with results obtained from XPS and other analytical techniques. In an effort to understand the energetics of F interaction with the Si lattice, we have also used cluster calculations to determine the most likely F sites.

11:40am **PS-FrM11 Operating High Density Plasmas in a Low Density Range : Applications to Metal Etch Processes***, **P. Czuprynski**,* France Telecom CNET/DTM/TFM, France*; O. Joubert, L. Vallier,* France Telecom CNET, France*; M. Heitzmann,* CEA LETI, France*; N. Sadeghi, J.P. Booth,* CNRS, France

In metal etching where complicated and thick metal stacks have to be etched on severe topography, selectivity between metal and resist is a critical problem. In practice, using standard Cl@sub 2@/BCl@sub 3@ etching chemistries and inductively coupled plasma sources (ICP) dedicated to metal processes, metal/resist selectivity higher than 3 are difficult to obtain. In this paper, we present a new way of operating high density plasma sources which greatly improve the selectivity issue of metal etch processes. The principal of the technique is to operate a high density plasma source in a low density mode (by strongly decreasing the RF power injected in the source, typically by a factor of 4) while keeping unchanged the RF power injected in the chuck to bias the wafer. Different techniques are used to compare the low density and high density modes. First, optical emission techniques are used to compare the dissociation efficiency of both modes and therefore get some information on the relative fluxes of Cl@sub 2@ and Cl species in the discharge. The ion current density (J@sub i@) and ion energy are also measured when the plasma source is operated in the low and high density modes (using identical chuck power conditions). The ion current density is measured using a new type of electrostatic probe whereas ion energy is simply estimated by measuring the self-bias voltage in the matching network of the chuck. The influence of low and high density modes on metal etch processes are evaluated using Cl@sub 2@/HCl chemistries. A strong increase in resist/metal selectivity is measured when the source is operated in the low density mode while perfectely anisotropic etching profiles of the metal stacks are still obtained. Finally, a simple model taking into account the chlorine coverage on the resist surface (as measured by in situ XPS), the ion density and ion energy is proposed to describe the resist etching rate. This simple model is useful to explain why operating ICP sources in a low density mode allows the resist consumption to be strongly decrease during etching processes. @FootnoteText@ This work has been carried out within the GRESSI consortium between CEA-LETI and France Telecom-CNET.

Surface Science Division
Room 308 - Session SS1-FrM
Surface Structure and Strain

Moderator: R.Q. Hwang, Sandia National Laboratories

8:20am **SS1-FrM1 Ultrathin Metal Films on W(111) and W(211): Nanoscale Faceting, Structure, Electronic Properties, and Reactivity@footnote 1@*,* *T.E. Madey,*** Rutgers, The State University of New Jersey **INVITED**

The W(111) surface is morphologically unstable when covered by monolayer films of certain metals (including Pt, Pd, Rh, Au), and develops nanoscale 3-sided pyramidal facets with mainly [112] faces upon annealing. In the present work, we focus on the structure, electronic properties and reactivity of planar and faceted W(111) and W(211) covered by ultrathin films of metals (0 - 8 ML, mainly Pt, Pd, Rh) and non-metals (S, O). The measurements include UHV-STM, soft XPS (SXPS) using synchrotron radiation, Auger spectroscopy, LEED, and thermal desorption spectroscopy. The observed formation of 3-sided pyramids with both [110] and [112] facets, as induced by 1 ML of overlayer metal, is predicted also by recent first-principles calculations of surface energetics. The faceting is caused by an increased anisotropy in surface free energy that occurs for the film-covered surfaces. The adsorption of S induces a different reconstruction with nanoscale texturing of the surface. At coverages above 1 ML, SXPS data indicate that interfacial alloys are formed upon annealing films of Pt and Pd, but not Au. These findings are discussed in terms of structural and electronic properties of bimetallic systems. The relevance to the surface chemistry of a structure-sensitive reaction (acetylene cyclization to benzene over Pd/W) is also discussed. @FootnoteText@ @footnote 1@Supported in part by US DOE, Office of Basic Energy Sciences @footnote 2@Collaborators include C.-H. Nien, J.J. Kolodziej, K. Pelhos, I. Abdelrehim, H.-S. Tao, R. Barnes (Rutgers); J. Keister, J.E. Rowe (NC State); J. Eng, J.G. Chen (EXXON); C-T. Chan (HKUST)

9:00am **SS1-FrM3 Determination of Thin Film Interface Structure by the Quantum Size Effect in Electron Reflectivity*,* *M.S. Altman,*** *W.F. Chung,* Hong Kong University of Science and Technology, Hong Kong*; H.C. Poon, S.Y. Tong,* University of Hong Kong, Hong Kong

It has long been recognized that it is very difficult to obtain detailed structural information of buried interfaces. The quantum size effect (QSE) in electron reflectivity offers some interesting insight into this and other structural features of thin films. The QSE has been understood qualitatively in the past to be an interference phenomenon between the electron waves which are reflected from the surface of a thin film and from the interface between film and substrate. The prominent QSE interference peaks which occur at very low energies are sensitive indicators of film thickness. We have examined the QSE in electron reflectivity from Ag films on the W(110) surface using the low energy electron microscope (LEEM) as an electron interferometer. This approach allows the reflected intensity from regions of different film thickness to be distinguished with atomic precision. Fundamental disagreement was found between the unique experimental data provided by LEEM and the predictions of the simple free electron model which has been invoked in the past to explain the QSE. A quantum mechanical Kronig-Penney model is presented as the first step towards a better understanding of the QSE. An analysis of the QSE peak positions by dynamical theory, aided by R-factors, also provides an accurate determination of the Ag-W interface spacing as a function of the Ag film thickness.

9:20am **SS1-FrM4 Interaction of Dislocations on Strained Metal Films*,* *J. de la Figuera,*** *K. Pohl, A.K. Schmid, N.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

Misfit dislocations appear in thin film growth to relieve the mismatch between substrate and film. A general family of dislocation networks has been found on substrates with triangular symmetry such as Pt(111), Ru(0001) and Au(111). A common uncertainty in understanding the observed surface structures is the stacking sequence followed by each adlayer, information that is relatively simple to extract for single layer films but requires more detailed information in multilayer films. Another recurrent question is the role played by the substrate in the network structure and periodicity, as some networks are attributed to ``long range elastic effects'' on one hand,@footnote 1@ but in other cases can be explained disregarding those effects.@footnote 2@ Cu on Ru(0001) presents a variety of different networks as a function of film thickness,@footnote 3@ and can be considered a testbed for the study of misfit dislocations on a triangular substrate. But even in this case, most of the studies have not dealt in detail with the stacking sequence in the first few layers (other than by assuming that the dislocations observed are present at the interface between the substrate and the Ru film). We will discuss how one can use STM to unambiguously determine the stacking sequences in films thicker than one monolayer. We then proceed to determine the range of dislocation interactions. On the basis of these measurements it is possible to compare the model of long ranged dislocation interactions due to Ru substrate relaxations versus local exponentially decaying interactions between dislocations due to 2-D distortions within the Cu film. @FootnoteText@ @footnote 1@S. Narasimhan and D. Vanderbilt, Phys. Rev. Lett. 69, 1564 (1992). @footnote 2@J. C. Hamilton and S. M. Foiles, Phys. Rev. Lett. 75, 882 (1995). @footnote 3@C. Günther et al, Phys. Rev. Lett. 74, 754 (1995).

9:40am **SS1-FrM5 Low Energy Electron Microscope Measurements of Oxygen-Induced Strain Relief on Si(001)***, J.B. Hannon, B.S. Swartzentruber,* ***G.L. Kellogg,*** Sandia National Laboratories

Real-time observations of step configurations on Si(001) with the low energy electron microscope (LEEM) show a continuous and irreversible change in the populations of the (1x2) and (2x1) domains (i.e., the ratio of adjacent terrace widths) upon exposure to oxygen at elevated temperatures. In the initial configuration, populations of the two domains differ significantly due to an external strain field. Exposure of the surface to ~10@super-8@ Torr oxygen at temperatures between 750-850 C causes the domains to become approximately equal in area. Based on previous LEED and STM measurements,@footnote 1,2@ we conclude that the progression towards equal domain populations results from the removal of the external strain. During equilibration, the potential in which the step moves is determined from the step velocity. The measured exponential time dependence of the equilibration rate is consistent with step motion in the presence of the step-interaction potential proposed by Alerhand et al.@footnote 3@ This agreement implies that strain relief takes place on a time scale of a few seconds. We propose that the mechanism of strain relief is an oxygen-induced change in the shear threshold of Si due to dissolution of oxygen into the bulk. The ability to modify the elastic properties of materials with common adsorbates such as oxygen is important in heteroepitaxy where strain is known to play a key role in defining the properties of the epitaxial film. 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@F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. 61, 2469 (1988). @footnote 2@B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, JVST A8, 210 (1990). @footnote 3@O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. 61, 1973 (1988).

10:00am **SS1-FrM6 The Strain Effect on Ge-covered Si(001) Surface*,* *F.-K. Men,*** *C.-R. Hsu,* National Chung Cheng University, Republic of China

By loading the free end of a cantilevered bar, we have studied the effect of strain on the Ge-covered Si(001) surface. On this surface, strain produces a reversible change in the relative population of the 2xn and nx2 domains. This change is driven by the relaxation of the energy associated with a long-range strain field extending into the bulk due to the anisotropy of the intrinsic stress tensor of the two reconstructed domains. The dependence of the surface stress anisotropy, defined as the difference of the components of the surface stress tensor parallel and perpendicular to the dimer bond, on the Ge overlayer thickness has been studied. By varying the separation between two neighboring dimer vacancy lines (DVL's) we have investigated the DVL-DVL interaction. Based on a linear-dipole-force model for the step-step interaction and the theory of long-range elastic relaxation of orientationally inequivalent domains, we have estimated the DVL formation energy and the DVL-DVL interaction strength. We have also studied the change in the relative population of the two orthogonal domains as a function of time at different temperatures. Results on the kinetics of the step migration will be presented.

10:20am **SS1-FrM7 Spontaneous Domain Formation on Ge(001)***, **H.J.W. Zandvliet**,* University of Twente, The Netherlands*; B.S. Swartzentruber,* Sandia National Laboratories*; E. Zoethout, G. Rosenfeld, B. Poelsema,* University of Twente, The Netherlands

Scanning tunneling microscopy measurements of Ge(001) reveal the presence of an ordered domain pattern consisting of c(4x2) and (2x1) domains arranged in stripes with a width of several dimer row spacings, oriented along the dimer rows. We suggest that the existence of a soft domain wall between the domains combined with a difference in the stress component along the dimer bond for the (2x1) and c(4x2) domains, respectively, can produce such an ordered domain phase. We have observed fluctuations of the domain walls indicating that the system is in thermal equilibrium. A simple model based on strain relaxation explains the observed size of the domain pattern.

10:40am **SS1-FrM8 New Results for Analytical Approximants of Terrace-Width Distributions on Vicinal Surfaces, and Some Consequences@footnote 1@***, **T.L. Einstein**, O. Pierre-Louis,* University of Maryland, College Park*; B. Joós,* University of Ottawa, Canada

Quantitative measurement of the equilibrium terrace width distribution P(L) of vicinal surfaces has proved a powerful and convenient way to investigate the interactions between steps. Most analyses have relied on simple analytic results based on the Gruber-Mullins approximation: one "active" step wandering between two fixed straight steps separated by twice the average step spacing . For non-interacting, free-fermion (FF)-like steps, P(L) corresponds to the ground-state density of a confined fermion, going like sin@super 2@(@pi@L/2), while for significant repulsions decaying as A/L@super 2@, this density is a Gaussian.@footnote 2@ For both cases, P(L) vs. L/ can be written as a "universal function." Rather complicated analytic expressions can be written for FF@footnote 3@ and for a special value of A. For FF, H. Ibach concocted a simple but excellent approximation for P(L) involving a power law and a gaussian decay.@footnote 4@ This expression turns out to be the celebrated "Wigner surmise" for the distribution of energies in gaussian unitary ensembles, long known to correspond to free fermions. Based on this recognition and results from random-matrix theory, we present a general universal expression that has just one fitting parameter, the power, from which A can be easily estimated. We provide calibrations at the values of A for which exact solutions exist. We use these results to clarify recent controversies@footnote 5@ about how to extract A from P(L). We also discuss what can be learned from the third moment of P(L) and from the covariance of adjacent terrace widths. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surface Sci. 240, L591 (1990). @footnote 3@B. Joós, T. L. Einstein, and N. C. Bartelt, Phys. Rev. B 43, 8143 (1991). @footnote 4@H. Ibach, private communcation; M. Giesen, Surface Sci. 370, 55 (1997). @footnote 5@L. Masson, L. Barbier, J. Cousty, and B. Salanon, Surface Sci. 317, L1115 (1994); L. Barbier, L. Masson, J. Cousty, and B. Salanon, Surface Sci. 345, 197 (1996); T. Ihle, C. Misbah, and O. Pierre-Louis, Phys. Rev. B 58, xxx (1998).

11:00am **SS1-FrM9 Enantiospecific Adsorption of Chiral Hydrocarbons on Naturally Chiral Pt and Cu Surfaces***, T.D. Power, **D.S. Sholl**,* Carnegie Mellon University

Many stepped metal surfaces exhibit chiral step structures which can, in principle, affect the properties of adsorbed chiral molecules@footnote 1@. These highly characterizable systems may be useful for isolating the fundamental mechanisms of enantiospecific reactions in chirally active heterogeneous catalysts. We have used Monte Carlo simulations to examine the energetic and entropic contributions to the free energy of adsorption of several chiral hydrocarbons adsorbed on naturally chiral Pt and Cu surfaces. By simulating both enantiomeric forms of the adsorbates, we are able to directly probe the enantiospecific nature of the adsorbate/surface interactions. These simulations have allowed us to explore the roles of adsorbate size and surface step spacing. Our results indicate that many examples of enantiospecific adsorption exist in which the energy shifts between enantiomers should be readily detectable using standard experimental tools such as Temperature Programmed Desorption. @FootnoteText@ @footnote 1@ C. F. McFadden, P. S. Cremer, and A. J. Gellman, Langmuir, 12 (1996) 2483.

11:20am **SS1-FrM10 Xe Adsorption Sites on Metal Surfaces***, **M. Caragiu**, Th. Seyller, R.D. Diehl,* Pennsylvania State University*; P. Kaukasoina, M. Lindroos,* Tampere University of Technology, Finland

Based on an adsorbate-substrate potential which consists of the attractive van der Waals interaction and a repulsive interaction due to wave function overlap, the equilibrium site for physisorbed noble gases would be expected to be a high-coordination site. The presumption which arose from this expectation, that physisorbed atoms prefer high-coordination sites, has been a great hindrance to the development of physisorption potentials since it has delayed experiments to measure the adsorption geometries of physisorbed atoms. Several years ago, a top-site geometry was proposed for Xe/Pt(111) based on He-atom diffraction intensities from an incommensurate phase, although this assignment was disputed by a later SPLEED study. Nevertheless, a density-functional theory cluster calculation suggested that a preference for top sites in this case may arise from the hybridization of the Xe 5p electrons with the Pt 6d states. Recently it has been shown that Xe on Ru(0001) adsorbs in the top-site geometry in the (@sr@3x@sr@3)R30° phase. If hybridization with substrate d-states is the origin for top-site adsorption, then Xe would not be expected to occupy the top sites on Cu surfaces where the d-states are several eV below the Fermi energy. We present the findings of LEED I(E) studies of Cu(111)-(@sr@3x@sr@3)R30° and Pt(111)-(@sr@3x@sr@3)R30° which were carried out to test this hypothesis and to resolve the disagreement on the adsorption site for Xe on Pt(111). These LEED studies indicate that Xe occupies the top site in both cases. Since it is unlikely that Xe atoms hybridize appreciably with the deep d-levels in Cu(111), we propose a new model for Xe adsorption on metal surfaces in which the hybridization occurs between the occupied part of the excited Xe 6s resonance (which extends below the substrate Fermi energy) and the unoccupied substrate orbitals near the Fermi level.

11:40am **SS1-FrM11 A NIXSW Study of the InP(001)-(4x2) and InP(001)-(1x1)-Cl Surfaces***, A.A. Davis, C.J. Fisher, **R.G. Jones**,* University of Nottingham, United Kingdom*; G. Scragg, J. Ludeke, D.P. Woodruff,* University of Warwick, United Kingdom*; B.C.C. Cowie,* Daresbury Laboratory, United Kingdom

The Normal Incidence X-ray Standing Wave (NIXSW) technique has been used to study the reconstructed, indium terminated InP(001)-(4x2) surface and the InP(001)-(1x1)-Cl chemisorbed surface, using the (002), (20-2) and (113) Bragg reflections. Auger electrons and photoelectrons from the In, P and Cl were used to monitor the X-ray absorption profiles. The reconstructed, indium terminated surface was found to contain In dimers orientated in the direction of the four times periodicity, which is in contrary to earlier studies, but in agreement with the findings of Sung et al.@footnote 1@ The chemisorbed chlorine surface had chlorine bonded to the top layer In atoms with the In-Cl bond probably extending along the [110] substrate direction. The inadvisability of using low energy Auger peaks, and the effects of non-dipole photoemission in XSW determinations, are also discussed. @FootnoteText@ @footnote 1@M. M. Sung et al; Surface Sci. 322(1995)116

Surface Science Division
Room 309 - Session SS2-FrM

Water and Ice Interfaces

Moderator: B. Mason, North Carolina State University

8:20am **SS2-FrM1 Dielectric Response and Ionization of Water Adlayers in High Electric Fields: Calculations and Experiments***, T.D. Pinkerton, D.L. Scovell, V. Medvedev, **E.M. Stuve**,* University of Washington

Water/metal interfaces typically support high surface electric fields on the order of 1-3 V/Å (100-300 MV/cm) - fields strong enough to make or break chemical bonds. While the surface electric field depends upon electrode potential and the nature of both electrode and electrolyte, the response of the electric field to these parameters and its subsequent influence in electrochemical processes remain unknown. Controlled high surface electric fields can be obtained on sharp field emitter tips in vacuum through potentials of 1-5 kV applied to tips of radius 100-1000 Å. The response of both thin and thick water layers adsorbed on these tips thereby allows the influence of electric field to be probed directly. Theoretical and experimental results show the transition of the location of the field from the water/vacuum interface for thin water layers to the metal/water interface for water layers above 500 Å thickness. Ionization at the water/vacuum interface represents UHV adsorbed water, whereas ionization at the metal/water interface represents an electrochemical response. The field required for onset of ionization increases linearly with adlayer thickness, in agreement with calculations. With increasing field strength water ionizes to form H@sub 3@O@super +@, OH@super -@, and H@sub 2@O@super +@. These results demonstrate the electrochemical response of water as a function of field and have implications in basic electrochemistry, nanolithography, and the design of tips for field emitter arrays.

8:40am **SS2-FrM2 Crystallization Kinetics of Amorphous Solid Water: The Effect of Underlying Substrate***, **Z. Dohnálek**, G.A. Kimmel, K.P. Stevenson, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Thermally induced crystallization of ultra-thin amorphous solid water (ASW) films grown from a directed H@sub 2@O(g) beam is investigated. The temperature programmed desorption (TPD) spectra of N@sub 2@(g) physisorbed on ASW and crystalline ice (CI) surfaces exhibit striking differences in their lineshapes. The spectroscopic sensitivity of the N@sub 2@(g) TPD provides a unique opportunity to study the ASW crystallization with high sensitivity at temperatures well below H@sub 2@O desorption. The ASW crystallization kinetics are followed isothermally on Pt(111) and CI substrates as a function of temperature and ASW film thickness. The crystallization kinetics are strongly substrate dependent. On Pt(111), the data is consistent with the 3-dimensional crystallization model with the nucleation occurring in the bulk of the ASW film as shown previously.@footnote 1@ In contrast, on the CI substrate we observe that the CI surface serves as a 2-dimensional nucleation center and the crystallization proceeds from the ASW/CI interface towards the ASW surface. The activation barrier of the crystallization process on the CI substrate is significantly lowered as compared to the Pt(111) due to the presence of the crystalline template. @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, Surf. Sci. 367 (1996) L13.

9:00am **SS2-FrM3 A Study of Amorphous Solid Water (ASW) Morphology using N@sub 2@ Gas Adsorption and Thermal Desorption***, **K.P. Stevenson**, Z. Dohnálek, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

We have probed the morphology of amorphous solid water (ASW) thin films grown below 140 K using N@sub 2@ gas adsorption and temperature programmed desorption (TPD). Surprisingly, we find that ASW films grown with increasing angles of incidence from a directed vapor source show 20-100 fold increase in the uptake of N@sub 2@ gas at 26 K. The integrated N@sub 2@ TPD signals obtained from subsequent thermal desorption experiments reflect significant increases in the available surface area and porosity of ASW films with increasing incident angle. In comparison, ASW films grown by ambient H@sub 2@O backfilling of the experimental apparatus show integrated N@sub 2@ signals most comparable with ASW films grown at oblique angles of incidence. This observation has important implications for those studying ASW in laboratory settings, since the angle of incidence as an experimental control variable has not been widely appreciated in the preparation of ASW thin films. Further, we have investigated the affects of growth temperature, film thickness, and annealing on ASW morphology. The available ASW film surface area is observed to decrease with increasing growth temperature until 80 K where it becomes relatively constant thereafter. For a given incident angle, a roughly linear increase with increasing film thickness is observed for ASW films grown at 22 K. ASW films annealed above 120 K show a significant collapse of the micropore structure consistent with previously published accounts. These results have important implications for understanding the chemical and physical properties of ASW found in astrophysical media such as comets, planetary satellites, and interstellar grains. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

9:20am **SS2-FrM4 Origin of Non-Zero-Order H@sub2@O Desorption Kinetics from Crystalline Ice Multilayers on Ru(001)***, **F.E. Livingston**, J.A. Smith, S.M. George,* University of Colorado, Boulder

Recent studies have reported non-zero-order kinetics for H@sub2@O desorption from crystalline ice multilayers on Ru(001). To understand the origin of the non-zero-order kinetics, D@sub2@O desorption from ultrathin crystalline D@sub2@O ice multilayers on Ru(001) was measured using a combination of laser-induced thermal desorption (LITD) spatial probing and isothermal desorption flux analysis. The ice multilayers were grown on Ru(001) using either backfill D@sub2@O vapor deposition or multichannel capillary array dosing methods. The ice multilayers grown via backfill vapor deposition were smooth and highly uniform. The LITD and isothermal desorption flux studies demonstrated that D@sub2@O desorption from these uniform ice multilayers exactly followed zero-order kinetics. Slight deviations from zero-order desorption kinetics were observed only at low D@sub2@O coverages of @<=@5 BL D@sub2@O. In contrast, the ice films prepared using capillary array dosing were spatially non-uniform and exhibited a decreasing multilayer coverage versus distance from the center of the substrate. This initial non-uniform D@sub2@O coverage distribution had a dramatic impact on the isothermal desorption flux measurements and produced non-zero-order desorption kinetics. The deviations from zero-order kinetics were directly related to changes in the ice film surface area as the non-uniform initial multilayer coverage is completely desorbed at various positions on the Ru(001) substrate at different times. The previous reports of non-zero-order kinetics on Ru(001) are assigned to a non-uniform initial D@sub2@O multilayer coverage distribution.

9:40am **SS2-FrM5 Low Energy Dynamics through the Verwey Transition : Water Adsorbed on Fe@sub 3@O@sub 4@(100)/MgO(100)***, **C.J. Hirschmugl**, M. Takasaki, M. Collins,* University of Wisconsin, Milwaukee*; C.H.F. Peden, S.A. Chambers,* Pacific Northwest National Laboratory

The far- and mid-infrared broadband absorptions and discrete vibrations have been studied for water adsorbed on an epitaxial 2000 Å Fe@sub 3@O@sub 4@(100) film using infrared synchrotron radiation. Water on Fe@sub 3@O@sub 4@ represents an ideal example both practically and fundamentally, as Fe@sub 3@O@sub 4@ is a prominent subsurface mineral (magnetite), and the material exhibits an interesting electronic transition. Specifically, the substrate undergoes a metal-semiconductor (Verwey) transition at 120 K (ten-thousand-fold change in conductivity from approximately 10@super 2@ [ohm-cm]@super -1@ to approximately .01 [ohm-cm]@super -1@), while water adsorbed on the surface is stable in vacuum until above 350 K. The frequency-dependent conductivity in normal-incidence reflectance measurements follows a Drude behavior above the transition, and is non-Drude below the transition. Hence, the infrared response of this system, both above and below the transition, provides a comparison of the water-substrate interaction in the metallic and semiconducting states. The present infrared studies employ synchrotron radiation, which can extend traditional IRAS measurements to below 400 cm@super -1@ with noise levels of approximately .01% attainable in 100 seconds measuring time. In addition, these measurements are complemented by TPD and concurrent resistivity measurements. Notably, three distinct cation adsorption sites are available on the reconstructed Fe@sub 3@O@sub 4@(100) surface: a tetrahedrally bonded Fe@super 2+@; a tetrahedrally bonded Fe@super 3+@; and an octahedrally bonded Fe@super 3+@. Molecularly adsorbed water is shown to sequentially fill these sites. In addition, adsorbed multilayers of water reveal large anti-absorption resonances in the infrared spectra for the molecular vibrations and the substrate phonons.

10:00am **SS2-FrM6 Surface Restructuring of Magnesium Oxide at the Interface with Water***, **J. Jupille**,* CNRS, France*; P. Nael, D. Abriou,* Laboratoire CNRS/Saint-Gobain, France*; H. Arribart,* Saint-Gobain Recherche, France

Interactions of water with oxide surfaces are among the most common chemical reactions since they can be observed at any time in the surrounding medium. Nevertheless, despite their apparent simplicity, they often lack microscopic description. A well known example is the adsorption of water on magnesium oxide. Cleaved MgO samples, which show mostly flat (100) terraces, undergo dramatic rearrangements upon exposures to surrounding atmosphere. Their surfaces are becoming very rough, so that flat (100) terraces are no longer visible. These changes in morphology are usually suspected to arise from the reaction with water molecules present in the ambient air. However, according to theory, water is not expected to dissociate on the dense (100) faces of MgO, but only on sites of lower coordination numbers. To demonstrate that water adsorption induces a restructuring of the MgO(100) surfaces, the behaviour of cleaved MgO surfaces which have been brought in contact with water have been examined by atomic force microscopy. It has been observed that pits are formed along directions. Moreover, rearrangements along similar directions have been seen by exposing cleaved MgO surfaces either to the ambient air or to moist nitrogen. Consistently with calculations relative to hydroxylated MgO surfaces, the orientation of the pits suggests that the driving force for the restructuring is the change in surface energy upon water adsorption.

10:20am **SS2-FrM7 Interaction of Water and Dimethyl Sulfoxide with Gold Surfaces***, **A.A. Gewirth**, N. Ikemiya, S.K. Si,* University of Illinois, Urbana

We discuss recent results examining the initial stages of water and dimethyl sulfoxide adsorbtion on Au surfaces. We show that water first adsorbs on Au at low temperature as a planar, amorphous, monolayer-high film. The subsequent growth of water clusters occurs atop this film, but not on the bare metal surface. The growth and structure of dimethyl sulfoxide on Au surfaces is surface-structure dependent with more highly corrugated faces providing localized electron density yielding ordered arrays. Results obtained at room temperature from bulk liquid dimethyl sulfoxide are in close correspondance with low temperature UHV measurements.

10:40am **SS2-FrM8 Coadsorption of Water and Hydrogen on Pt(110)***, **P. Blowers**, N. Chen, R. Masel,* University of Illinois, Urbana

In previous papers, various investigators have discovered a new species when hydrogen and water coadsorb on various faces of platinum. However, the exact nature of the species is still in dispute. In this paper we combine high quality HREELS spectra with abinitio calculations to try to identify the species. The EELS spectrum of coadsorbed water an hydrogen shows peaks at 1180 and 3340 cm-1 which are not seen with water or hydrogen alone. The peaks shift with deuteration in a way expected for compound formation between water and hydrogen. Abinitio methods at the MP2/6-31G* level are used to identify the species. We have not found any (H2O)nH clusters, radical species or negative ions with vibrations near 1180 cm-1 However, cationic species e.g. [H3O]+, [H5O2]+, [H7O3]+ give vibrations in the right range. A detailed comparison of theory and experiment suggests that a number of hydrated ions form during the coadsorption process, with [H5O2]+, and [H7O3]+ being the most important.

11:00am **SS2-FrM9 Equilibrium Water Structures at Well-Defined Organic Surfaces***, **D.L. Allara**, T.J. Boland,* Pennsylvania State University

We report combined in-situ infrared vibrational spectroscopic and coverage measurements, from submonolayer to near condensation, of equilibrium water adsorption at well-defined organic surfaces synthesized by molecular self-assembly. The adsorption isotherm data were used to develop thermodyamic parameters of the adsorbed films while the IR data give information on the water structures. The IR spectra were interpreted quantitatively by using modeling based on electromagnetic theory and the known optical function spectra of various phases of water. The results reveal a range of water structures from ice-like to clathrate-like and liquid-like depending on the water chemical potential, the chemical functionality of the surface and on the presence of dilute inorganic salts dissolved in the near water films. In the case of hydrophobic methyl-terminated surfaces, the water adopts a liquid-like structure from submonolayer to near-condensation coverages in surprising contradiction to the traditional view of ordered water at hydrophobic surfaces. In contrast, for polar surfaces such as CO2H, the water adopts a strongly H-bonded structure up to the condensation point. The incorporation of dissolved salts at the interfaces serves to broaden the range of water structures observed.

11:20am **SS2-FrM10 Effect of Boron on the Surface Chemistry of Single Crystal Ni@sub 3@(Al,Ti)***, **B. Zhou**, J. Wang, Y.W. Chung,* Northwestern University

Previous work demonstrated that water dissociates into atomic hydrogen on Ni@sub 3@(Al,Ti)(100). 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 show that boron addition to these alloys increases ductility. Therefore, it is reasonable to expect that boron may affect the production of atomic hydrogen from water vapor dissociation and its surface mobility. To explore the effect of boron, we first dosed the surface of clean Ni@sub 3@(Al,Ti)(100) with controlled amounts of boron, using a specially designed low-energy boron ion source, followed by low-temperature exposure to D@sub 2@O and temperature-programmed desorption. The state of the surface was determined by x-ray photoemission. These studies show that addition of boron reduces the production of atomic hydrogen. The significance of this observation in explaining the beneficial effect of boron will be discussed.

11:40am **SS2-FrM11 Interactions of 50-2500 eV Electrons with Ice***, **C.D. Wilson**, C.A. Dukes, R.A. Baragiola,* University of Virginia

We investigate the interactions of 50-2500 eV electrons with vapor deposited ice by means of Electron Energy Loss Spectroscopy (EELS), Auger Electron Spectroscopy (AES), and Secondary Electron Emission (SEE). The EELS data is used to measure low lying excitations and to ascertain the production of radicals in the near surface region. This is done by observing the appearance of energy loss features in the band gap region as a function of irradiation fluence. We will discuss electrostatic charging and chemical alterations during irradiation and relate the results to astronomical problems.

Thin Films Division

Room 310 - Session TF-FrM

Thin Film Deposition from Chemical Precursors

Moderator: A. Belkind, Stevens Institute of Technology

8:20am **TF-FrM1 Annealing of Copper Electrodeposits***, **C.H. Seah**, S. Mridha,* Nanyang Technological University, Republic of Singapore*; L.H. Chan,* Chartered Semiconductor Manufacturing Ltd., Republic of Singapore

Cu is the best metallization candidate to replace Al and its alloys because of its lower resistivity and better electromigration resistance. Significant progress has been made in building multilevel Cu interconnection systems for advanced microelectronics. As a result, it is important to understand how the morphology of the electroplated Cu films and its properties change after annealing at high temperatures. The properties of annealed electroplated Cu films, together with the diffusion barrier performance, have been studied. Electroplating of Cu films was performed onto p-Si with Cu and W seed layers. The barriers film are either TiN, Ta or TaN. The specimens were then annealed at 600 and 700°C in N@sub 2@ atmosphere for grain growth study. The average grain size of the as-plated Cu films was found to be different; larger Cu grains were formed on W seed layer compared to that formed on Cu (600 vs 200 nm). After annealing, all the Cu films recrystallized readily and grain growth occurred. Regardless of the initial grain size of the electroplated Cu films, the final grain size after annealing was found to be similar in both seed materials. The grain sizes were about 1.0 and 1.2 µm after annealing at 600 and 700°C respectively. The driving force for grain growth is the surface energy release from elimination of grain boundaries and thus achieving an equilibrium state. The annealed films produced a layered microstructure, together with the presence of pinholes and cavities. Results show that all the diffusion barriers remained intact after annealing at 600°C. The CVD TiN barrier appeared to fail at 700°C annealing if the film stack contains only 100 Å thick barrier layer. The resistivity of the electroplated Cu films was also found to be reduced from 2.1 microhm-cm to 1.9 microhm-cm after annealing at both temperatures.

8:40am **TF-FrM2 Polymerized C-Si Films on Metal Substrates: Cu Adhesion/Diffusion Barriers for ULSI?***, L. Chen, **J.A. Kelber**,* University of North Texas

The increasing demands of ULSI have created a need for Cu diffusion/adhesion barriers which are consistently effective at thicknesses of several hundred angstroms or less. Further, the integration of Cu with low-dielectric polymers requires the reliable adhesion at the Cu/polymer interface. We have recently synthesized polymeric C-Si films which are resistant to thermal diffusion of Cu at temperatures below 800 K, even at thicknesses less than 100 Å. These films also show potential for providing a covalently bonded interphase between Cu and, e.g., fluoropolymer dielectrics. The films are created by electron or UV photon bombardment of condensed vinyl silane derivatives. The films are not SiC, and have chemical compositions very close to those of the vinyl silane precursors (e.g., Si:C = 1:4 for vinyltrimethylsilane(VTMS)-derived films). TPD data show that polymerization occurs via the vinyl group. Films derived from VTMS are adherent and stable on Ta substrates until 1000 K in UHV. Diffusion of Cu is not observed below 800 K. Cu adhesion to the substrate is relatively good, with dewetting of deposited overlayers occuring only at temperatures above 600 K in UHV. Perfluorobenzene moieties can also be incorporated into the growing film with good thermal stability, indicating that these films have potential to adhesively couple Cu surfaces to vapor-deposited fluoropolymer films. Opportunities for molecular tailoring of electronic and mechanical properties via systematic variation of precursor structure will be discussed.

9:00am **TF-FrM3 Ultra High Rate, Wide Area, Plasma Polymerized Films from High Molecular Weight/Low Vapor Pressure Liquid or Solid Monomer Precursors***, **J.D. Affinito**, M.E. Gross, P.A. Mounier, S. Stockhause,* Pacific Northwest National Laboratory **INVITED**

A new process has been developed for the high rate vacuum deposition of solid films from high molecular weight/low vapor pressure liquid, or even solid, monomer precursors. The gas resulting from the flash evaporation of a liquid monomer mixture, or from a suspension of liquid monomer and insoluble solid particles, is used as the support medium for a glow discharge in a Plasma Enhanced Chemical Vapor Deposition-like (PECVD) process. Due to the high molecular weight/low vapor pressure nature of the precursors, the plasma of the flash evaporated gas cryo-condenses at extremely high rate on substrates at ambient, and higher, temperatures. Upon condensation the liquefied plasma immediately begins to polymerize to form a solid film due to the high concentration of radicals and ions contained in the liquid film. The process has been successfully implemented in a vacuum roll coating system in a roll-to-roll deposition process. Polymer films, and Molecularly Doped Polymer (MDP) composite films of polymer and light emitting organic molecules, have been deposited at thickness' ranging from 0.1 microns to 24 microns at webs speeds as high as 100 linear meters per minute. This new deposition process will be discussed along with some properties of the films fabricated with this new process.

9:40am **TF-FrM5 Effects of Temperature (350 - 25°C) on OH Incorporation and Electrical Performance of Plasma Deposited Silicon Dioxide Thin Films for Applications on Plastic Substrates***, **A. Gupta,** C.G. Makosiej, G.N. Parsons,* North Carolina State University

Very low temperature PECVD SiO@sub 2@ may be useful on plastic substrates for gate dielectrics for polysilicon thin film transisitors, or for barrier or insulating layers in organic LED displays. We have used SiH@sub 4@/N@sub 2@O/He/H@sub 2@ mixtures in a parallel plate rf plasma CVD reactor to form SiO@sub 2@ on silicon, and examined the effect of substrate temperature between 350°C and 25°C, rf power, and gas ratios on the chemical composition, refractive index, etch rate, chemical stability, deposition rate, and I-V and C-V characteristics. Low temperature films have also been deposited on PET and polycarbonate substrates to examine adhesion and stress. Films deposited at 350°C show good insulating properties with breakdown fields >8 MV/cm. As temperature is decreased to 100°C, an increase in charge trapping is observed. The decrease in temperature also results in an increase in deposition rate from 65 to 100 Å/min, and a decrease in refractive index from 1.47 to 1.43, indicating a less dense structure. Infrared spectroscopy shows a correlation between OH concentration and the Si-O stretch peak position. At 90W, as the temperature decreases from 350 to 250°C, the Si-O stretch mode position decreases from 1063 to 1056 cm@super -1@, indicating an increase in bond strain. As temperature is decreased from 250 to 25°C, the Si-O peak increases from 1056 to 1065 cm@super -1@, due to an increase in OH incorporation during deposition. After deposition, the OH concentration increases with ambient exposure, and decreases slightly during annealing at 300°C. Process variations, including H@sub 2@ and He dilution, and time modulated deposition and H@sub 2@ exposure cycles to decrease OH incorporation have been tested. Films with less OH in the as deposited condition show a greater resistance to post-deposition oxidation, and show improved electrical properties. Films with good leakage characteristics (

10:00am **TF-FrM6 Structural and Electrical Properties of SrTiO@sub 3@ Thin Films Prepared by Plasma Enhanced MOCVD***, D.O. Kim, **Y-.B. Hahn,*** Chonbuk National University, Korea

Dielectric SrTiO@sub 3@ ultra thin films having 30 - 75 nm thickness were deposited on Pt/Si and Ir/Si substrates by plasma enhanced MOCVD using high purity Ti(O-i-C@sub 3@H@sub 7@)@sub 4@, Sr(tmhd)@sub 2@ and O@sub 2@. The structural and electrical properties of SrTiO@sub 3@ films were studied in terms of crystallinity, microstructure, current leakage, and dielectric constant. For the case of Pt/Si substrate, the peaks of (100) and (111) SrTiO@sub 3@ together with TiO2 and SrCO@sub 3@ peaks started to appear at 500 @super o@C, and at 550 @super o@C for (110) and (211) peaks without TiO@sub 2@ and SrCO@sub 3@ peaks. For Ir/Si substrate, peaks of (100) SrTiO@sub 3@ and TiO@sub 2@ appeared at 500 @super o@C, and at 550 @super o@C for (110), (111) and (210) SrTiO@sub 3@. Dielectric constants decreased as the film thickness decreased. The leakage current density of the SrTiO@sub 3@ films decreased with increasing deposition temperature up to 550 @super o@C, but somewhat increased at > 550 @super o@C. It was found that the electron current was limited by tunneling effect for films thinner than 30 nm, but limited by Schottky emission for films thicker than 30 nm. The electron affinity and depletion layer of SrTiO@sub 3@ films, based on the electron current mechanism, were 4.0-4.3 eV and 15 nm, respectively.

10:20am **TF-FrM7 Thermal Stability of MOCVD TiN/PECVD SiOF Interface for Cu Metallization***, **K.H. Kim,** S.J. Park, G.S. Lee,* Louisiana State University

RC delay based on Al and SiO@sub 2@ interconnection system comprises a great portion of the total delay as circuit density increases. RC delay can be reduced by using low resistance metal or low dielectric constant insulator, or both. Thus, Cu and SiOF are preferred to be used as low resistance and low dielectric materials, respectively. However, Cu metallization system needs a stable diffusion barrier. Meanwhile, it is known that the properties of MOCVD TiN film are affected largely by the substrate material. In this study, we investigated the interface stability of MOCVD TiN/PECVD SiOF film for the possibility of integration. The SiOF film of 100 nm thickness was deposited using TEFS with Ar as a carrier and O@sub 2@ as a reactant. The MOCVD TiN film of 50 nm thickness was coated using TDEAT and He carrier at substrate temperature of 350°C. The TiN/SiOF film was annealed in the temperature range of 200 - 600°C for 30 min. in vacuum. The effect of annealing was investigated by FTIR, four point probe, C-V measurement, and AES. It was observed that the sheet resistance of the TiN film increased and the dielectric constant of the SiOF film decreased at annealing temperature above 500°C. After the TiN film was removed from the annealed TiN/SiOF film, FTIR showed unknown peak which increased as a function of annealing temperature. The results of C-V measurement also showed unstable interface at annealing temperature above 500°C. We demonstrated that the properties of MOCVD TiN/PECVD SiOF film were affected by annealing, which may be due to diffusion and interaction at interface.

10:40am **TF-FrM8 Assessment of As-deposited Polycrystalline Silicon Films on Polymer Substrates using ECR-PECVD***, **S.H. Bae,** S.J. Fonash,* The Pennsylvania State University

As-deposited polycrystalline silicon (poly-Si) films have been successfully grown on polymer substrates at 120 and 200 °C using ECR (Electron Cyclotron Resonance) PECVD. PES (polyethersulfone) and PET (polyethylene terephthalate) substrates have been used in this work. To block diffusion and degassing from the polymer substrates, 1000 Å ECR-PECVD silicon nitrides (refractive index = 1.9) have been coated on the substrates prior to Si film depositions. Then, Si films have been deposited with SiH@sub 4@/H@sub 2@ ECR plasmas. The structural, opto-electric and electrical characteristics of Si films have been assessed by X-ray diffraction, photoluminescence, and electrical conductivity measurements, respectively. X-ray diffractions for 3500 Å Si films grown at 120 and 200 °C have shown (111), (220), (311) and (331) peaks which are the primary diffraction peaks of crystalline Si materials. We have explored the effect of the 13.56 MHz RF substrate bias during growth of Si films. According to X-ray diffraction patterns, low RF substrate bias and high substrate temperature are favorable for high degree of crystallinity of Si films. It is noted that RF substrate bias during ECR plasmas may tailor electrical properties of as-deposited poly-Si films; as the RF substrate bias is applied and increased, conductivities are improved and activation energies are decreased. In photoluminescence spectra of Si films, the intensity of luminescence is enhanced as RF bias is increased. Since intensity of photoluminescence is related to defect density of Si films; the more defects offer the more alternative paths for non-radiative recombination which compete with radiative recombination paths, enhancement of photoluminescence intensity with applying RF bias may mean that degree of defect passivation during Si film growth is controlled by RF substrate bias.

11:00am **TF-FrM9 A Novel Method For Determining Kinetic Rate Expressions For CVD Processes Using a Combination of Step Coverage Measurements and Computer Simulation***, E.J. McInerney, **G. Ramanath,** D.C. Smith,* Novellus Systems

There is an increasing need for understanding reaction kinetics and mechanisms during chemical vapor deposition (CVD) to accurately predict deposition rate, uniformity, step coverage, and reactor throughput. We present a novel method for determining reliable kinetic rate expressions by a combination of transport modeling and experimental measurements of step coverage and planar deposition rate. We demonstrate the method by applying it to W CVD during H@sub 2@ reduction of WF@sub 6@ to elucidate -- for the first time -- two distinct kinetic mechanisms operating in different WF@sub 6@ flow regimes. Rate expressions deduced from deposition rate measurements on planar geometries often fail to accurately predict step coverage due to incorrect assumptions of near-surface concentration N@sub s@ of reactants. As direct measurements are difficult, modeling species transport in the reactor is necessary to estimate N@sub s@. However, this method by itself is inadequate because small errors in the model can lead to large errors in the rate expression. In our method, we obviate the limitations of traditional modeling by utilizing experimentally measured step coverage values to model species transport within topological features in addition to that in the reactor. In this way N@sub s@ is calculated self-consistently, allowing the determination of the reaction order n and kinetic mechanisms. Despite numerous studies of the H@sub 2@-WF@sub 6@ reaction over the last 30 years, the order of WF@sub 6@ concentration dependence on W deposition rate has been unresolved between n=0, 1/6, and 1. Our results reveal two distinct mechanisms: at high WF@sub 6@ flows the rate is HF desorption limited (n=1/6), while at low flows WF@sub 6@ adsorption is the limiting step (n=1).

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