Sunday Morning, November 2, 2003

Workshop on Sputtering
Room Constellation C, Hyatt Regency - Session WS-SuM

Workshop on Sputtering (Morning Session)

Moderator: W.D. Sproul, Advanced Energy Industries, Inc.

10:00am **WS-SuM1 Basic Understanding of Reactive Sputtering Processes*,* *S. Berg*,** *T. Nyberg,* Uppsala University, Sweden **INVITED**

Reactive sputtering is a mixed physical and chemical vapour deposition process. It is frequently used in a wide variety of industrial applications. It is not, however, a simple matter to combine high rate reactive sputter deposition and process stability. The reactive gas may easily poison the target causing the deposition rate to decrease sometimes as much as a 5-20 times. In addition the process exhibits a hysteresis behaviour in the relations between the primary processing parameters. In a large volume production situation this may cause serious problems. There must be some sort of built in control system to force the process to avoid being trapped in the hysteresis loop and entering too far into the target poisoned mode. Process modeling of the reactive sputtering process may serve to illustrate the influence of different processing parameters on the overall behaviour of the process. A quite successful model for the basic behaviour of the reactive sputtering process have been suggested by Berg and co-workers. It is frequently referred to as Berg´s model. This model enables to predict the general shapes of most experimental reactive sputtering processing observations. It may predict the complex realations between the partial pressure and supply of the reactive gas as well as the fraction of target poisoning and the composition and deposition rate of the growing film. Knowing the actual relations between these parameters significantly assists in designing reliable control systems for reactive sputtering processes. A detailed analysis suggests that there exist several ways of eliminating the hysteresis in reactive sputtering processes. Increasing the pumping speed of the system will ultimately result in elimination of the hysteresis. Decreasing the effective sputter erosion zone at the target may also result in elimination of the hystereis. Hysteresis or no hysteresis depend on a critical balance between the gettering of the reactive gas by compound formation of the growing film and the amount of the supplied reactive gas eliminated from the processing chamber by the external pump. There exists several ways of "twisting and turning" this balance. This will be shown in this presentation. Sputtering from more than one target (co-sputtering of different elements) and/or the use of more than one reactive gas in a reactive sputtering process will significantly increase the complexity of the process. Reproducing deposition rate and film composition under such conditions may be hazardous. Input processing parameters interact with each other in such a way that not only their absolute values are important but also the sequence in wich that they are varied must be taken into account. This makes process control quite problematic. We will illustrate how such conditions occur and suggest how to be in full control of the process. @FootnoteText@ 1. Computer modeling as a tool to predict deposition rate and film composition in the reactive sputtering process.: S. Berg, T.Nyberg, H-O.Blom and C.Nender; J.Vac.Sci.Technol.A16(3)May/June 1998,p1277-85 2. Modeling of the reactive sputtering process: S. Berg, T.Nyberg, H-O.Blom and C.Nender Handbook of thin film process technology, Edited by D.A.Glocker and S.I.Shah, Inst.of Physics, 1998, pp A5.3:1-15 3. Review article to appear in the journal Thin Solid Films in spring 2004.

11:00am **WS-SuM3 Shallow Implantation as a Mechanism for Target Poisoning in Reactive Sputtering*, R. De Gryse*,** *D. Depla, J. Haemers, G. Buyle,* University Ghent, Belgium **INVITED**

Up to now, reactive sputtering and in particular the target poisoning effect has been described in terms of gettering and chemisorption. It is modelled by a set of linear differential equations@footnote 1@ which predict the non linear poisoning behaviour as a function of the mole fraction of the reactive gas (RG). From this picture it also follows that a decrease in sputter rate as well as a decrease in absolute target voltage (ATV) is expected. The expected decrease in ATV relies on the fact that it is widely accepted that the ion induced secondary electron emission coefficient (ISEE) of compounds is larger as compared to the ISEE of the corresponding metal. However, the experiment shows that several combinations of metal - (R.G.) give rise to an increase in ATV upon poisoning. In systems such as Nb/O@sub 2@@footnote 2@; Sn/O@sub 2@@footnote 2@;Si/N@sub 2@; etc. the ATV is reported to increase when poisoning occurs. Recently it has been suggested that the poisoning instability is not always due to the chemisorption effect but can also be ascribed to the combined effect of target etching, preferential sputtering of metal vis a vis compound and shallow implantation of reaction gas into the target near surface region. This D.R.@footnote 3@ model also leads to a poisoning instability without any need of wall gettering and also two levels in sputtering speed depending on the fraction of (RG) i.e. a high sputtering speed for low mole fractions and a low sputtering speed for higher mole fractions. This behaviour has been simulated by means of the TRIDYN code.@footnote 4@. The transition between metallic and compound or poisoned regime can be predicted as a function of an experimental parameter which contains quantities such as pumping speed, wall area, discharge current, sputter efficiency etc. In this model it is assumed, and shown experimentally, that non bonded RG can be present in a shallow surface layer. It is also shown that this non bonded RG is a component which can give rise to an increase in ATV upon poisoning. Also chemisorption, if present, can give rise to an increase in ATV. Reality will probably be best modelled by a combination of the gettering model and the D.R. model.@footnote 5@ In metallic mode, the magnetron discharge can be described quite accurately and several tools are at our disposal varying from Analytical models over Fluid models, Boltzmann models, Monte Carlo models/Particle in cell (MC-PIC) models to Hybrid models (MC-Fluid). All these models are in some or other way a trade off between speed and accuracy. However in pure metallic sputtering the accuracy and speed of the analytical approach is surprising.@footnote 6@ Modelling of the magnetron discharge in poisoned or compound mode requires the correct picture of the poisoning mechanism. This will allow to predict over the full range of reactive gas flows quantities such as number densities, energy and directivity of the different material fluxes towards the substrate. This in turn will give an estimate of the expected deposition speeds, coating homogeneity, target consumption and will eventually predict the growth mechanism of the coating. The ultimate goal is to develop for every particular application a stable running magnetron. @FootnoteText@ @footnote 1@S. Berg et al., J. Vac. Sc. Technol. A5(2), 1987, p. 202. @footnote 2@"Sputter Deposition" by W. Westwood ISBN 0-7354-0105-5. @footnote 3@D. Depla et al., Vacuum 66 (2002) p. 9. @footnote 4@Z.Y. Chen et al., Nucl. Instr. Meth. In Physd. Res. B: in press. @footnote 5@D. Depla, R. De Gryse, submitted for publication in Surface and Coatings Technology. @footnote 6@G. Buyle et al., J. Vac. Sci. Technol., A21(4), July/August 2003.

11:40am **WS-SuM5 Modeling of Sputtering Equipment and Processes as an Engineering Tool: Building a Virtual Sputter Tool*, J.C.S. Kools,*** Veeco Instruments **INVITED**

In recent years, computational modeling has emerged as an attractive engineering tool to substantially reduce the development time and cost for both equipment and process development of industrial thin film deposition and etch. Furthermore, due to the dramatic increase in computing power available, advanced computational techniques such as Molecular Dynamics have migrated from the academic community to the engineering community, bringing more realistic models within its reach. Our goal is to build a "virtual sputter tool" that could predict the sputter equipment behavior and film properties. Fig.1 sketches the outline of a virtual sputter tool. As can be seen, such a Multiscale/Multiphysics model comprises both advanced computational techniques, such as Particle-In-Cell Monte-Carlo (PIC-MC) and conventional continuum descriptions such as Finite Element Analysis (FEA). In this talk, we will review the progress that has been made towards building a virtual sputter tool, comparing modeling and experimental results. We will put most emphasis on the right hand side of the diagram, namely the modeling of film properties, in the context of industrial application. We will discuss the future outlook towards completion of the virtual sputter tool.

Sunday Afternoon, November 2, 2003

Workshop on Sputtering
Room Constellation C, Hyatt Regency - Session WS-SuA

Workshop on Sputtering (Afternoon Session)

Moderator: W.D. Sproul, Advanced Energy Industries, Inc.

1:30pm **WS-SuA1 Control of Microstructural Evolution during Film Growth*, I. Petrov,*** University of Illinois at Urbana-Champaign **INVITED**

Microstructure is critical for polycrystalline thin film applications and its control during kinetically-limited, low-temperature deposition has been an important goal of materials science in the past decades. In this part of the workshop we will review the fundamental film growth processes - nucleation, coalescence, competitive growth, and recrystallization - and their role in thin film microstructure evolution as a function of substrate temperature. We discuss, further, atomistic mechanisms through which reactive deposition and low-energy ion/surface interactions modify growth kinetics and, thus, allow to controllably manipulate microstructural evolution. Special attention will paid to in-situ substrate treatment by ion-irradiation and its effect on film microstructure and adhesion.

2:30pm **WS-SuA3 Advances in Sputtering Power Supply Technology*, R. Scholl,*** Advanced Energy Industries, Inc. **INVITED**

Plasma power supplies display a marked interaction with the plasma and other elements of the system, and a clear understanding of the important parameters and characteristics of the power supply is a considerable aid in designing and operating a plasma system. In this presentation the basic characteristics of DC, midfrequency, and high frequency (RF) supplies will be outlined, and the key parameters vis-à-vis plasma interactions presented. Instrumentation and matching issues in RF systems will be discussed; in particular a presentation will be made on forward, reflected and load power and their significance in plasma systems. Finally, special and emerging power technology will be covered in a special section, including balancing systems for dual magnetron sputtering, multiple anode sputtering, and ultrahigh power pulsed DC, among others.

3:30pm **WS-SuA6 Cathodic Arcs and High Power Pulsed Magnetron Sputtering: A Comparison of Plasma Formation and Thin Film Deposition*, A. Anders,*** Lawrence Berkeley Laboratory **INVITED**

Film formation by energetic condensation has been shown to lead to well-adherent, dense films. Films are often under high compressive stress, but stress control is possible by pulsed high-voltage biasing, for example. Control of film growth via tuning the kinetic energy of condensing species is most efficient when the condensing species are ions, and when the degree of ionization of the plasma is high. Cathodic arc plasmas are fully ionized; they even contain multiply charged ions. The streaming plasma is supersonic, with kinetic ion energies in the range 20-150 eV, and additional energy can be provided via substrate bias. Ion formation at cathode spots and the dependence of plasma properties on the cathode material will be discussed. Along with ions, macroparticles are produced at cathode spots. This highly undesirable feature can be mitigated by plasma filters and other approaches, however, there is strong motivation to find alternative ways of producing fully ionized plasmas of condensing species. High power pulsed magnetron sputtering (HPPMS) may be one possible way of achieving this goal, at least for some target materials. In HPPMS, the power density at the magnetron target is pulsed to power levels exceeding the average power by about two orders of magnitude. Thermalization of sputtered atoms appears to be needed to accomplish ionization, and self-sputtering during each power pulse may be an important feature of HPPMS.

4:30pm **WS-SuA8 Progress and Prospects for Ionized Physical Vapor Deposition*, J. Hopwood,*** Northeastern University **INVITED**

For somewhat more than a decade, the intentional ionization of sputtered neutral atoms has been exploited to improve the directionality of sputter deposition. In addition to directional control, once a sputtered atom is ionized it is relatively easy to control its energy of deposition. Ionized sputtering is a subclass of the deposition technique commonly known as ionized physical vapor deposition (IPVD). The common characteristic of the many various IPVD techniques is that a neutral vapor, created by physical means including evaporation, sputtering, and ablation, is partially ionized using an intense secondary plasma. As the neutral vapor traverses this secondary discharge, the atoms are ionized by collisions with energetic electrons and metastable atoms. Due to the low ionization potential of most metals, the ionizing discharge need only have about 10@super 12@ electrons per cm@super 3@ with an electron temperature of ~ 2 eV. Atoms with high ionization potentials and small ionization cross sections, however, require significantly more intense secondary discharges. For this reason, reactive sputtering using IPVD may produce a high flux of oxygen or nitrogen atoms, but IPVD typically does not significantly ionize the reactive gas flow. Nonetheless, the depositing flux of metal may be as much as 80-90% ionized using IPVD. The physical mechanisms responsible for ionization will be briefly reviewed in the context of reactor design and process development. A primary user of IPVD is the semiconductor industry. The driving force for adopting IPVD was the need to deposit thin films into the high aspect ratio microstructures commonly found on modern integrated circuits. Conventional sputtering exhibits a cosine angular distribution of sputtered atoms that makes deposition of material into the bottom of deep submicron trenches and vias impossible. By simply applying a negative bias voltage to the wafer, however, ionized sputtered material can be accelerated perpendicular to the wafer surface such that the depositing flux provides adequate bottom coverage of microstructures. The common applications of IPVD include the deposition of copper seed layers used for the subsequent electroplating of copper interconnects, as well as the deposition of adhesion layers and barrier layers using reactively sputtered metal-nitrides. Examples of successful semiconductor processes that use IPVD will be discussed. Because many IPVD process tools require a complete sputtering system plus additional hardware for producing the secondary ionizing plasma, IPVD is a more complex and expensive process than conventional PVD. The secondary ionizing plasma may be produced by inductively coupled plasma, helicon resonators, or ECR plasma - all of which add cost and complexity. Recent advances, however, exploit single power source sputtering in which the secondary plasma is produced by the sputtering source. These simple techniques may allow for the broader use of IPVD in cost-sensitive applications.

Biomaterials Plenary Session
Room 307 - Session BP-SuA

Biomaterials Plenary

Moderator: H.J. Griesser, University of South Australia

3:00pm **BP-SuA4 New Perspective on Hydrogen Bonding in Water using X-rays*, A. Nilsson,*** Stanford Synchrotron Radiation Laboratory **INVITED**

Hydrogen bonding (H-bonding) in water and at interfaces provides the mechanism for many processes of great importance for biological system. Recent experiments using x-ray and electron spectroscopy have raised the question whether we really understand the nature of H-bonding and the structure of liquid water. Using x-ray absorption spectroscopy (XAS) together with density functional theory (DFT) calculations we have demonstrated the appearance of specific spectral features that can be related to asymmetric H-bonding configurations. These can be seen at the surface of ice and in the liquid phase showing the existence of broken H-bonded local structures. The surprising result for the liquid phase is the large number of broken H-bonded species compared with the established wisdom based on molecular dynamic (MD) simulations. We find that most molecules in the liquid are in two-hydrogen-bonded configurations with one donor and one acceptor hydrogen bond compared to the four-hydrogen-bonded tetrahedral structure in ice. Measuring XAS spectra through x-ray Raman scattering (XRS), where inelastic scattered x-rays cause a core excitation, different samples can be studied in air using hard x-rays. This provides means to study water at various temperatures and pressures. From x-ray emission spectroscopy (XES) and photoelectron spectroscopy (PES) studies of ice, providing information of the occupied orbitals projected onto the oxygen atoms, a deeper insight into molecular orbital rearrangements upon H-bonding could be obtained. The decrease in repulsive interaction through charge transfer and rehybridization is essential for a strong attractive electrostatic interaction. The new applications of x-ray spectroscopy (both XAS and XES) and PES to water based systems provides a unique opportunity to obtain new information that has not been accessible previously. A perspective of implications to interfaces will be given.

3:40pm **BP-SuA6 Synthetic Receptors for Biosensor Surfaces*, I. Lundstrom,*** Linkoping University, Sweden **INVITED**

Several biosensor principles are based on biomolecular interactions on surfaces or in thin sensing layers. One of the most wellknown techniques for the direct elucidation of biomolecular interactions utilizes optical changes in a thin hydrogel (dextran) sensing layer occurring upon the binding of biomolecules to the ligands in the sensing layer. Labelling one of the molecules in an interaction pair with fluorescent groups leads, however, to a large sensitivity, and forms therefore the basis for several detection schemes. Molecular beacons, for example, utilize changes in fluorescence resonance energy transfer or quenching for the detection of structural changes in a biomolecule upon binding to a ligand or upon hybridisation. We are developing synthetic helix-loop-helix polypeptide scaffolds, which show promise as a vehicle for new biosensor principles. Their interesting property is that (arbitrary) ligands can be site selectively introduced in a predetermined order into the scaffold using simple solution chemistry, based on active esters, and without need of protecting groups. The scaffolds are also easily functionalised for covalent binding of them to different types of surfaces and hydrogels. In the talk the use of these versatile scaffolds for biosensing purposes will be described after a short introduction to their chemistry. The coupling of the scaffolds to gold surfaces and to dextran matrices and their use for non-labelling biospecific interaction analysis are touched upon. It will furthermore be shown how the scaffolds can be provided with a binding ligand for a molecule and a (fluorescent) reporter group, indicating that binding has occurred.. In the example an inhibitor, benzenesulfonamide, is used as the ligand for an enzyme, carbonic anhydrase, and dansyl as the fluorescent reporter group. The use of arrays of scaffolds with ligands with different affinities for different biomolecules to enable "diagnostic chips" will finally be discussed.

4:20pm **BP-SuA8 Polyvalency in Biochemistry*, G.M. Whitesides,*** Harvard University **INVITED**

Polyvalent or multivalent interactions are the simultaneous association of multiple ligands on one entity (a molecule or a surface) to multiple receptors on another entity. Multivalent interactions are ubiquitous in biology - in infectious disease, in processes involving antibodies, in blood clotting, metastasis, platelet activation, inflammation, and in many conditions in which cells interact with surfaces- and have become a focus of study in molecular biochemistry. Multiple simultaneous interactions have unique collective properties that are qualitatively different from the properties of their monovalent constituents. Monovalent interactions- generally small molecules directed towards a single receptor site- are clearly fundamental, but understanding them is not necessarily sufficient to understand multivalency and its importance in biology. Our group is interested in confirming, understanding, and quantifying the importance of multivalency in biological interactions, defining the range of biological systems in which it is important, and moving this fundamental knowledge towards applications in the design of drugs and materials.

Monday Morning, November 3, 2003

Applied Surface Science
Room 324/325 - Session AS-MoM

Practical Surface Science

Moderator: P.M.A. Sherwood, Kansas State University

8:20am **AS-MoM1 Aqueous-derived Planar Proxies: A Connection between Surface Science and Real World Catalysts***, C.F. Conrad,* Virginia Institute of Marine Science*; C.J. Chisholm-Brause, **M.J. Kelley**,* College of William & Mary

Real catalysts typically comprise metal or metal oxide nanoclusters on a high-surface area insulator oxide support, prepared by aqueous chemistry. Researchers seeking to overcome the experimental difficulty of studying such materials with surface science techniques have made model catalysts by physical deposition, akin to microfabrication technology. It has now become possible to prepare planar proxies by all-aqueous methods, closely akin to those for real catalysts. After obtaining a hydrous gamma alumina layer on a metal foil, established aqueous solution techniques were used to prepare planar proxy and high surface area materials together. To verify their equivalence, both sets of materials were examined by ToF/SIMS, XPS, SEM/EDS and EXAFS, and by response to organic probe molecules.

8:40am **AS-MoM2 The Role of XPS in Materials Characterization in an Industrial R&D Setting***, **M.C. Burrell**,* GE Global Research **INVITED**

X-ray photoelectron spectroscopy (XPS) is a widely used method in fundamental surface science and applied materials characterization. As an analytical technique, XPS is an integral part of a modern materials research laboratory. Characterization of complex materials usually requires combinations of analytical methods to provide an understanding of structure-property relationships. In this talk, I will review the types of information provided uniquely by XPS, and illustrate how this information is coupled with data provided from other methods in the characterization of surfaces and thin films. Some examples will be selected from the author's own experience as an XPS expert within a larger materials characterization group at a major industrial R&D site. In this setting, a wide variety of sample types and issues are encountered. The variable degrees of success in the application of XPS to quantitative analysis, determination of oxidation states and functional groups, and thin film compositions will be described. In addition, the current and prospective applications in emerging fields such as biotechnology and nanotechnology will be discussed.

9:20am **AS-MoM4 Quantitative Depth Distribution Analysis of Hg and Na in Glass***, **T.A. Dang**, T.A. Frisk, M.W. Grossman, C.H. Peters,* Osram Sylvania

Fluorescent lamps use mercury for efficient conversion of electrical power to light. During lamp operation, some Hg is consumed through interaction and/or deposition on lamp components. One of the primary sites for interaction is the soda lime glass used as a lamp tube. The association of Hg and Na from the glass has been observed by XPS mapping.@footnote 1@ It is of particular interest to also evaluate the relationship of these two elements in deeper layers. A depth distribution analysis of Hg and Na would readily provide such information. It has always been a challenge to obtain the depth distribution of Na in glass using sputtering techniques. Due to the high mobility of Na, a soft sputtering condition, which minimizes Na diffusion, is generally required. Unfortunately, this also decreases the sensitivity for Hg, whose intensity is several orders of magnitude lower than that of Na. Simultaneous measurement of Na and Hg is strongly desirable because of the non-uniform nature of the interaction. In this presentation, we are going to compare the depth distribution analysis of Na and Hg using Secondary Ion Mass Spectrometry (SIMS) and High-Frequency Square-Wave Sputtered Neutral Mass Spectrometry (HFSW-SNMS). The advantages and disadvantages of each technique will be discussed. Samples included in the evaluation are composed of both quartz and soda lime glass wafers implanted with Na and Hg respectively as well as the real soda lime glass lamp tube subjected to normal lamp operation. @FootnoteText@ @footnote 1@ T. A. Dang, T. A. Frisk and M. G. Grossman, Anal. Bioanal. Chem., 373, 560 (2002).

9:40am **AS-MoM5 Rutherford Backscattering Quantification of Mercury Interaction with Fluorescent Lamp Materials***, **C.H. Peters**, M.W. Grossman, T.A. Dang, T.A. Frisk,* Osram Sylvania Inc.

Understanding mercury interactions with lamp materials is essential to reducing the amount of Hg required for operation of fluorescent lamps as well as improving light output. Rutherford backscattering spectrometry (RBS) is especially well suited to quantification of heavy elements such as Hg or Ba in a light matrix (e.g. soda lime glass). It provides quantitative measurement of trace amounts of mercury and non-destructive depth distribution information. We have developed a method to quantify buried Hg layers in glass under intact 1 to 2 µm thick alumina particulate coatings without the need to remove the coating layer. In uncoated lamps RBS can measure Hg uptake in soda lime glass within the first hour of operation. We have used RBS to characterize the effectiveness of coating layers in reducing interaction between Hg and the glass lamp envelope. Results from actual fluorescent lamps will be compared with quartz and soda lime glass wafers implanted with known amounts of mercury.

10:00am **AS-MoM6 Investigation of the Tribological System of Roller Bearings with TOF-SIMS***, **U. Gunst**, D. Lipinsky,* Westfälische Wilhelms-Universität Münster, Germany*; W.-R. Zabel, G. Poll,* Universität Hannover, Germany*; H.F. Arlinghaus,* Westfälische Wilhelms-Universität Münster, Germany

Tribology is a term describing an important and often complicated set of topics involving friction, lubrication, and wear. The surface characterization of tribological systems is of high importance to enhance their lifetime and to reduce economical loss. We have used time-of-flight secondary ion mass spectrometry (TOF-SIMS) in order to characterize the composition of tribosurfaces and of tribointerfaces of high speed rolling element bearings. Different TOF-SIMS methods (static TOF-SIMS, imaging, and depth profiling) were applied to investigate the elemental and molecular surface compositions as a result of interacting surfaces, friction, lubrication, and wear. Using static TOF-SIMS, semi-fluid lubricants, additives, the bearing steel, and the cage material were analyzed to establish reference information. The greases and roller bearing steel surfaces were investigated again after performing tribological test runs with real bearings under almost real application conditions. For these tests the additivation of the lubricants was varied using different primary, ashfree antioxidants. We used TOF-SIMS imaging for the characterization of these tribosurfaces within the race way of angular contact ball bearings. The depth composition of tribological boundary layers was analyzed by performing TOF-SIMS dual beam depth profiling on the top of roller bearing balls, as well as in the bearing race ways. Significant elemental and molecular species were found for lateral and depth distributions of different tribological layer regions - giving correlations to tribological models and interaction mechanisms.

10:20am **AS-MoM7 Interfacial Analysis between Amorphous Carbon Films and Glass by XPS and Improvement of Adhesion Strength at the Interface by Plasma Treatment***, **S. Takeda**, S. Suzuki,* Asahi Glass Co., Ltd, Japan

Amorphous carbon (a-C) films are widely applied in data storage and microelectronic industries because of their unique properties such as excellent hardness, good wear resistance, low friction coefficient, good chemical resistance and high electrical and thermal conductivities etc. However, in case of deposition of the a-C films onto glass, adhesion strength of the films to glass substrate is very poor and the film is easily delaminated at the interface between the film and glass. This is a serious problem for practical applications. Namely, improvement of the adhesion strength is a key issue to apply the a-C films to practical products. In order to overcome this problem, we investigated the effects of plasma treatment in Ar, N2 and O2 prior to the film deposition on the adhesion strength of the films to glass substrate. In the presentation, we report a major factor governing the adhesion strength based on the interfacial analysis between the a-C films and glass by X-ray photoelectron spectroscopy.

10:40am **AS-MoM8 Determination of SiGe Film Composition and Thickness by Combined AES and Multiple-Voltage X-ray Emission Analysis***, **J.T. Armstrong**, S.A. Wight, R.B. Marinenko, D.S. Simons, E.B. Steel,* National Institute of Standards and Technology

SiGe epitaxially grown on Si is used for bandgap-engineered devices with significant potential in a variety of microelectronic products. The composition of SiGe layers is often determined by RBS; however, the analytical accuracy is limited to ~5-10%, in part due to the lack of suitable standards. We are working on development of higher accuracy analytical procedures to characterize SiGe films being considered as NIST reference materials (50-150 nm, 3-40 atom % Ge, grown on Si substrates). We use a combination of Auger electron spectroscopy, multiple voltage x-ray emission analysis, and SIMS to determine their homogeneity, thickness and composition. Results are compared to measurements made on a series of bulk SiGe alloys also being investigated as possible NIST reference materials. The new generation of field emission scanning Auger microprobes (FE-SAM) provides superior capabilities for this type of analysis. With our newly installed FE-SAM, we are able to simultaneously perform Auger electron spectroscopy and high precision and accuracy EDS x-ray analysis at beam energies ranging from <1 to 25 keV. Using low voltage EDS analysis (2-4 keV) (augmented by the lack of contamination enabled by UHV and incorporating our newly refined correction procedures) we are able to determine the film compositions to better than 2% relative. By multiple higher voltage x-ray analysis (5-25 keV) on the FEASAM and electron microprobe, we are able to determine the lateral homogeneity and thickness. By AES and SIMS we are able to determine the in-depth homogeneity of the films and separately estimate their thickness. Preliminary results show good agreement among these measurements.

11:00am **AS-MoM9 Carbon Gold Sulfide by 13.56 MHz Plasma CVD and Sputtering Process***, **M.A. Kashem**, S. Morita,* Nagoya University, Japan

Co-operation process of plasma CVD and sputtering is a well-known technique to fabricate metal containing carbonaceous film, however the metal was mixed in the film with polycrystalline structure at content more than a few atomic %.@footnote 1@ CH@sub 4@ and SF@sub 6@ mixture gas plasma induced a unique reaction of HF dissociation and carbon sulfide could be synthesized.@footnote 2@ A new carbon gold sulfide film was formed with using CH@sub 4@, SF@sub 6@ and Ar mixture gas plasma CVD and gold plate discharge electrode. The process was observed and discussed with using a mass spectroscopy. The gold atom was observed to distribute uniformly caused on chemical bond with carbon and sulfur. The carbon gold sulfide structure was confirmed by x-ray diffraction, XPS analysis and refractive index measurement on the effect of thermal treatment at 200 °C. The chemically bonded carbon gold sulfide suggested to be conductive. Therefore, the density of carbon gold sulfide molecular group was observed to affect on a dielectric and conductive property. @FootnoteText@@footnote 1@L. Marutinu, Solar Energy Materials 15, p.21 (1987). @footnote 2@M. Matsushita, Md. Zarid. Bin Harum, Md. Abul Kashem and S. Morita; J. Photoplolym. Sci. and Tech., 12 (1) (1999) pp.11-14.

11:20am **AS-MoM10 Thickness, Dose and Distribution Measurements of Silicon Oxynitride Ultra-thin Films***, **R.K. Champaneria**, P. Mack, R.G. White, J. Wolstenholme,* Thermo Electron, UK

The continuing requirement for smaller equivalent oxide thickness (EOT) for transistor gate dielectrics has lead to the introduction of new materials with higher dielectric constants than silicon dioxide (high-k dielectrics). At present, silicon oxynitride is an important material for this application. X-ray photoelectron spectroscopy (XPS) is a well-known surface analytical technique. It can provide quantitative information, not only about chemical elements but also their chemical state. The information depth of the technique varies with the material under investigation but is in the region of 5-10 nm for materials commonly encountered in semiconductor device fabrication. This information depth can be controlled by means of the angle at which the photoelectrons are collected (angle resolved XPS or ARXPS) and, by collecting the signal at a number of angles, it is possible to generate a concentration depth profile. Since no material is removed in the generation of the concentration profile, the method is essentially non-destructive. Data will be shown to illustrate how ARXPS can provide accurate and precise measurements of thickness and nitrogen dose in oxynitrides. It will be shown that XPS measurements at a single angle cannot provide accurate measurements of the dose. Using line scans or maps, the uniformity of thickness and dose across a wafer can be measured. ARXPS data can also be used to reconstruct concentration depth profiles. These profiles reveal both the total dose and the distribution of nitrogen in each of its chemical states. It will be shown that methods of profile generation involving sputtering can produce misleading results.

Biomaterial Interfaces
Room 307 - Session BI-MoM
Protein-Surface Interactions

Moderator: A. Chilkoti, Duke University

8:20am **BI-MoM1 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Surface Plasmon Resonance (SPR) Determination of Surface Bound Anti-Lysozyme Orientation***, **N. Xia**, N.T. Samuel, P.S. Stayton, D.G. Castner,* University of Washington

Static time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and surface plasmon resonance (SPR) were used to analyze the orientation of immobilized proteins. A model protein with a well-define structure, the Fv fragment of a humanized anti-lysozyme (HuLys), was used. A His-tag linked to the C-terminal of the heavy chain was located opposite to the lysozyme binding domain (complementarity-determining region, CDR). We immobilized nitrilotriacetic acid (NTA) onto a self-assembled monolayer (SAM) of oligo(ethylene glycol)-terminated (OEG) thiol on Au. OEG provides a low-fouling background and NTA binds nickel ions, leaving two coordination sites available for interaction with the His-tag of HuLys. SPR experiments showed after nickel activation the NTA/OEG surface specifically bound HuLys Fv via the His-tag and that the immobilized HuLys Fv had nearly full antigen (lysozyme) binding capacity, suggesting a uniform CDR-exposed orientation of HuLys Fv on the surface. For comparison, we also activated the OEG SAM with carbonyldiimidazole (CDI), which binds protein via amine/imidazolyl carbamate chemistry and should result in a random protein orientation. This was supported by the SPR results, which showed that only ~50% of HuLys Fv immobilized on the CDI/OEG surface had antigen binding capability. The ToF-SIMS spectra of HuLys Fv immobilized on NTA/OEG and CDI/OEG surfaces were then compared. It was found that the peaks at m/z=81, 82 and 110 had lower intensities in the spectra of HuLys Fv immobilized on the NTA/OEG surface. These peaks all correspond to the primary mass fragments from the amino acid histidine. Since wild-type Hulys Fv has only 2 histidine residues, the ToF-SIMS results confirmed that HuLys Fv was immobilized onto the NTA/OEG substrate via the His-tag, which should be located at the bottom of the protein layer.

8:40am **BI-MoM2 Identification of Proteins in the Presence of Topographic Features using TOF-SIMS***, **S. Rangarajan**, B.J. Tyler,* University of Utah

In an earlier study, we had demonstrated the use of statistical modeling using mixture models and Principal Components Analysis (PCA) in characterizing samples having a relatively simple chemistry and coupled with topographical features. This study involves a very important extension to analysis of samples with more complex chemistry, such as with proteins. ToF-SIMS has been extensively used to characterize proteins, in spite of the inherent difficulties associated with spectral interpretation.@footnote 1,2@ Multivariate methods have also proved to be invaluable in the discrimination of adsorbed proteins on flat substrates.@footnote 3@ In this study, Polystyrene micro-spheres were adsorbed with different proteins and statistical models as well as discriminant techniques such as PCA were used to analyze the ToF-SIMS images. Discrimination of protein spectra from the images was then performed using the afore mentioned techniques, without a priori information about the type of protein adsorbed onto the sphere surfaces. Some of the models, such as the multinomial mixture model were found to yield more information than previously thought. References. @FootnoteText@ @footnote 1@ M.S.Wagner and D. G. Castner, Langmuir 17, 4649 (2001). @footnote 2@ D. S. Mantus and B. D.Ratner, Analytical Chemistry 65, 1431 (1993).@footnote 3@ M.S.Wagner, B.J.Tyler, and D. G. Castner, Analytical Chemistry 74, 1824 (2002).

9:00am **BI-MoM3 Immobilized Microarrays of Capture Agents for Bioassay: A Return to the Past for Protein Surface Stability?***, **D.W. Grainger**, P. Gong,* Colorado State University*; M. Lochhead, S. Metzger,* Accelr8 Technology Corporation **INVITED**

Microarrays of antibodies, nucleic acids, and antigens all encounter problems with prolonged bioactivity and desired capture sensitivity in immobilized formats. Surface chemistry is used to produce high target capture activity (high signal sensitivity) with low non-specific binding (noise). These surfaces can exhibit shelf-life problems limited, for example, by intrinsic hydrolysis of amine-reactive coupling chemistry (active esters, aldehydes) even under protective conditions. Reactive commercial array surfaces targeting amine-reactive nucleic acids or proteins have been regenerated in situ using N-hydroxysuccinimide to re-activate amine reactivity, improving functionalization of the commercial surfaces and improving immobilization of amine-terminated probes above original capacity. XPS and ToF-SIMS results for surface re-derivatization are correlated with DNA probe immobilization and target capture efficiencies. In a second effort, contact printed immobilized antibodies against a probe analyte on commercial polymer microarraying surfaces (70-micron spots) were assayed for model target capture (goat IgG) in sandwich immunoassay with fluorescently labeled secondary antibodies in full goat serum, imaged by fluorescence scanning. Off-array noise and on-array signal were compared as a function of printed antibody concentration. Despite masking with prescribed protocols (e.g., BSA or polymer masking), assay signal:noise was markedly improved on a non-masked three-dimensional polymer hydrogel commercial chemistry. Last, commercial arraying surfaces were used to exploit nucleic acid amplification (PCR reaction)on-array, capture fluorescently labeled target amplicons with printed probes, and rinse away all PCR reaction reagents in a single-step assay without prior separations or compromise to signal:noise performance. This provides substantial advantages in time and effort should sufficient signal:noise be achieved without costly, tedious PCR separation steps.

9:40am **BI-MoM5 Limitations of Molecular Streptavidin/Anti-biotin Antibody Architectures using Micro-contact Printed Biotinylated Thiols***,* ***Ch. Grunwald****,* Ruhr-University Bochum, Germany*; N. Opitz,* Max-Planck Institute for Molecular Physiology, Germany*; S. Herrwerth, W. Eck,* University of Heidelberg, Germany*; J. Kuhlmann,* Max-Planck Institute for Molecular Physiology, Germany*; Ch. Woell,* Ruhr-University of Bochum, Germany

Atomic force microscopy (AFM) and confocal fluorescence microscopy have been used to study the interaction of streptavidin and anti-biotin antibodies with a patterned, biotinylated organic surface. This system presently attracts considerable interest because of its potential for molecular architectures employing protein-protein interactions. The substrates were prepared by first using the µCP technique to print a periodic pattern of an oligoethylenglycol (OEG) self-assembled monolayer (SAM) on clean gold surfaces. The pattern consists of squares (40 µm x 40 µm) which are separated from each other in each direction by 10 µm. By immersing the stamped substrates into a mixture of OH-terminated and biotinylated organothiols a patterned SAM is obtained. These 2D-SAM patterns have been imaged via contact atomic force and lateral force microscopy as well as with tapping-mode AFM. The patterned SAMs were then incubated with two fluorescence-labelled proteins exhibiting a strong affinity towards biotin, streptavidin and anti-biotin antibody. Incubation time, temperature and concentration of the protein solution as well as the biotin surface concentration were varied systematically. The comparison of the AFM-data with the results of the fluorescence microscopy allows for important conclusion on the protein-protein binding, in particular concerning reproducibility, unspecific binding and protein resistance.

10:00am **BI-MoM6 A Comparison of Microcontact Printed and Solution Adsorbed Cytochrome c Protein Films on Indium Tin Oxide Electrodes***,* ***A. Runge****, S. Saavedra,* University of Arizona

The immobilization of proteins on a surface in a controlled way that retains their function is one of the challenges in making a functioning biosensor. Electrochemical biosensors use redox active proteins to impart selectivity to the electrode surface on which they are immobilized (either adsorbed or covalently attached). The orientation of proteins on the surface is presumed to be important for proper functioning of the device. We are investigating using microcontact printing as a way of immobilizing cytochrome c onto indium tin oxide electrodes in order to determine how the method of immobilization affects the orientation and function of the protein. We are presenting the results of three different methods for forming protein films on indium tin oxide that have been characterized and compared using cyclic voltammetry and X-ray photoelectron spectroscopy. Preliminary results from surface sensitive polarized spectroscopic studies will also be discussed. Protein films formed by adsorption of cytochrome c out of solution and by microcontact printing with both hydrophobic and hydrophilic PDMS are compared in terms of total and electrochemical surface coverage, standard reduction potential and rate of electron transfer with the ITO surface. Plasma treatment of the PDMS stamps, which makes them hydrophilic, dramatically increases the surface coverage of printed films to the level of solution adsorbed films. We have demonstrated that a redox active protein can be microcontact printed onto an electrode surface with its capability for direct electron transfer with the surface intact. The total surface coverage of the different films were compared using X-ray photoelectron spectroscopy.

10:20am **BI-MoM7 Using Nanografting to Position with Predictable Orientation, De-novo Proteins on Gold***,* ***Y Hu****, M. Case, G. McLendon, T.K. Vanderlick,* Princeton University*; D. Vanderah,* National Institute of Standards and Technology*; B. Nickel,* Princeton University*; M. Mrksich,* University of Chicago; *G.Y. Liu,* University of California, Davis*; G. Scoles,* Princeton University

An extensive research effort has been trying to make biosensors at the nanometer scale, especially selective detection devices with molecular recognition sites. We have approached this problem from a unique angle by using nanografting, which is to use an AFM tip to remove thiol molecules from a designated area of a self-assembled monolayer (SAM) while different thiol molecules from a contacting solution will self-assemble onto the exposed gold sites. By incorporating cysteine residues at the end of the peptide chains of [Fe(V@suba@L@subd@C-long)@sub3@]@super2+@, the proteins acquire the possibility to stand vertically on a gold surface. By using nanografting, the proteins could be patterned into islands about tens of nm wide and their properties could be measured in a differential way using the surrounding SAM as a reference. The height of these islands measures 3.2nm±0.4nm which, added to the 2.2 nm of the C@sub18@ SAM, corresponds well with the model height of the proteins. Effectively maximizing the signal-to-noise ratio of biosensors depends also on the ability to prevent protein nonspecific surface adsorption. It has been found that SAMs of thiols containing short oligomers of the ethylene glycol group prevent the adsorption of most proteins under a wide range of conditions. However the mechanism has not been clearly explained. It is observed that both SH(CH@sub2@)@sub11@(EO)@sub3@-OH and SH(EO)@sub6@-(CH@sub2@)@sub17@-CH@sub3@ reversibly compressed to half of their height under small imaging forces(0-10nN) in ethanol or 2-butanol. When the force is increased to over ~50nN, irreversible compression happened. Moreover, when the solution is changed to water mixture, the SH(EO)@sub6@-(CH@sub2@)@sub17@-CH@sub3@ is found to decrease its height significantly, and become much less compressible. By offering a model to explain the compressibility changes observed, we hope to offer some insight into the protein resistant properties of PEG-containing layers.

10:40am **BI-MoM8 Nanoscale Control of ECM Proteins for Cell Adhesion***, H. Wang, L. Liu,* ***S. Chen****, T. Barker, H. Sage, B.D. Ratner, S. Jiang,* University of Washington

Osteopontin (OPN) is an important extracellular matrix protein shown to function in wound healing, inflammation and foreign body reaction and has been identified as a potential target for engineered biomaterials. The secreted protein acidic and rich in cystein (SPARC/osteonectin/BM-40) is associated with events characterized by changes in cell shape and mobility. In the work, we first report control of OPN orientation and conformation on charged self-assembled monolayers (SAMs) for cell adhesion. Our atomic force microscope (AFM) results show that the amount of adsorbed OPN on -COOH surface is slightly less than that on -NH2 surface. Results from in vitro cell adhesion assays show that on NH2 surface BAEC adhesion and spreading are more. By comparing these results, it is suggested that the orientation/conformation of OPN on -NH2 positively charged surface is more favorable for cell interactions than on -COOH negatively charged surface. Second, AFM is used to image the binding of OPN onto individual triple-helical collagen I monomer on freshly cleaved mica for the first time. We also use anti-OPN antibody to assist for better visualization. Analysis of AFM results clearly shows binding patterns of OPN to collagen I. Finally, the interactions of SPARC with ECM proteins, such as collagen I and fibronectin, are characterized and quantified using AFM and surface plasma resonance (SPR). Cell culture and adhesion assays are used to study SPARC as a modulator of the adhesive process of cells seeded on ECM proteins. The influence of SPARC-collagen I interaction is studied using smooth muscle cells while the influence of SPARC-fibronectin interaction is studied using endothelial cells.

11:00am **BI-MoM9 Activity of the Model Enzyme Urease Adsorbed on Different Colloidal Oxide Particles***,* ***K. Rezwan****, J. Voros, M. Textor, L.J. Gauckler,* ETH Zurich, Switzerland

Whilst metal oxides are directly used for applications where their extreme hardness is necessary (e.g. femoral head replacement), most metallic biomaterials are themselves covered by a protective, stable oxide film such as titanium oxide on titanium. In these cases proteins only interact with the oxide film and not with the underlying metal. Closer investigations of the protein - oxide interface are therefore vital to the biomaterials field as it strives to make the transition from merely bio-inert to fully bioactive implant materials. It is assumed, that not only the amount of adsorbed protein but also its conformation is important for cell proliferation. A change of protein structure would hamper the cell receptors (situated within the cell membrane) to recognize the specific protein function. As a consequence, the cell would not adhere and proliferate on the preliminary adsorbed protein layer and not accept the adsorbed proteins as body own proteins but rather see them as intruders. This fatal mistake, made by the cell, is assumed to be one of the reasons which promotes local inflammation and tissue mutations. Assessing the conformational changes of a protein after adsorption is a delicate matter and can be measured by using for instance circular dichroism. In the case of enzymes, one can also measure the activity of the enzyme before and after adsorption. We used the model enzyme urease for our studies where the catalysis of urea was monitored by measuring the electrical conductivity as a function of time. The aim of this study was to compare the activity (and hence the conformational state) of urease after adsorption onto different colloidal oxide particles. We found that urease adsorbed onto TiO2 showed the highest activity and urease on Al2O3 the lowest. The measurements showed also an adsorption time dependency, which indicated further conformational changes after adsorption.

11:20am **BI-MoM10 In situ Real-time Atomic Force Microscopy Studies of Lysozyme and RR02 Protein Crystal Growth at Surfaces***, T.R. Keel, S. Allen, M.C. Davies, C.J. Roberts,* ***S.J.B. Tendler****, P.M. Williams,* University of Nottingham, UK

The successful application of crystallography to fields such as structural biology and rational drug design has been largely due to the availability of single crystals of the macromolecule of interest. However, relatively little is understood about the fundamentals of macromolecular crystal growth. Here, we have utilized the technique of atomic force microscopy (AFM) to study protein growth at surfaces. Two different protein systems, at both the micro- and nanometre scale have been investigated. The first is a model system, lysozyme. We have investigated two polymorphs of the lysozyme crystal and present data concerning the effect of supersaturation (@sigma@) on the growth rates and mechanisms of growth of the crystals. Molecular resolution studies have also been carried out and the observed periodicities are in good agreement with the known unit cell dimensions. Also presented are preliminary results from a second protein system, RR02, which is a response regulator protein found in streptococcus pneumoniae. RR02 is relatively straightforward to crystallize, but unlike lysozyme, many of the grown crystals diffract poorly and x-ray studies yield little structural data. We have used the AFM to investigate these crystals and compare the results with the lysozyme studies.

High-k Gate Dielectrics and Devices Topical Conference
Room 317 - Session DI-MoM

Electronic Properties of High-k Dielectrics and their Interfaces

Moderator: R.L. Opila, University of Delaware

8:20am **DI-MoM1 Attempting the Unthinkable: Replacing SiO@sub 2@ with High-k Materials as the Gate Dielectric for Scaled Devices***,* ***G.D. Wilk****,* ASM **INVITED**

The rapid pace of scaling CMOS technology has led to considerable attention in the area of high-k gate dielectrics. Since SiO@sub 2@ gate dielectrics are expected to have unacceptably high leakage current for most applications, high-k materials are of interest for producing lower leakage currents while maintaining similar device performance to SiO@sub 2@. Various high-k materials have been studied for this purpose recently, but it is clear that many important characteristics, which are already well known for SiO@sub 2@, have yet to be understood for any high-k material. To date, most high-k materials systems have exhibited the expected gate leakage reduction compared to SiO@sub 2@ of the same equivalent oxide thickness (EOT), but significant issues remain with respect to mobility degradation and threshold voltage shifts. Progress toward understanding these issues has been made over the past few years, yet controlling regions at both the channel and gate Si interfaces is still of critical importance to the success of any high-k material. Both physical and electrical analysis will be presented to highlight the key fundamental properties of high-k gate dielectrics, and how processing optimization has improved film quality. Characterization techniques such as electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM), medium energy ion scattering (MEIS), X-ray Photoelectron Spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) as well as electrical device properties will be presented.

9:00am **DI-MoM3 Challenges and Progress on High-K Devices and Materials***,* ***H.-H. Tseng****,* Motorola **INVITED**

High-K gate dielectric research is critical for advanced technology because the standby power increases significantly for ultra-thin SiO2 based gate dielectric. Although progress has been made in the past, there are huge challenges remained to be solved. This paper presents the challenges and progress of High-K devices and materials. Issues related to High-K device performance such as transconductance and mobility degradation, and high threshold voltage will be discussed. Challenges of reliability related topics such as threshold voltage instability, negative bias temperature instability (NBTI), stress-induced leakage current (SILK) will also be presented. Recent progress to address these challenges will be discussed. Finally, new research directions of High-K/gate electrode stack to meet the future technology requirements will be outlined.

9:40am **DI-MoM5 First Principles Studies of the Electronic and Atomic Structures of ZrO@sub 2@/Si and ZrSiO@sub 4@/Si Interfaces***,* ***R. Puthenkovilakam****, Y.-S. Lin, J.P. Chang,* University of California, Los Angeles

First principles simulations using density functional theory is employed to investigate the electronic properties of ZrO@sub 2@/Si and ZrSiO@sub 4@/Si interfaces for their potential applications in metal-oxide-semiconductor field effect transistors. Tetragonal zirconia and zircon are used to model ZrO@sub 2@ and ZrSiO@sub 4@, respectively, and the interfaces are formed by lattice matching their (001) surfaces to the Si(100) surface. The electronic structure of ZrO@sub 2@/Si interfaces showed partial occupation of zirconium d states at the Fermi level when the zirconium coordination is different from its bulk coordination. These partially occupied states lie within the silicon band gap, forming conductive paths under an applied potential field, thus are detrimental to the device performance. However, ZrSiO@sub 4@/Si interface showed no partial occupation of zirconium d states at Fermi level. Hydrogen passivation of zirconium dangling bonds as well as oxygen bridging at the interface are shown to effectively remove the partial occupancy of d orbitals. The calculated band offsets of ZrO@sub 2@/Si interfaces showed asymmetric band alignments, with conduction band offsets between 0.73-0.98 eV and valence band offsets between 3.70-3.95 eV for different zirconium and oxygen coordinations at the ZrO@sub 2@/Si interfaces. The ZrSiO@sub 4@/Si interface resulted in a more symmetric band alignment with a much higher conduction band offset of 1.90 eV and a valence band offset of 2.98 V. These results suggest that ZrSiO@sub 4@ forms a superior interface with silicon compared to ZrO@sub 2@ and can be an ideal candidate for replacing SiO@sub 2@ as a gate insulator in silicon based microelectronics and additional interface preparation or post-deposition annealing are required for ZrO@sub 2@ to yield adequate electronic properties.

10:00am **DI-MoM6 X-ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE) Study of Hafnium Silicate Alloys Prepared by Remote Plasma Assisted Chemical Vapor Deposition: Comparisons between Conduction Band Offset Energies and Optical Band Gaps***,* ***J.G. Hong****, N.A. Stoute, G. Lucovsky, D.E. Aspnes,* North Carolina State University

Thin films of hafnium silicate alloys, (HfO@sub 2@)@sub x@(SiO@sub 2@)@sub 1-x@, were prepared by remote plasma enhanced chemical vapor deposition (RPECVD) using down-stream injected Hf t-butoxide as the Hf source gas and silane as the Si source gas; chemically-active species from a remotely excited O@sub 2@/He plasma were used to drive the CVD reaction. Alloy compositions were determined by Rutherford backscattering (RBS), and were used to calibrate Hf-to-O spectral ratios obtained by on-line Auger electron spectroscopy (AES). XPS spectra were then obtained for the O 1s, Si 2p, Hf 4d and Hf 4f core levels, and the core level binding energies of these features were analyzed as a function of the alloy composition x. All core binding energy levels decreased (i.e., became more positive) as the Hf fraction x increased, paralleling the behaviors previously reported for O 1s, Si 3p, and Zr 3d core level energy shifts in zirconium silicate alloys. The Hf silicate alloy shifts are consistent with the charge transfer expected on the basis of the relative electronegativities of Hf, Si and O. As in case of Zr silicates, the total shift of the O 1s core level in Hf silicates, ~3.1 eV, is larger than the average shift of the Hf 4d and Si 2p core levels, ~ 2 eV. Finally, the XPS results will be compared with on-line AES, X-ray absorption spectroscopy (XAS), and vacuum ultra-violet spectroscopic ellipsometry (SE) results to determine the compositional variations of the conduction and valence band offset energies with respect to Si, and to compare theses with the compositional variation of the optical band gap.

10:20am **DI-MoM7 Photoemission Study of High-k Gate Dielectric/Si(100) Heterostructures - Chemical Bonding Features and Energy Band Alignment***,* ***S. Miyazaki****,* Hiroshima University, Japan **INVITED**

The characterization of chemical and electronic structures of high-k dielectrics as well as the quantification of defect state distributions is of great importance for the implementation of the high-k dielectric gate stack in sub-100nm technology generations. For some high-k dielectrics such as Ta@sub 2@O@sub 5@, Al@sub 2@O@sub 3@, ZrO@sub 2@ and HfO@sub 2@, we have experimentally determined the energy band alignments to Si(100) with an thin interfacial Si-oxide or nitride from high-resolution XPS measurements and defect state distributions in the high-k dielectrics and at the interfaces form total photoelectron yield measurements.@footnote 1-3@ We have extended our research to characterize the chemical and electronic structures of Y@sub 2@O@sub 3@, Pr-silicates and Hf-aluminates on Si(100) including interfacial SiO@sub x@. In this presentation, recent our results will be review to demonstrate how the energy bandgaps of practically-thin high-k dielectrics such as

HfO@sub 2@ and Y@sub 2@O@sub 3@ and of an ultrathin Si-nitride barrier can be determined from the analysis of energy loss spectra of O1s (or N1s) photoelectrons and, for the system of Y@sub 2@O@sub 3@ formed on Si(100), how the energy band alignment can be determined with combination of the measured bandgap and the valence band lineup as obtained from the analysis of XPS valence band spectra of heterostructures with thin dielectrics. Also, we show that total photoelectron yield spectroscopy is a useful tool for quantifying the energy distribution of electronic defect states for thin high-k dielectric/Si(100) systems. @FootnoteText@@footnote 1@S. Miyazaki, J. Va. Sci. Technol. B19, (2001) 2212. @footnote 2@S. Miyazaki, M. Narasaki, M. Ogasawara and M. Hirose, Microelec. Eng., 59 (2001) 373. @footnote 3@M. Yamaoka, M. Narasaki, H. Murakami and S. Miyazaki, Proc. of 2nd Int. Semicond. Technol. Conf. (2002, Tokyo) Abst. No. 57.

11:00am **DI-MoM9 Separate and Independent Control of Interfacial Band Alignments and Dielectric Constants in Transition Metal-rare Earth Ternary Oxides**, ***D.G. Schlom,*** Pennsylvania State University*; J.L. Freeouf,* Oregon Graduate Institute*; G. Lucovsky,* North Carolina State University

The electronic structure of transition metal, Tm, and trivalent rare earth, Re, binary (TmO@sub x@ and Re@sub 2@O@sub 3@) and ternary mixed oxides (TmRe@sub x@O@sub y@) are qualitatively different from those of silicon oxide, silicon nitride, and silicon oxynitride alloys. The lowest conduction band states are associated with localized anti-bonding d*-states of the Tm/Re atoms, rather than extended Si 3s*-states, and/or O/N 2p*-states. Based on quantitative agreement between the Zr silicate anti-bonding state electronic structure obtained from Zr M@sub 2,3@ and O K@sub 1@ XAS spectra, and ab initio calculations on small clusters, the ordering and overlap of anti-bonding Zr 4d*- and 5s*-states, and Si 3s*-states in the O K@sub 1@ spectra is the same as the features of the conduction band electronic structure that determine band-offset energies at Si-Zr silicate alloy interfaces. These relationships have been extended to Re ternary oxide compounds, including LaAlO@sub 3@ and GdScO@sub 3@, through direct comparisons between O K@sub 1@ XAS spectra and band edge optical absorption constants obtained from analysis of SE measurements extending to 9 eV. As a result of near-neighbor interactions between Tm and Re d-states induced by bonding to a common O atom, ternary oxide minimum band gaps, and conduction band offset energies are increased in oxide phases containing Tm and Re species. This identifies new and technologically important opportunities for band gap engineering at the atomic scale. Relative energy shifts of coupled Re and Tm d*-states are important for the ultimate scaling of CMOS devices since they increase the effective band gaps/offset energies for ternary oxides containing highly polarizable Sc, Ti, Nb, and Ta atoms above what had previously been proposed as a fundamental limitation inferred from the band gaps and/or band offset energies of their respective binary oxides.

11:20am **DI-MoM10 A Materials and Electronics Properties Study of the ZrO@sub 2@/Si and SiO@sub 2@ Interfaces**, ***C.M. Lopez***, *N.A. Suvorova,* University of North Carolina, Chapel Hill*; A.A. Suvorova, M. Saunders,* University of Western Australia*; E.A. Irene,* University of North Carolina, Chapel Hill

Zirconia, ZrO@sub 2@, thin films were grown on single crystal MgO(100), Si(100) and on amorphous SiO@sub 2@ by ion beam sputter deposition of Zr metal at room temperature and subsequent oxidation both in-situ and ex-situ at 250°C and 600°C, respectively. The optical properties of MgO, sputter-deposited Zr, and ZrO@sub 2@ were determined by in-situ spectroscopic ellipsometry in the photon energy range of 1.5-4.5 eV. Based upon ellipsometric thicknesses obtained, a volume expansion of 1.28 Zr to ZrO@sub 2@ was observed. This value is in contrast to the value assuming bulk densities, 1.54. Refractive index values for ZrO@sub 2@ ranged from 2.18 to 2.52 for the given spectral range. Time of flight mass spectrometry of recoiled ions (TOF-MSRI), analytical electron microscopy, and spectroscopic ellipsometry were used to investigate the material properties of all samples with special attention to the composition and extent of the interface formed between ZrO@sub 2@ and the Si substrate. To compliment these techniques, electrical measurements were performed on fabricated Pt/ZrO@sub 2@/Si capacitors also prepared in vacuo to determine the interface trap state density, fixed charge, and dielectric constant for the overall film stack. The nature of the interface is correlated with the resultant electronic properties of the interface.

11:40am **DI-MoM11 Interface and Materials Properties of High-k Gate Stack Structures**, ***S. Sayan,*** *X. Zhao, R.A. Bartynski, T. Emge, M. Croft, T. Gustafsson, D. Vanderbilt, E.L. Garfunkel,* Rutgers University

In this presentation, we describe recent results using soft x-ray photoemission (SXPS), inverse photoemission (IPE), and x-ray absorption spectroscopy (XAS) to examine HfO2 gate dielectrics and their interfaces with silicon and metal layers. In selecting an alternative (high-K) gate insulator, many parameters in addition to dielectric constant and thermal stability must be considered, including the barrier heights for tunneling. The SXPS and IPES results are used to determine the densities of states above and below the Fermi energy, in particular to elicit useful information on barrier heights. We find that interface dipoles affect the "effective workfunction" of metals via change in electrostatic potential as well as the band alignments, where the specific alignment depends on the interface properties. We have also performed first-principles density functional calculations to study the properties of the crystalline phases of HfO2 and ZrO2. The densities of valence and conduction bands are calculated and compared to experimental measurements. The thickness, layered structure, and crystal phase of the as-deposited and annealed films have been studied by XRD, XAS, MEIS, RBS and HRTEM. The authors would like to acknowledge useful interactions with colleagues at and NCSU (J.P. Maria, G. Parsons, G. Lucovsky and A. Kingon), J.Robertson (Cambridge University.UK), R. Tung (CUNY) and K.P. Cheung (ECE, Rutgers University) We also acknowledge the SRC for financial support.

Manufacturing Science and Technology
Room 309 - Session MS-MoM

Process and Equipment Integration and Development

Moderator: E.G. Seebauer, University of Illinois at Urbana Champaign

8:40am **MS-MoM2 Development of Low Resistance Copper Thin Films Using a Strain Enhanced Grain Growth Technique**, ***M. Moriyama***, *M. Shimada, H. Masuda, M. Murakami,* Kyoto University, Japan

Copper is attractive as interconnect materials of future Si-ULSI (Ultra-Large Scale Integrated) devices with linewidth of less than 100nm. The advantage of using copper (over conventional Al-alloy) as the interconnect materials is that copper has lower electrical resistivity and higher reliability. However, we have serious concern with resistivity of the ultra-narrow Cu interconnects, because the resistivity of interconnects was observed to increase rapidly by reducing the linewidth of the interconnects. The reason is believed to be due to the relatively long mean free path (~39nm) of the conducting electrons of copper. When the linewidth is less than 100nm, the electron scattering by the surface (or interface) and grain boundary becomes dominant, causing significant increase in the resistivity of the copper interconnects. In order to realize nano-scaled Si-devices, development of low resistance ultra-narrow copper interconnects is essential. The purpose of the present experiment was to explore the possibility to prepare low resistivity copper interconnects, which satisfy the designer's requirement, by determine the primary factor (film thickness or mean grain size) which controls the electrical resistivities of copper films. The film microstructures were observed by atomic force microscopy and scanning ion microscopy. The film resistance was measured by a DC four-point probe method. Our experimental result concluded that the grain boundary scattering primarily increased the resistivity of the Cu thin films, indicating that large grained films were essential for low resistivity ultra-narrow copper interconnects. We succeeded to prepare the copper thin films with giant grains by the strain enhanced grain growth technique. This technique will be promising to develop the low resistance copper interconnects for the future Si-ULSI devices.

9:00am **MS-MoM3 Processing and Characterization of PMSSQ Based Materials for Nanoporous Low-K Dielectrics**, ***P. Lazzeri,*** ITC-IRST, Italy*; J.J. Park, Z. Lin, R.M. Briber,* University of Maryland*; L. Vanzetti, M. Anderle, M. Bersani,* ITC-IRST, Italy*; R.D. Miller,* IBM Almaden Research Center*; G.W. Rubloff,* University of Maryland

Nanoporous low-K dielectrics are an essential component in future interconnect technology. We have investigated the thermal transformations by which nanoporous polymethylsilsesquioxane (PMSSQ)-based low-K dielectrics are formed through spin-casting and curing in a mixture of PMSSQ with a poly(methylmethacrylate-co-dimethylaminoethylmethacrylate) random copolymer (PMMA-co-DMAEMA) as the porogen. ToF-SIMS shows a sequence of PMSSQ fragments which change with curing, as well as the evolution of porogen related species. Over the range 200-450C, both crosslinking to form the

SiO@sub 1.5@CH@sub 3@ matrix and decomposition/volatilization of the porogen occur. To understand the influence of PMSSQ precursor chemistry on the final low-K structure, we have compared two precursors with different initial SiOH content. ToF-SIMS shows the crosslinking kinetics to be faster for the high SiOH than for the low SiOH content material. The distribution of the porogen species also varies with the nature of the PMSSQ precursor: XPS reveals substantial surface depletion of porogen for the low SiOH but not for the high SiOH content material, and ToF-SIMS images indicate the formation of large porogen aggregates, but only for the low SiOH material. Thermal desorption mass spectrometry during curing shows the evolution of volatile byproducts, as expected for both the crosslinking reactions and the porogen degradation and desorption. These chemical analysis techniques yield information crucial to understanding the complex chemical and transport phenomena which determine the microscale and nanoscale properties of these nanoporous low-K dielectrics and their role in future interconnect technology.

9:20am **MS-MoM4 Multi-scale Modeling of Chemical Mechanical Planarization***, L. Jiang, H. Simka, S. Skokov, D. Thakurta,* ***S. Shankar,*** Intel Corp.

A coherent modeling approach is presented for mechanics and transport effects in CMP process. Different regimes of material removal are identified based on first-principle analysis on slurry transport, stress, and slurry flow. Important effects of pad, glazing, conditioning, and polisher design are demonstrated with oxide polish model results. We review multiple-scale model linking with an emphasis on the innovative methods to combine flow and stress analysis from feature to wafer scale. Micron-scale models developed at Intel are presented to illustrate the complexity of particle-level dynamics in CMP and the physical processes involved in patterned wafer planarization.

9:40am **MS-MoM5 Thermal Characterization of Stacked 3D System-in-Package***, J. Valtanen, J. Miettinen,* ***E.O. Ristolainen,*** Tampere University of Technology, Finland

Electronics development has been driven mainly by IC technology progress. Cell and line width have been continuously shrunk proving development trend called Moore's law. This has created increasing pressure to the first level interconnection. In future, traditional 2-dimensional (2D) packaging will limit product miniaturization. Therefore, components must be also joined to third dimension. A solution to this problem is a stacked System-in-Package (SiP). With this technology, great improvements over 2D packaging are achieved, such as greater packaging density, smaller size, and shorter interconnection length. The next evolution step comes in through following ways: to grind extra sand away from active ICs, to use flexible substrates and interposers. However, this technology has some problems that must be solved. For higher density of 3D package, increased power density brings new challenges to heat management. In this work, a stacked SiP structure has been studied. The package consists of three layers. In every layer, a silicon die of 3.7 mm x 8.3 mm has been joined with flip chip method onto an aramid-epoxy interposer of 6 mm x 10 mm. The silicon chips has been thinned down to 90 µm and the thickness of the interposer is 150 µm. The interposers are joined together using solder covered polymer spheres with diameter of 250 µm. So, the dimensions of whole package are 0.9 mm x 6 mm x 10 mm resulting in the total silicon efficiency of 150 %. Transient thermal responses have been measured by experiments and they are compared with simulations calculated with the FEM program Ansys. A constant heat power has been added to one chip at a time and temperature response has been measured in every chip. In this study, thermal responses, maximum temperatures, and chip-to-chip thermal interactions are achieved. In addition, differences between boundary conditions are discussed and certain design rules for chip placement are given.

10:00am **MS-MoM6 Advanced Clean Process by Supercritical Carbon Dioxide***,* ***H.-J. Tu,*** *P. Chuang, C.-Y. Wang, Y.-L. Lin, H. Lo, M.-S. Zhou, M.-S. Liang,* Taiwan Semiconductor Manufacturing Company, Ltd., Taiwan, R.O.C.

As device approaching nano-scale, it is more difficult to extend aqueous-based clean processes to future generations due to its high surface tension characteristics. An advanced clean process by supercritical carbon dioxide (SCCO@sub 2@) becomes a potential enabling technology in semiconductor industries for its specific capabilities of low surface tension, chemical inertness, and more friendly ESH (environment, safety, and health) which can overcome future wafer clean challenges. In the present work, we show that using SCCO@sub 2@ can successfully remove residue/polymer for advanced sub 100 nano-meter copper low-k interconnect fabrication. In addition, it appears that the low-k dielectric film is much less damaged by this novel technology than conventional clean process.

10:20am **MS-MoM7 Two-Gas Reactive Sputtering***, W.D. Sproul, D.J. Christie,* ***D.C. Carter,*** Advanced Energy Industries, Inc.

Reactive sputtering with two reactive gases and one target material presents special problems. Both reactive gases affect the state of the target surface and the plasma conditions, which means that both affect common feedback control signals such as the cathode voltage and optical emission signals. Modeling has shown that the way to control the two-gas reactive sputtering process is to produce individual control signals for each gas. Experiments have confirmed the model. The reactive sputtering of titanium or silicon in a combined oxygen/nitrogen atmosphere is shown. In this study, individual partial pressure signals for each of the oxygen and nitrogen reactive gases were available from a mass spectrometer. A combination where one of the gases is controlled in the partial pressure mode and the other in a flow mode can lead to unstable operating conditions under certain process conditions. The gas operating in flow control can trap the target in a poisoned state, and the target cannot return to the unpoisoned state until both gases are removed. Both target voltage and mass spectrometer data show the existence of a high partial pressure of the flow controlled reactive gas that traps the target in the poisoned mode even when the partial pressure controlled reactive gas is removed from the system. To have a fully stable process when two reactive gases are used requires that the partial pressure of each gas be controlled individually. When the individual partial pressures are controlled, the target does not get trapped in a poisoned state, and there is complete freedom to adjust the reactive gas partial pressures to achieve the desired film composition.

10:40am **MS-MoM8 Hydrogen Pressure Dependence of Trench Corner Rounding during Hydrogen Annealing***,* ***H. Kuribayashi,*** *R. Shimizu,* Fuji Electric Corporate Research and Development, Ltd., Japan*; K. Sudoh, H. Iwasaki,* Osaka University, Japan

Hydrogen annealing has become increasingly important for silicon device processes. Especially for trench gate MOSFETs, both trench corner rounding and sidewall surface smoothing are quite essential for the ruggedness and reliability of gate oxide. Though the evolution of crystal shape through surface self-diffusion during heating in vacuum has been extensively investigated, it has not been sufficiently studied in specific ambients, which are applicable to semiconductor processes. At the preceding meeting we studied shape transformation of silicon trenches with sidewall surface of (110) and (-110) during annealing in hydrogen ambient at 1000°C, and showed that the observed shape transformation can be simulated well with Mullin's continuum surface model@footnote 1@ with surface self-diffusion. In this work, to study the roll of hydrogen gas on the Si surface self-diffusion in more detail, we investigated both the hydrogen pressure dependence and the temperature dependence of the trench corner rounding for wider range of pressure (10-760Torr) and temperature (1000-1100°C), respectively. We found a remarkable effect of hydrogen on trench corner rounding. The curvature of a trench corner for a certain annealing time increases linearly with increasing hydrogen pressure. The diffusion coefficient at 1000°C deduced by the Mullin's formula decreased from 2x10@super 5@nm@super 2@/sec at 100Torr to 3x10@super 3@nm@super 2@/sec at 500Torr, which are much smaller than the one in vacuum@footnote 2@ by three to five orders of magnitude. The diffusion coefficients did not follow the Arrhenius relations for 1000-1100°C in the higher-pressure region above 100Torr, suggesting that more than one rate-limiting processes are involved in the temperature range. @FootnoteText@ @footnote 1@W.W.Mullins, J.Appl.Phys.28, 333(1957).@footnote 2@Y.-N. Yang, Elain S. Fu, and Ellen D. Williams, Surf. Sci. 356,101(1996) .

11:00am **MS-MoM9 Development of a Continuous Generation/Supply System of Highly-concentrated Ozone Gas for Low-temperature Oxidation Process***,* ***S. Ichimura,*** *H. Nonaka,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Y. Morikawa, T. Noyori, T. Nishiguchi, M. Kekura,* Meidensha Corporation, Japan

Ozone has various superior characteristics compared to oxygen molecules in ultrathin oxide film formation on silicon. It realizes rapid oxidation rate at low substrate temperature, very thin transition layer in the oxide film, high electrical quality of the oxide film, etc. Those characteristics have been proved using a highly concentrated (HC) ozone generator, which supplies almost 100% ozone gas at pressure lower than 1000 Pa. The generator utilizes vaporization of pure liquid ozone accumulated in an ozone vessel. Since the liquid ozone accumulation is limited to 5 ml because of safety, the generator can supply only about 360 l ozone gas at the pressure. Considering future need in practical low-temperature oxidation process, we have developed a new system which continuously generate/supply HC ozone gas. The system is equipped with 4 ozone-vessels, and each vessel temperature can be controlled separately. During continuous operation, the condition of each ozone vessel changes stepwise with the same time interval along the following mode sequence; 1) cooling the vessel from 120K to 90K, 2) accumulation of liquid ozone by distillation of ozone/oxygen mixture gas at 90K, 3) heating the vessel from 90K to 113K and vaporization of pure liquid ozone, and 4) heating the vessel from 113K to 120 K and evacuation of the vessel. Allocating one of the 4 modes to each of the 4 ozone vessels so as to cover all the modes simultaneously, the system can supply constant flow of HC ozone gas. The maximum flow rate of the gas is 60 sccm, being enough for single wafer processing, and the ozone concentration is over 99 vol.% at the output of the system. The characteristics of the system in the formation of ultrathin oxide on 4 inch silicon wafer is examined, together with the effect in low temperature oxidation of excited state atomic oxygen which can be generated/supplied by photo-dissociation of ozone at sample position. @FootnoteText@@footnote 1@T. Nishiguchi et al. Appl. Phys. Lett. 81, 2190 (2002).

11:20am **MS-MoM10 Profile Control for Deep Silicon Etch by Sidewall Passivation in High Density Plasma***, **M. Khbeis**, G. Metze,* Laboratory for Physical Sciences*; K. Powell, D. Thomas, A. Pentland, J. Hutchings,* Trikon Technologies, Ltd.

Deep silicon etching of micron-sized structures is a critical step in high-aspect ratio via fabrication. This paper shows that m=0 Resonant Induction (M0RI) plasma technology coupled with the use of both etch and passivation gases produced deep via holes with unscalloped sidewalls at non-cryogenic temperatures. Process development, operational parameters, and potential applications are discussed. Wafer level packaging of high density, complex systems-on-chip is of great interest to the microelectronics industry for the production of compact devices and electronic components.@footnote 1@ Vertical integration of various unpackaged integrated circuits can be accomplished through die attachment, wafer-to-wafer bonding, thinning, and lastly high-aspect ratio backside interconnects for signal communication. During the fabrication of these 3-D systems there is a need to provide high-aspect ratio backside metal interconnects at a depth of at least 20µm. The fabrication of interconnect via holes dictate that the following etches be performed; oxide mask etch, bulk silicon etch, and buried oxide layer etch. Other potential applications for deep silicon etch include bulk micromachining for MEMS, ground/power plane connections, or re-routing of signal lines for novel packaging. In this paper, development of the deep bulk silicon etch is emphasized. To accommodate subsequent dielectric passivation and metallization steps, via holes were specified to have a profile angle of 89 to 90 degrees with absolutely no sidewall scalloping. Sidewall scalloping will impede metal transport during a high-pressure reflow process. Since deep reactive ion etch (DRIE) processes, such as Bosch, induce scalloping, alternative etch technologies that do not require switching of etchants and passivants are mandatory. @FootnoteText@@footnote 1@ J. Reche E. Korczynski, High-Density Thru-Silicon Interconnects, HDI Expo Proceedings,(2000).

11:40am **MS-MoM11 The Study on Deformation of ArF Photo Resist in Dry Etching***, **C.-H. Shin**, G.J. Min, C.J. Kang, J.T. Moon,* Samsung Electronics Co., Ltd., Korea

193nm ArF lithography has been introduced in DRAM industry for sub-90nm patterning. However, it has several issues in the substrate fabrication of sub-90nm patterning. First, the physical thickness of resist has been decreased less than 3000Å, which is critical point for stable pattern transfer. Second, durability of resist in the plasma was reduced due to the increase of Ohnish parameter. Third, resist is subjected to deformation when it is exposed to the plasma due to its soft chemical structure. All these factors limit the application of ArF lithography. Etching was performed in the commercially available dual frequency plasma based on O2, Ar, CO and C4F6 single gas chemistry, respectively. It was found that supply of bias power in the argon gas system led to the severe deformation of ArF photo resist. Novel techniques for the formation of protective layer will be discussed in this paper in order to suppress resist deformation with enhanced etch selectivity.

Nanometer Structures
Room 316 - Session NS-MoM

Quantum Dots and Nanoscale Devices

Moderator: E.T. Yu, University of California, San Diego

8:20am **NS-MoM1 Conductance and Stability of Atom-sized Al Contacts under High Biases***, J. Mizobata,* Toshiba Corp., Japan*; A. Fujii, S. Kurokawa, **A. Sakai**,* Kyoto University, Japan

Single-atom contacts (SACs) of metals are known to exhibit various unique properties and considered to be a candidate of interconnects in nanoelectronics. In our previous experiments, we studied high-bias conductance of Au and Au-alloy SACs and showed that they can be observed up to 2 V. In order to know the maximum rating of other metal SACs, we carried out conductance measurements of Al SACs for biases from 0.1 to 0.8 V and investigated the formation and the lifetime of Al SACs as a function of the bias voltage. All measurements were made in UHV at room temperature on breaking Al pin-plate contacts, where SACs were observed just before their complete breakage. We found that the formation probability p@sub Al@ of Al SACs decreases with increasing the bias and leads to the suppression of the first peak in the conductance histogram. Both p@sub Al@ and the first peak vanish at around 0.8 V. On the other hand, the average lifetime of Al SACs, <@tau@@sub Al@>, decreases almost linearly with increasing the bias but remains finite at 0.8 V. For comparison, we re-measured the high-bias conductance of Au SACs and found that p@sub Au@ and <@tau@@sub Au@> show similar bias dependence to that of p@sub Al@ and <@tau@@sub Al@>, respectively, though the relevant bias range is much higher for Au SAC: p@sub Au@, for example, survives up to 2.4 V. We consider that the reduction of p@sub Au@ and p@sub Al@ is due to a contact instability induced by electromigration, which fractures contacts in the middle of their deformation and hence reduces the chance of forming SACs. On the other hand, we found it difficult to explain the observed linear bias dependence of <@tau@@sub Al@> and <@tau@@sub Au@> by a simple rate theory since we know little about the effective contact temperature under high biases.

8:40am **NS-MoM2 In-situ Monitoring of Quantum Conductance in Electrodeposited Magnetic Point Contacts@footnote 1@***, **C.-S. Yang**, J. Thiltges, B. Doudin,* University of Nebraska, Lincoln*; M. Johnson,* Naval Research Laboratory

The goal of our research is to investigate the magnetoresistance properties of magnetic quantum point contacts. A two-steps fabrication process is used. First, a 50 nm gap between two planar Au electrodes of 1-2 microns widths is patterned using focused ion beam milling. Second, a metallic film is slowly electrodeposited over the electrodes. In-situ measurements of the inter-electrodes impedance monitors the contact resistance during the growth. Keeping electrochemical control of the electrodes ensures optimum purity of the nanocontact, as well as the absence of oxides. Experiments are performed under sweeping magnetic field reaching 1600 Oe amplitude. Quantum conductance steps in Au and Ni point contacts are observed. For Ni, we find that an external field is helpful to observe quantum conductance in multiples of e@super 2@/h, lifting the spin degeneracy. Opening and closure of nanocontacts seldomly occur during the magnetic field sweeping. No significant magnetoresistance was observed for samples of conductance values smaller than 50 e@super 2@/h. Optimizing the measurement speed, we show that no magnetoresistance values larger than 10 % occur when the resistance is stabilized at quantum plateau values during a few magnetic field sweeps. @FootnoteText@ @footnote 1@This research is supported by ONR and NSF MRSEC.

9:00am **NS-MoM3 Quantum Dot Nucleation and Growth in a Microfluidic Reactor***, **T.L. Sounart**, J.A. Voigt, T.A. Michalske,* Sandia National Laboratories

Semiconductor quantum dots have the potential to transform important technologies including (bio-)chemical sensors, efficient light sources, catalysts, and supercapacitors. The current ability to control nanoparticle properties, however, is at a state of infancy. Quantum dots are synthesized in batch operations with no feedback and poor control of thermal, chemical, and fluid transport, resulting in a distribution of particle size and batch-to-batch variations. Microfluidic technology, which has revolutionized analytical chemistry and only more recently has been applied to chemical synthesis, offers numerous potential advantages over existing techniques. It is expected that laminar flow, high heat transfer rates, and short mixing lengths can be exploited to precisely control crystal size and morphology, and that microreactor conditions can be adjusted instantaneously to tune output particle properties in real time. In addition to providing better control of reactor conditions, microfluidic systems provide a unique platform for investigation of fundamental reaction processes. Using optical measurement techniques, which are particularly suitable to quantum dot synthesis, we present here for the first time, an on-chip analysis of the nucleation and growth of nanoparticles. CdS early growth processes that are too fast to observe transiently have been resolved spatially in a continuous flow microreactor, and examined by imaging the fluorescence field in the microchannel upon excitation at 365 nm. Early results indicate, e.g., that cysteine-capped quantum dots are formed in less than a second of contact between Na@sub 2@S and CdSO@sub 4@. We are currently analyzing the fluorescence field using hyperspectral imaging to extract data on particle size and concentration variations within the reactor for different chemistries and flow rates. This data is being incorporated into microreactor models to learn how to control quantum dot size and morphology.

9:20am **NS-MoM4 Formation of 31P Qubit Test Structures by Single Ion Implantation***, **T. Schenkel,*** Lawrence Berkeley National Laboratory*; J. Bokor,* UC Berkeley and Lawrence Berkeley National Laboratory*; D.H. Schneider,* Lawrence Livemore National Laboratory*; A. Persaud,* Lawrence Berkeley National Laboratory*; S.-J. Park,* UC Berkeley and Lawrence Berkeley National Laboratory*; J. Nilsson,* Lawrence Livemore National Laboratory*; J.A. Liddle,* Lawrence Berkeley National Laboratory

Electron and nuclear spins of 31P atoms in silicon are promising candidates for the realization of a scalable solid state quantum computer architecture. Single ion implantation with low energy (<10 keV), highly charged ions offers a path to the formation of single 31P atom arrays. We describe our development of single ion placement technology and the integration of atom arrays with control gates and single electron transistor readout structures. Silicon nanowire based single electron transistors are formed in SOI (silicon on insulator) by electron beam lithography and stress limited oxidation. We will discuss critical process integration issues. @footnote 1@ @FootnoteText@ @footnote 1@ We thank the staff of the UC Berkeley Microlab for technical support. This work was supported by the National Security Agency and Advanced Research and Development Activity under Army Research Office contract number MOD707501, and by the U. S. Department of Energy under contract No. DE-AC03-76SF00098. Work at LLNL was performed under the auspices of the U. S. Department of Energy under contract No. W-7405-ENG-48.

9:40am **NS-MoM5 Spin Based Qubit Fabrication in SiGe***, **L.J. Klein,** K.A. Slinker, J.L. Truitt, M. Friesen, D.W. van der Weide, S.N. Coppersmith, R. Joynt, M.A. Eriksson,* University of Wisconsin, Madison

A promising approach to solid-state implementation of quantum computers is electron spins in silicon devices. The design incorporates vertical and lateral tunneling into quantum dots defined by nanostructured top gates in the 2DEG of a strained Si quantum well. The potential in the two-dimensional electron gas is modulated by the voltages applied to the top metallic gates. Work is underway to fabricate quantum point contact and quantum dots in strained Si layer and quantum phenomena are investigated related to discrete charge variations. The ultimate goal is the fabrication of qubit: a quantum dot with single electron occupancy with a well defined spin state which is immune from decoherence. This scalable approach allows entanglement of two qubits by varying the voltage applied to top gates separating two quantum dots. Recent measurements of spin lifetime in stained SiGe structures shows decoherence times larger than micro seconds. This large decoherence time should allow many qubit logic operations, initialization, and read-out of a single spin qubit.

10:00am **NS-MoM6 A Systematic Study of SiGe Quantum Fortresses and Possible Applications to Quantum Cellular Automata***, **T.E. Vandervelde**, P. Kumar, T. Kobayashi, J.L. Gray, T.L. Pernell, R. Hull, J.C. Bean,* University of Virginia

In this study we detail conditions that result in the generation and evolution of novel hetero-epitaxial surface structures in SiGe/Si created either by spontaneous self-assembly or by ion beam seeding. These self-assembled structures strongly resemble the proposed parameters for a Quantum Cellular Automata (QCA) unit cell. Specifically, we define the growth conditions (i.e. temperature, epi-layer thickness, Ge concentration, and growth rate) under which self-assembly of strain-stabilized quantum fortresses (QFs) and their precursors form. This growth progression can be dissected into a series of surface features that evolve before and after the appearance QFs. These kinetically limited configurations exist over a wide range of growth conditions, however they are destabilized by excessive adatom surface mobility or strain relaxation resulting from the introduction of misfit dislocations. To characterize these self-assembled structures and their destabilization, we have systematically studied and are basing simulations on their basic dimensional parameters, within this functional space. One natural application would be to use QFs in QCA based architectures. A fully developed QCA circuit requires arrays of QF-like structures, but nature only provides us with isolated randomly located QFs. To overcome this limitation we also report work directed at a guided self-assembly technique that relies on gently altering the substrate before growth. This is achieved using a 25 KeV in-situ Ga+ focused ion beam to locally enhance Ga+ concentration and alter the substrateâ€™s surface topography. The intent is to use the surfactant-like nature of low Ga doses, to cause local nucleation of Ge clusters without greatly disturbing surface topology. We also explore the effects of higher Ga+ dosages, which cause the appearance of significant surface topology, on the localization of Ge cluster nucleation. This work, in part, was supported by NSF through FRG and MRSEC grants.

10:20am **NS-MoM7 Current Challenges in Nanocrystal-Quantum-Dot Lasing***, **V.I. Klimov,*** Los Alamos National Laboratory **INVITED**

Semiconductor quantum dots (QDs) offer important advantages for lasing applications that are associated with their size controlled emission wavelengths (and, hence, output color) and low, temperature-insensitive optical-gain thresholds. QDs have been fabricated using epitaxial techniques (epitaxial or self-assembled QDs) or using chemical synthesis routes [nanocrystals or nanocrystal QDs (NQDs)]. Despite the impressive success of laser technologies based on epitaxial QDs, the first unambiguous demonstrations of amplified spontaneous emission@footnote 1@ and lasing@footnote 2@ involving chemically synthesized NQDs were performed only recently. The difficulties in achieving lasing in NQDs are due to both materials-quality issues and the existence of intrinsic physical mechanisms that complicate the development of stimulated emission. One such complication is ultrafast gain decay due to highly efficient, nonradiative, multi-particle Auger recombination. In our work we explore "geometrical" methods (e.g., nanocrystal shape control) for suppressing the multi-particle recombination. In particular, we study the effect of the zero- to one-dimensional (1D) transformation on Auger decay using series of elongated semiconductor nanocrystals (quantum rods). We observe an interesting new effect, namely, the transition from a three- to a two-particle recombination process as the nanocrystal aspect ratio is increased. This transition implies that in the limit of 1D confinement, Auger decay is dominated by Coulomb interactions between 1D excitons that recombine in a bimolecular fashion. One consequence of this effect is strongly reduced decay rates of higher order multi-particle states that lead to the increased optical gain lifetime and efficient light amplification due to excited-state transitions. These unique rod properties suggest that shape control may be key to developing practical lasing applications for nanocrystals. @FootnoteText@ @footnote 1@ V. I. Klimov et al., Science 290, 314 (2000). @footnote 2@ H.-J. Eisler et al., Appl. Phys. Lett. 80, 4614 (2002); M. Kazes et al., Adv. Mater 14, 317 (2002); A. Malko et al., Appl. Phys. Lett. 81, 1303 (2002).

11:00am **NS-MoM9 Si Nanocrystal Synthesis in an Oxide Matrix: A Multiscale Computational Study***, **D. Yu**, G.S. Hwang,* University of Texas at Austin

Nanocrystalline Si (nc-Si) embedded in a SiO@sub2@ matrix is receiving great attention due to its interesting fundamental physical properties and promising applications for advanced microelectronic devices and optoelectronic devices. The unique electrical and optical properties of embedded Si nanocrystals appear to be strongly influenced by their crystallite size, shape, density as well as Si/SiO@sub2@ interface structures. It is therefore necessary to develop a detailed understanding of the nc-Si growth and Si-SiO@sub2@ interfacial interactions. Although experiments offer many clues to the nanocrystal formation and interface properties, their interpretations often remain controversial. In this talk, we will present our multiscale computational model for the synthesis of Si nanoclusters in an oxide matrix. Our multiscale model integrates various state-of-the-art theoretical methods at different time and length scales, such as first principles quantum mechanics, molecular mechanics, and kinetic Monte Carlo. Using the multiscale approach, we have examined i) formation mechanism of Si clusters in silicon suboxide, ii) shape evolution of embedded nanoclusters, iii) Si-SiO@sub2@ interface structure and strains. Our simulations show that small silicon clusters agglomerate very rapidly at the early stage of thermal annealing mostly via coalescence. As the Si cluster density gets lower, the coalescence becomes less probable and the cluster growth continues mainly by Ostwald ripening (which appears be several orders of magnitude slower than the initial stage coalescence). Our theoretical study also demonstrates that the average size of silicon clusters is a strong function of the initial silicon supersaturation. Our results are in good agreement with recent experimental observations.

11:20am **NS-MoM10 Nanocrystalline Structures in Amorphous Silica**, ***J.Y. Cheng***, Rensselaer Polytechnic Institute; *M.M.J. Treacy,* NEC Research Institute; *P.J. Keblinski,* Rensselaer Polytechnic Institute

We conduct the metamict transformation of crystalline silica in a transmission electron microscope. In this experiment, an alpha quartz crystal was transformed into an amorphous phase by electron irradiation at high dose. In the meantime, diffraction patterns of these phases were taken throughout the process. After that, we measured image fluctuations in dark field for the amorphous structure. From the images, the amorphous silica is "nanocrystalline." From the diffraction patterns, these crystallites are randomly oriented. Our results also show that the original alpha phase has ultimately disappeared in the new structure.

11:40am **NS-MoM11 Investigation of Nucleation and Growth of Si(Ge) Nanocrystals Embedded in HfO@sub 2@ as Floating Gate for Flash Memory Devices**, ***R. Gupta***, National University of Singapore; *L.K. Bera,* Institute of Microelectronics, Singapore; *W.J. Yoo,* National University of Singapore, Singapore; *D.S.H. Chan,* National University of Singapore; *N. Balasubramanian,* Institute of Microrelectronics, Singapore

Charge storage in semiconductor nanocrystals is a very critical property to determine electrical performance of non-volatile memory devices. Nanocrystals embedded in high dielectric constant materials are not only effective to scale down the device size but also to enhance the programming and retention properties. Also, it is known that Si(Ge) nanocrystals of size @<=@ 10nm can have much better charge storage capability at room temperature than Si nanocrystals. This study is focused on understanding mechanisms to control shape, size, and composition of Si(Ge) nanocrystals that will be used for improving device properties of non-volatile memories. The Si(Ge) nanocrystals were deposited using Silane & Germane at the pressures of 0.5Torr - 5Torr and at the temperatures of 500°C-600°C on 40Å of either thermally grown SiO@sub 2@ or MOCVD HfO@sub 2@. The deposition time was varied from 5 seconds to 70 seconds at different flow rates of Silane & Germane. It was found that the evolution of size and density of Si(Ge) nanocrystals was dependent on pressure, deposition time, and substrate material. We found, as the deposition pressure decreased from 5 Torr to 0.5 Torr, the minimum size of Si(Ge) nanocrystal on SiO@sub 2@ decreased from 50 nm to 2 nm while density increased from 10@super 8@/cm@super 2@ to 10@super 11@/cm@super 2@. We observed that nanocrystal size increased in early stages but agglomeration took over with the further increase of deposition time. For SiO@sub 2@, we found that Ge atomic percent decreased from 18.4% to 14.6% as the deposition time increased from 5 seconds to 15 seconds at 5 Torr. However, Ge atomic percent on HfO@sub 2@ at same conditions at 5 seconds was lower at 12.3 %, showing significant difference in kinetics of the Si(Ge) nanocrystal formation between HfO@sub 2@ and SiO@sub 2@ substrates. Details on nucleation, growth, and electrical results on charge storage of Si(Ge) nanocrystals on HfO@sub 2@ will be presented.

Contacts to Organic Materials Topical Conference
Room 318/319 - Session OM-MoM

Contacts to Molecules and Molecular Films (I)

Moderator: A. Kahn, Princeton University

8:20am **OM-MoM1 Coupling Molecules to Electronic Materials Chemical Bonding and Polarization Effects at Metal-Molecular Monolayer-Semiconductor Junctions**, ***D. Cahen***, Weizmann Institute of Science, Israel **INVITED**

All-molecular nm scale optoelectronic devices face many practical and fundamental obstacles, which,however,do not preclude use of molecules to control hybrid devices. In such systems nm- or even sub-nm molecular structures need to be incorporated in device structures. Judicious choice of such systems allows, apart from potentially practical possibilities, fundamental investigations of the effects, limitations and possibilities of molecules in optoelectronics. By placing molecules at metal-semiconductor interfaces, even if only as poorly organized, partial, rather than ideal monolayers, they can control these interfaces electronically.@footnote 1@ This is primarily because electron energetics at interfaces determine the electronic behaviour of semiconductor & metal contacts.@footnote 2@ Normal requirement for (near-)ideally structured monolayers can be relaxed because the molecules can act as "gatekeepers", i.e., electrostatically rather than -dynamically. This leads to molecular devices, with no current flow through molecules.@footnote 1@ Devices are made reproducibly because soft contacting methods were developed.@footnote 3@ These also show how intimate contact between molecules and metal can polarize the contacts.@footnote 1,3@ In systems with near-ideal molecular films, molecules electronic transport through molecules is often by "through bond" tunneling.@footnote 4@ Experimental evidence is accumulating both from our and other groups, that in most devices with molecules, the nature of the molecule/electrode contact is crucial for the resulting junction.@footnote 4,5@ @FootnoteText@ @footnote 1@ A.Vilan et al. Nature404(2000)166;J.Phys.Chem B, in press; G.Ashkenasy et al. Acc.Chem.Res.35(2002)121@footnote 2@ D.Cahen, A.Kahn, Adv. Mater.,14(2003)271@footnote 3@ A.Vilan, D.Cahen, Adv.Funct.Mater.12(2002)795; H. Haick et al., to be published@footnote 4@ Y.Selzer et al.,J.Phys.Chem.B 106(2002)10432;D.Cahen,G.Hodes, Adv.Mater. 14(2002)789@footnote 5@ Y.Selzer et al.,Angew.Chem.Int.Ed., 41(2002)827.

9:00am **OM-MoM3 Long Range Electronic Coupling at Molecule-metal Interfaces: C60/Cu(111)**, *G. Dutton,* ***X.-Y. Zhu***, University of Minnesota

It is well-recognized that electronic interaction at molecule-metal interface is one of the key factors governing the performance of molecular-semiconductor devices. The efficiency or rate of injection at such an interface is determined by (1) the energet ic alignment of molecular orbitals to the metal Fermi level, (2) the electronic coupling strength (wavefunction mixing) between molecular orbitals and metal bands, and (3) the dynamics of charge carrier localization at the interface. While energetic align ment has been probed by photoemission spectroscopies, electronic coupling strength and charge localization dynamics remain largely unknown at the present time. We attempt to address these issues in the present study using the model system of C60/Cu(111) a nd the experimental technique of time-resolved two-photon photoemission (2PPE) spectroscopy. The lowest unoccupied molecular orbital (LUMO) and LUMO+1 levels in C60 are transiently populated via the creation of charge-transfer excitons, with lifetimes < 1 00 fs. The lifetimes decrease substantially as film thickness decreases, due to quenching by the Cu substrate; this effect is seen for films as thick as 50 @Ao@. Such a long-range effect is attributed to charge transfer between the Cu substrate and electronic bands in C60.

9:20am **OM-MoM4 Molecule on Metal versus Metal on Molecule: The Sexiphenyl/Al Interfaces**, *B. Winter, J. Ivanco, F.P. Netzer,* ***M.G. Ramsey***, Karl-Franzens University, Austria

Here the formation of both the organic/metal and metal/organic interfaces has been investigated with particular attention given to both their electronic and geometric structure as elucidated by angle resolved UV-photoemission and low energy electron diffraction. Despite the weak electrostatic bond found, a dense well ordered wetting monolayer results for sexiphenyl (6P) on single crystal Al(111), irrespective of growth temperature. The interface dipole of this layer determines the band alignment for the subsequent films that develop. For the converse, Al on 6P, a similarly weak bonding interaction is observed with no evidence for the commonly invoked scenarios of either a strong chemical bond formation or diffusion into the organic film. Under UHV growth conditions a wetting layer is impossible to achieve and the Al balls-up on the organic film. In spite of this weak interaction the evaporation of Al disturbs the surface of the crystalline 6P film, changing the conformation of the molecules at the surface and thereby effecting a 0.6 eV change in the HOMO binding energy and concomitantly the band alignment. If oxygen is introduced at the interface a change of up to 2 eV in the band alignment results, due to both a change in the interface dipole and in the ionisation potential of the interfacial molecules brought about by an increase in their conjugation. Not only does the oxygen improve the electron injection ability at the Al interfaces, the changes in surface energy allows the formation of a metallic wetting layer. Acknowledgments: Supported by the Austrian Science Foundation SFB Electroactive Materials

9:40am **OM-MoM5 Adsorption of Sexithiophene on Clean and Potassium-Dosed Al(111)**, ***J.E. Whitten***, *H. Ahn, S.K. Sengupta,* University of Massachusetts, Lowell

Oligo- and polythiophenes are finding important organic electronic device applications that include light-emitting diodes, photovoltaics, and field-effect transistors. Low work function vacuum-deposited metals, such as aluminum, are commonly used as electrode materials, and understanding the nature of the organic/metal interface may lead to improved device performance. In this study, we have taken the approach of adsorbing the organic layer on top of bulk metal in order to obtain complementary information to previous investigations of aluminium deposition on sexithiophene. X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) have been used to study the interfaces between sexithiophene sublimed in ultrahigh vacuum onto clean and potassium-doped Al(111) surfaces at 130 K. These investigations demonstrate that sexithiophene adsorbs very weakly on the clean surface, as suggested by minimal work function changes and a lack of shifts in the binding energies of the C1s and S2p core levels and in the frontier valence orbitals of the adsorbate. In contrast, even a small amount of deposited potassium leads to strong interaction between the surface and interfacial sexithiophene. The adsorption of this oligomer on the K-doped aluminum surface has been studied as a function of potassium dose. Even at low potassium coverage, strong interaction of sexithiophene with the surface is indicated by low binding energy components in the C1s and S2p peaks and the emergence of a potassium-induced peak near the Fermi level.

10:00am **OM-MoM6 Interaction between Metals and Organic Semiconductors Studied by Raman Spectroscopy***, **D.R.T. Zahn**, G. Salvan, B. Paez,* Technische Universität Chemnitz, Germany

Silver and indium were deposited onto molecular layers of two perylene derivatives, viz. 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,@ag N@-dimethylperylene 3,4,9,10-dicarboximide (DiMe-PTCDI). The interaction between the metals and the organic semiconductors was probed in situ by Raman spectroscopy. The molecular structure is found to be preserved when Ag or In are deposited onto PTCDA and DiMe-PTCDI layers. For In this is in contrast to previous suggestions of strong reactivity with PTCDA and covalent bond formation between In and O atoms in PTCDA.@footnote 1,2@ However, the molecules having direct contact with the metal are involved in a weak ground state dynamical charge transfer with different strength for Ag and In, resulting in a breakdown of vibrational selection rules. A significant enhancement of Raman internal vibrational modes is observed both for Ag and In deposition as a result of metal-induced surface enhanced Raman scattering (SERS). The enhancement factors observed for the internal modes reflect a rough morphology of the metal films which is influenced by the morphology of the underlying organic film, i.e., Ag on PTCDA grows predominantly (111) oriented, while Ag on DiMe-PTCDI has a much more polycrystalline nature. Moreover, conclusions regarding the interdiffusion of the two metals can be drawn from the comparison of the breakdown of the selection rules for the internal modes and the spectral evolution of the external molecular modes. @FootnoteText@@footnote 1@Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, and S.R. Forrest, Phys.Rev. B 54, 13748 (1996)@footnote 2@S. Kera, H. Setoyama, M.Onoue, K. Okudaira, Y. Harada, N. Ueno, Phys.Rev. B 63, 115204 (2001).

10:20am **OM-MoM7 Electronic Structure and Hole Injection Barriers for Pure and Substituted Phenylene Ethynylene Oligomer Self-Assembled Monolayers***, **S.W. Robey**, C. Zangmeister, R.D. van Zee,* National Institute of Standards and Technology

Ultraviolet photoelectron spectroscopy was used to determine the electronic structure of self-assembled monolayers (SAMs) of phenylene ethynylene oligomers on Au. Monolayers comprised of the three ring oligomer (OPE) and molecules with -NO@sub2@ (NO@sub2@-OPE) substitutions on the central ring were investigated. This study provides the first glimpse of the electronic structure and band alignment for SAMs of these molecular systems linked to interesting transport characteristics in nanoscale junctions.@super1@ For the unsubstituted oligomer, the electronic structure is interpreted using simple molecular systems and related polymers as guidance. The states above ~ 5 eV binding energy are primarily C-C and C-H @sigma@ bonding states. Their polarization dependence is found to be consistent with a nearly upright orientation. Near the Fermi level (E@subf@), orbitals traceable to benzene e@sub1g@ @pi@ states are split by the C-C coupling along the backbone into density localized primarily on the ortho-carbon atoms of individual phenyl rings (at ~ 3.9 eV) and potentially delocalized @pi@ levels along the backbone that can provide the primary channels for transport. The hole injection barrier (energy separation between E@subf@ and the HOMO level) is about 0.8 eV. Substitution of electron withdrawing groups on the central ring induces negative differential resistance in transport measurements.@footnote 1@ The effects on electronic structure were investigated in monolayers of the NO@sub2@-OPE oligomers. Compared to the unsubstituted OPE, there is an overall shift of intensity for @pi@ states near E@subf@ to higher binding energy by about 0.5 eV. The hole injection barrier also appears to increase to approximately 1.0 eV. Connections with calculations of transport properties for related molecular systems and experimental and theoretical results for substituent effects in conjugated polymers will be discussed. @FootnoteText@@footnote 1@Chen et al.,Science 286,1550(1999).

10:40am **OM-MoM8 Direct Double-Bond Contacts to Metal Carbides: A New Surface Functionalization Reaction***, M. Siaj, H. Oudghiri Hassani, **P.H. McBreen**,* Universite Laval, Canada

Functional nanoelectronics devices require optimal electrical contact between their components as well as adequate protection from the environment. In the context of SWCNT-based field-emission transistor devices, metal carbides can be used as chemically bonded high-transmission source/drain contacts.@footnote 1@ We will present results showing that organic layers can be attached to the surface of molybdenum carbide via a metal-carbon double bond. This new surface reaction involves the insertion of a surface metal atom into the carbonyl bond of ketones or aldehydes, as in the following process; R2C=O + Mo yields R2C=Mo=O. Furthermore, the R2C=Mo surface groups (termed surface alkylidenes) are found to be thermally stable to above 900 K, if the surface is rendered inert though carbon deposition.@footnote 2@ The fact that the contact between the organic layer and the carbide is a double bond points to three advantages. First, a double bond is intuitively a better electrical contact than a sulfur atom. Second, it is possible to form carbides from a wide variety of metals. Third, we have demonstrated that alkylidene functionalized molybdenum carbide is active for metathesis reactions. Thus, ring opening polymerization (ROMP) can be used to grow polymeric layers directly from the carbide surface. Extensive results obtained using RAIRS and XPS will be presented to describe these new methods for the preparation of double bond contacts on a technically relevant substrate. @FootnoteText@@footnote 1@R. Martel, V.Derycke, C. Lavoie, J. Appenzeller, K. K. Chen, J. Tersoff and Ph. Avouris, Phys. Rev. Lett. 87, 256805, 2001. @footnote 2@E. Zahidi, H. Oudghiri Hassani and P. H. McBreen, Nature, 409,1023,2001.

11:00am **OM-MoM9 Study of Transport Through Organic Molecules on Semiconductor Surfaces Using STM-SPV***, **I. Nevo**, S.R. Cohen, D. Cahen, G. Haase,* Weizmann Institute of Science, Israel

Mapping the potential of semiconductor surfaces using STM provides the ability to investigate electron transport properties through single molecules. The potential mapping is preformed by monitoring the tip-surface bias required to maintain a constant tunneling current under illumination termed - surface photovoltage (SPV). There is currently great interest in electron conduction through organic molecules attached to inorganic surfaces. However, many experiments probe an ensemble of nano-scale systems, thus, the effect of interface inhomogeneity is averaged out. Namely, it is not clear if and which of the molecular states participate in the electronic current passing through a system of a single molecule confined between two electrodes. Moreover, of the effect of an organic molecule on the local potential is unknown. In this work we investigate the transport properties of poly-aromatic molecules adsorbed on GaAs(110) and GaP(110) surfaces in ultra high vacuum and room temperature conditions. The bias dependence of the SPV images that are acquired simultaneously with the topography images indicates different tunneling mechanisms: direct tunneling, and resonant tunneling involving the molecular states. In addition, the potential surface varies with bias due to the changing overlap of molecular states with the tunneling energy interval.

11:20am **OM-MoM10 Contact Effects in Molecular Junctions***, **C.D. Frisbie**,* University of Minnesota **INVITED**

The importance of metal-molecule interfaces in determining the current-voltage (I-V) characteristics of molecular junctions has been made clear in theoretical work over the past 5 years. Yet systematic experimental investigations, in which the contact effects are mapped out as a function of the metal work function and the type of surface linker used to bind the molecules to the electrodes, have not been carried out. This talk describes a conducting probe atomic force microscopy (CP-AFM) approach to the experimental examination of contact effects in molecular junctions. Junctions are fabricated by contacting self-assembled monolayers (SAMs) on metal substrates with metal-coated AFM tips; it is possible to contact SAMs with any metal that can be coated onto an AFM tip. Contact resistances are estimated by measuring total junction resistance (at different bias voltages) as a function of the length of the molecules between the tip and substrate contacts, and then extrapolating resistance versus length plots to zero length. We find that contact resistances in molecular junctions are sensitive to the metal work function, the type of surface linker (e.g., -SH vs â€“NC), and the bonding in the molecular backbone (i.e., conjugated vs saturated). Importantly, the work function dependence allows qualitative estimation of where the Fermi level of the junction lies with respect to the HOMO and LUMO of the molecules. We will summarize our findings to date on contact effects in junctions composed of molecules with alkane or oligophenylene backbones.

Plasma Science and Technology
Room 315 - Session PS-MoM
Critical Dimension Etching

Moderator: K. Seaward, Agilent Laboratories

8:20am **PS-MoM1 Not Quite 50 Years of Plasma Etching**, ***R.A. Gottscho***[1], Lam Research Corp. **INVITED**

Since the advent of plasma etching in the manufacturing of semiconductor devices in the 1970s, both industry and technology have changed dramatically. In the '70s, integrated device manufacturers (IDMs) dominated the industry. IDMs built systems by starting with "sand" and using equipment of their own design and fabrication. For example, hexode etchers were created by Bell Labs, the Reinberg reactor came from Texas Instruments, and electrostatic chucks came from IBM. Today, IDMs buy plasma processing equipment with processes developed, at least partly, by the equipment companies. Fabless companies have sprouted and grown ubiquitous as foundries have become a dominant source of chip supply. In the early '80s, debates raged over the relative merits of single wafer processing for 4-6" wafers. Today, batch etchers cannot be found in the fab despite their inherent throughput advantages. Single wafer processing of 12" wafers with unprecedented control is the norm. Now, we see the advent of integrated metrology and even more advanced process control. Over this time period, gate lengths have shrunk from >1 um to

9:00am **PS-MoM3 Chemical Topography Analyses of Photoresist Patterns Exposed to HBr/O2 and Cl2/O2 Trimming Plasma Processes**, ***E. Pargon***, *O. Joubert, L. Vallier,* CNRS/LTM, France*; S. Xu,* Applied Materials

Nowadays, a way to bypass the lithography limitation in typical gate etch processes is to introduce a step of "resist trimming" prior all the other classical etch steps. Resist trimming induces a lateral erosion of the photoresist mask to reach a range of dimension smaller than the resolution of the lithography. To better understand the mechanisms involved in this process, an experimental procedure based on XPS has been developed to determine the chemical composition and thickness of the reactive layers formed both on top and sidewalls of the resist features during the process. The processes are performed in a high density plasma source (ICP) and two trim chemistries are investigated: HBr/O@sub2@ and Cl@sub2@/O@sub2@. The XPS analyses show that the transformations occurring on the resist sidewalls can well explain the faster trim rate obtained with a HBr/O@sub2@ chemistry. Indeed, the XPS results reveal that HBr/O@sub2@ is a very reactive chemistry leading to the formation of very thin (0.5 @nm@) reactive layers on the resist sidewalls, while when using Cl@sub2@/O@sub2@, there is a competition for the adsorption sites between atomic Chlorine and Oxygen leading in this case to thick (1.5 @nm@) carbon rich chlorine reactive layers on the resist sidewalls. Other plasma parameters (pressure, bias and source powers) have also been studied and we have obtained good correlations between the trim rate and the modifications measured by XPS on the resist sidewalls. In most cases, with the Cl@sub2@/O@sub2@ chemistry, a decrease in trim rate is well correlated with an increase in reactive layer thickness on the resist sidewalls and with a decrease of the O/Cl ratio in the reactive layer. Finally, this XPS experimental procedure enables us to better understand the mechanisms involved in resist triming processes and to determine the key plasma parameters that drive such processes.

9:20am **PS-MoM4 Aspect Ratio Dependent Etching in the Si-Treatment Process of the Source and Drain Area of sub 90 nm Devices**, ***K.H. Bai***, *M.C. Kim, B.Y. Nam, K.K. Chi, C.J. Kang, W.S. Han, J.T. Moon,* Samsung Electronics Co., Korea

As feature dimension shrinks down to nano scale of sub 90 nm, the aspect ratio increases up to more than 10 even at the source/drain area of the self-aligned contact (SAC) sturcture of the DRAM devices. The small open areas of the contact holes for the sub 90 nm devices require enough Si-treatment at the source/drain area to get a reliable contact resistance. However, usually the low-biased etching condition of the soft etch plasma has severe aspect ratio dependent etching (ARDE) phenomena, leading a lot of Si3N4 loss at the shoulder of SAC sturcture. To overcome the severe ARDE in the high aspect ratio structure, we investigated the ratio of radical to ion flux at the top and bottom surface of the contact holes. Because the low bias of the soft etching condition, the radicals collide to the side wall surface multiple times before reaching the hole bottom. Therefore, the radical flux at the bottom of the hole is affected by the sticking coefficient controlled by the surface temperature. However, another important key factor controlling the ARDE is the radical density in the plasma. We found that the surface coverage of the contact hole is greater than 1, the temperature becomes a less important factor in controlling the ARDE. In this work, we investigated the ARDE of our Si-treating plasma in our sub 90 nm scale devices as functions of the radical density and temperature, finding a condition nearly free from ARDE. As a result, the loss of Si3N4 at the shoulder of the gate electrode was reduced by 70%, also improving contact resistances at the source/drain more than 10%.

9:40am **PS-MoM5 Loading Effect Study on Cl@sub 2@+HBr Plasma Etching of Polysilicon**, ***W. Jin***, *H.H. Sawin,* Massachusetts Institute of Technology

The effect of etching product buildup, i.e. loading effect, in an inductively coupled plasma etcher for polysilicon etching with Cl@sub 2@+HBr chemistry is studied. In addition to the depletion of reactants, etching products can be fragmented upon collision with energetic electrons into various Si-containing species, with subsequent deposition on the substrate and chamber walls. The role of Si-containing species on the plasma-surface interaction has to be included in the surface kinetic model database for the simulation of etching process. This work uses real plasma beam/QCM to measure the etching yield under different ion bombardment energy and temperatures, and adds SiCl@sub 4@ in Cl@sub 2@/HBr feed gas to mimic the effect of Si-loading observed in a real ICP etcher. The study indicates that the Si-loading can reduce the etching yield significantly, due to the ion-enhanced deposition of Si-containing species on the substrate. The effect of etching yield reduction is more pronounced at lower Si-loading. The plasma beam composition was measured with a mass spectrometer as a function of feed gas composition and Si-loading. The reduction of etching yield at different Si-loading can be explained by the relative concentration of Si, SiCl and SiCl@sub 2@ species at different Si-loading. The surface composition was measured with X-ray photoelectron spectroscopy after etching. The surface composition does not show significant change with Si-loading. A surface kinetics model was developed to relate the etching yield to the beam composition, ion energy and substrate temperature. The insensitivity of surface composition to the Si-loading can also be explained by this model.

10:00am **PS-MoM6 Pattern Deformations during Resist Trimming Process and its Suppression by He-diluted O@sub 2@/SO@sub 2@ Chemistry**, ***H. Morioka***, *M. Tajima, M. Terahara, M. Nakaishi, I. Hanyu,* Fujitsu Limited, Japan

In addition to CD control, accuracy of pattern transcription in resist trimming and gate etching process, what is called pattern fidelity, has become more important with scaling of ULSI devices. Various pattern deformations during resist trimming, such as line-end shortening, often become serious obstacles to high-density device integration because they narrow the alignment margin and prevent the scaling of design rule. We measured line width reduction (amount of trimming) and the line-end shortening during trimming and gate etching process. Experiments were performed on an ICP etcher. O@sub 2@-base chemistry was used to "trim" resist patterns. The gate stack consisted of 1nm gate oxide, 100nm Poly-Si, and 30nm SiO@sub 2@, which was coated by organic BARC and patterned by ArF lithography. We found that the line-end shortening was larger than the line width reduction, and this disparity increased with increasing trimming time, which was accompanied by pattern deformations in specific patterns, such as L-shape corner. This pattern dependent resist erosion can be related to excessive etchant flux in the convex area. In order to suppress these disparity and pattern deformation, we investigated He/O@sub 2@/SO@sub 2@ chemistry, in which SO@sub 2@ was a source of lateral etching inhibitor that is mild to ArF resist, and oxygen was main etchant of trimming. He-dilution was used to control the trimming rate and suppress condensation of sulfur compounds. Optimizing etchant/inhibitor ratio by means of O@sub 2@/SO@sub 2@ ratio, we have succeeded in reducing line-end shortening and suppressing pattern deformations for trimming of sub-100nm resist patterns. In optimized conditions, trimming amount was almost the same as line-end shortening, and proximity effect (dense-iso differnce) of trimming was smaller than 5nm. Therefore we have fabricated

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[1] **AVS 50th Anniversary Invited Speaker**

25nm gate poly-Si patterns by He/O@sub 2@/SO@sub 2@ trimming (from 80nm to 25nm) and conventional poly-Si gate etching process.

10:20am **PS-MoM7 On the Roughness of Etched Silicon***, **A.A.E. Stevens**, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

The smaller the etched features, the more important the roughness of the etched feature surface becomes. Not only for integrated circuits, but also for, e.g., photonic crystals, the surface roughness might limit the device quality. By using in situ (spectroscopic) ellipsometry and mass spectrometry, the effect of Ar@super +@ ions and XeF@sub 2@ etch precursor on the etch mechanism has been studied, simultaneously collecting information regarding the roughness evolution. Analysis of the XeF@sub 2@ reactivity and SiF@sub x@ products in contrast to the reaction layer composition shows that the reaction layer thickness, i.e. the surface fluorine content, scales with the roughness. This implies, that the SiF@sub x@ layer build up suggested in literature can be explained by the increasing roughness of the surface, thus the effective surface area increase of the etched Si samples. Furthermore, the etched Si samples have been analyzed with an AFM for comparison with the in situ ellipsometry results. The same trends in roughness evolution have been observed for the ellipsometry measurements and the AFM measurements, corroborating the used ellipsometry models. To learn about the role of the etch precursor and ions in the roughening of the surface during etching, the Family-Vicsek scaling theory of the surface roughness has been applied. The scaling coëfficients @alpha@ and @beta@, representing lateral correlations on the surface and time dependent roughness evolution, respectively, have been derived from the AFM data analysis. Since specific @alpha@ and @beta@ values are related to the surface processes occurring during the etching, the application of the scaling theory aids in understanding the role of the ions and etch precursor in the roughening process.

10:40am **PS-MoM8 Investigation of Trim Etching Process for Formation of Si/High-K Gate Stack***, **K.M. Tan**,* National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; L. Chan,* Chartered Semiconductor Manufacturing, Singapore

In recent years, a photoresist trimming technique based on the current 248nm and 193nm lithography technology are being developed to achieve smaller gates. In this work, we investigated the trimming technique to directly apply to the etching of the Si/SiO@sub 2@ and Si/HfO@sub 2@ gate stacks to further reduce the gate length. The trimming process developed using an industry standard ICP etcher consists of a main etch step followed by a trimming step using HBr, SF@sub 6@ and Cl@sub 2@. When HBr and SF@sub 6@ were used, a Si layer was trimmed at the rate of 17nm per minute at a pressure of 80mTorr, a bias power of 60W and an inductive power of 400W. A higher trim rate was obtained by using a higher inductive power and also by replacing HBr with Cl@sub 2@. However, the use of Cl@sub 2@ resulted in the decrease of the selectivity of Si to the underlying SiO@sub 2@, and thus reduced the maximum allowable trimming time. The trimming rate varied with pressure with an initial increase from 40mTorr to 70mTorr and a subsequent decrease from 70mTorr to 80mTorr. According to the results obtained for all the etch conditions used, HfO@sub 2@ produced a much slower etch rate than SiO@sub 2@ regardless of whether Cl@sub 2@ or HBr was used, and this resulted in a higher etch selectivity of Si to the underlying dielectric. As a result, a longer trimming time was allowed for HfO@sub 2@ than SiO@sub 2@. It was interesting to find out that an etching profile after the trimming step could be more anisotropic than that before the trimming step. Further studies are in progress to obtain 65nm trimmed gate structures from 130nm patterns using the 193nm photolithography technology.

11:00am **PS-MoM9 50nm Gate Electrode Patterning using a Neutral Beam Etching System***, **S. Noda**, S. Samukawa,* Tohoku University, Japan*; H. Nishimori, T. Ida, T. Arikado,* Semiconductor Leading Edge Technologies, Inc. (Selete), Japan*; K. Ichiki,* Ebara Research Co., Ltd., Japan

The increased packing density of ultra large-scale-integrated circuits (ULSI) requires ultra thin dielectric films that have low leakage current and are extremely reliable in metal-oxide-silicon (MOS) devices. High-k dielectrics films have been identified as leading candidates to replace conventional SiO@sub 2@ gate dielectrics in future ultra large-scale integrated circuits. However, the high-k films are more fragile and defective materials in comparison with the SiO@sub 2@-based thin films. As a result, the process-induced damages are very serious problems, such as charge-build-damages, changes in film quality and generation of defects by the irradiation of charged particles (ions and electrons) and VUV photons during the plasma etching processes. To break-through these problems, we developed a high-efficiency neutral beam etching system using negative ions generated in the pulse-time-modulated inductively coupled plasma (TM-ICP).@footnote 1@ In this system, high-density (1-4mA/cm@super 2@) and low-energy (10-100eV) neutral beams are effectively extracted from the pulsed plasma. It is expected that the neutral beam etching is promising candidate for the damage-free high-k gate electrode patterning. In this paper, we evaluated characteristics of the poly-Si gate etching using fluorine (SF@sub 6@) and chlorine (Cl@sub 2@) based gas chemistries. Highly anisotropic 50nm poly-Si etching profiles could be obtained with no degradation of extremely fine resist patterns in the case of the chlorine based neutral beams. The electrical properties of MOS capacitors will also be presented in comparison with the results in the conventional plasma etching systems. @FootnoteText@ @footnote 1@ S. Samukawa, K. Sakamoto and K. Ichiki, J. Vac. Sci. Technol. A20, 1566 (2002).

11:20am **PS-MoM10 Surface and Reactor Dynamics Governing Photoresist Trim and Organic BARC Open Plasma Processing***, **D.J. Cooperberg**,* Lam Research Corporation*; S. Johnston, D. Horak,* IBM Microelectronics*; V. Vahedi,* Lam Research Corporation

Photoresist trimming is employed to obtain acceptable feature profiles in sub-130nm linewidths. For logic applications, the process offers a means of shrinking gate length to values that are smaller than can be printed directly with a chosen lithographic technology. When organic bottom anti-reflective coatings (O-BARC) are used to assist photolithography the photoresist trimming can be performed before, during, or after an in-situ O-BARC opening process. The trimmed PR and opened O-BARC are used as a mask for either a hardmask open or a gate etch process. In this talk we will present process trends for O@sub 2@/CF@sub 4@/N@sub 2@ photoresist trim and O-BARC open plasma processing. We have measured the effect of several reactor settings as well as wafer topology on vertical and trim (lateral) etch rates. Reactor settings studied include inductively coupled power, bias power, gas mixture, and electrode temperature. In addition, the effects of variations in exposed area, local pattern density, and microloading or aspect ratio have been studied. It will be shown that local pattern density gradients over a length scale @>=@ the gas mean free path can effect etch uniformity. Trim rates are measured during the O-BARC open process and the trim process separately. It will be shown that the dependence of trim rate on aspect ratio changes dramatically during these two steps. Our experiments are used to identify the appropriate semi-empirical models for the surface kinetics and intra-feature transport which govern feature scale profile evolution. Additionally our experiments can be used to partially characterize reactor dynamics and the transport of the primary etchant, O atoms.

11:40am **PS-MoM11 3-Dimensional Modeling of Pulsed Inductively Coupled Plasmas: A Method to Improve Uniformity@footnote 1@***, **P. Subramonium**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Continuous wave (CW) operation of inductively coupled plasma (ICP) reactors having asymmetric pump ports or feedstock gas injection may produce asymmetric densities of radicals and fluxes to the substrate. These asymmetries are often intensified by positive feedback between regions of higher conductivity producing higher power deposition and higher ionization rates, which in turn increase the conductivity. Pulsed ICPs have been investigated as a means to extract negative ions to the substrate to reduce charging damage. Pulsed ICPs may also provide a means to reduce or eliminate asymmetries by reducing this positive feedback. In this paper, results from a 3-dimensional model for pulsed ICPs having such asymmetries will be discussed. As these long-term phenomena are difficult to resolve in multi-dimensional plasma equipment models a computationally parallel hybrid model has been developed to both speed the calculation and to better represent the physical processes. Results for pulsed ICPs in Ar, Ar/Cl@sub 2@, Ar/C@sub 2@F@sub 6@ gas mixtures will be discussed while varying pulse repetition frequency (5 - 20 kHz), duty cycle (10% - 70%), power (200 - 800 W) and pressure (5 - 20 mTorr). We found that the non-uniformities in species densities which feedback through the plasma conductivity are generally reduced during the afterglow of the pulsed plasma. In the afterglow, without the nonuniform source function, diffusion smooths the plasma density profile, providing a more uniform set of initial conditions for the next power pulse. The ionization source during the subsequent power pulses is therefore more uniform. As a result, time averaged plasma properties for pulsed plasmas are more uniform compared to CW excitation. Uniformity generally improves with decreasing duty cycle and decreasing repetition rate. @FootnoteText@ @footnote 1@ Work supported by Semiconductor Research Corporation and National Science Foundation.

QSA-10 Topical Conference
Room 320 - Session QS-MoM

Advances in Quantitative Surface Analysis

Moderator: C.J. Powell, National Institute of Standards and Technology

8:20am **QS-MoM1 Modules for an XPS Expert System: Applications in Corrosion Science*, J.E. Castle,*** University of Surrey, UK **INVITED**

Expert Systems (ES) can guide users in application of XPS.@footnote 1-6@ Guidance requires modules of the ES to be tailored to a particular group, e.g., corrosion scientists. This group, which has defined needs and a history of using XPS, could benefit from automated knowledge retrieval. In creating a set of rules, the requirements are defined and matched to the information that might be delivered by XPS, e.g.: the mean surface composition and relation to the bulk; the location of any marker elements; the thickness of overlayers, e.g., a contamination layer and an oxide or similar layer; evidence for graded composition such as enrichment of an alloying element in the oxide or metallic undersurface; valance states and a trial stoichiometric composition. Reminders of further opportunities should also be provided, possibly by use of on-screen wizards.@footnote 4,5@ In proposing this ES module emphasis will be placed on the cost-effective provision of basic information from the 'survey scan'. The rules have provenance from prior discussion and publication by international workshops such as those sponsored by IUVSTA.@footnote 1,3,6@ The rule base will be most useful when it is embedded in the controlling system for the spectrometer, so that some degree of knowledge based acquisition is possible, but would be equally suitable for stand alone, retrospective analysis. Both outcomes make a demand on costly resources that in the end will have to be provided by the user community. It is hoped that this feasibility study will show that, for corrosion scientists, this is worthwhile. @FootnoteText@ @footnote 1@M-G Barthes-Labrousse, Surf.Interface Anal. 26 p72 - 91 (1998) @footnote 2@J.E.Castle and M.A.Baker, J. Elec Spec Rel. Phenom., 105 p245 - 256 (1999) @footnote 3@L.Kover, Surf. Interface Anal. 29 p671 - 716 (2000) @footnote 4@J. E. Castle, PV 2001 - 5, C.R.Clayton et al. Eds. The Electrochemical Soc., NJ. pp1-14(2001) @footnote 5@J.E.Castle, Surf.Interface Anal. 33 pp 196 - 202 (2002) @footnote 6@ Report of St Malo Workshop, to be pub.

9:20am **QS-MoM4 Auger Electron Spectroscopy: Reducing Measurement Uncertainty*, J.D. Geller,*** Geller MicroAnalytical Laboratory **INVITED**

Quantitative analysis using Auger electron spectroscopy (AES) is most commonly performed using pure element sensitivity factors. The accuracy of the technique can be quite good for materials such as stainless steels where many of the elements have adjacent atomic numbers and similar densities. However, in most other materials errors well over 100% of the accepted true value are commonplace. The reasons for this will be discussed and different methods for quantifying data will be compared for their effectiveness. Accuracy, defined as the difference between the accepted true value and the result of an analysis, with Auger electron spectroscopy has seen very slow improvements over the years. There have been relatively very few technical papers addressing this important subject. By contrast, highly accurate quantitative analysis with the electron probe micro analyzer (EPMA) developed very quickly to the point where accuracies in the range of a few percent on a relative basis are commonly reached. Programs for converting x-ray intensities to concentrations following the ZAF (where Z is atomic number correction, A the absorbance correction, and F the fluorescence correction) procedures are available both in the public domain as well as from all the manufacturers of x-ray spectroscopic equipment. For AES there are no commercially available programs beyond the sensitivity factor approach. This work evaluates the current matrix effect corrections approaches (Sekine, et al) to that using elemental sensitivity factors from measurements with compounds. Sensitivity factors for several experimentally collected stoichiometric carbides, silicides, phosphides and sulfides are compared with those calculated from pure element sensitivity factors using matrix effect corrections. The factor with the greatest uncertainty was found to be preferential ion sputtering which is not included in any of the corrections. Sekine, et al, Evaluation of Correction Accuracy of Several Schemes for AES Matrix Effect Corrections, Surface and Interface Analysis, Vol. 15, 466-472 (1990).

10:20am **QS-MoM7 Molecular Characterization of Biomaterials with ToF-SIMS Imaging*, N. Winograd,*** Penn State University **INVITED**

It is now feasible to employ ion beams to desorb molecules directly from a variety of complex matrices. Here we show that it is possible to examine frozen-hydrated biological interfaces prepared using a special freeze-fracture protocol. The results demonstrate that it is possible to unravel dynamical events such as chemical fluctuations associated with domain structure in cellular membranes. This strategy allows the distribution of molecules within these matrices to be determined with high lateral resolution. Fracturing criteria for preserving chemical distributions have proven to be much more stringent than morphological cryo-electron microscopy studies. Two examples will be discussed. In the first instance, we report on the characterization of liposome particles that are about 50 microns in diameter. We have captured each stage of a fusion event between two liposomes and have shown that membrane structure during fusion ranges from specific domains that then migrate across the interface to produce a homogeneous, fluid-mosaic membrane. In the second instance, several different possible fracture planes from single biological cells have been imaged to understand further the process of freeze fracture and TOF-SIMS imaging of cellular membranes. Sensitivity is still problematic for this type of mass spectrometry. We present recent imaging data using a C60+ ion source that increases the yield of biomolecules by more than a factor of 1000. Combined with the freeze-fracture protocols, this technology holds the promise to define the biology of cellular membrane surfaces at the molecular level.

11:20am **QS-MoM10 Extrinsic and Intrinsic Excitations in Ge and Si Photoelectron Spectra*, L. Kövér,*** *Z. Berényi,* Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary*; S. Tougaard,* University of Southern Denmark, Denmark*; F. Yubero,* Institutio de Ciencia de Materiales de Sevilla, Spain*; I. Cserny, J. Végh, J. Tóth, D. Varga,* Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary*; W. Drube, T. Eickhoff,* HASYLAB at Deutsches Elektronen-Synchrotron DESY, Germany

Studying excitations accompanying deep core photoemission and Auger transitions in solids of great practical interest is important for understanding solid state effects@footnote 1@ on such transitions and for revealing the electronic structure of these systems. Here we report our results for (Ge 1s,2s; Si 1s) core photoelectron spectra excited by X-rays of different energies. Photoelectron spectra were obtained using the Tunable High Energy XPS facility at the BW2 beamline of HASYLAB,@footnote 2@ while the electron energy loss spectra reflecting the effects due to inelastic scattering (extrinsic losses) were measured with the home built ESA-31 electron spectrometer.@footnote 3@ The background corrected spectra are compared to model spectra calculated within the frame of a theory@footnote 4@ developed to describe both extrinsic and intrinsic (due to the appearance of the core hole) losses in XPS experiments. In addition, the ratio of the probabilities of extrinsic and intrinsic plasmon creation has been derived analyzing the excited plasmon spectra and is compared to the ratio obtained from the theory and from an other experimental approach. In a reasonable agreement with the theory, our analysis of the measured spectra shows a significant contribution from intrinsic excitations. Supported by OTKA T038016 and IHP-Contract HPRI-CT-1999-00040/2001-00140 (EC). @FootnoteText@ @footnote 1@ L. Kövér, Zs. Kovács,J. Tóth, I. Cserny, D. Varga, P. Weightman and S. Thurgate, Surf. Sci., 433-435(1999)833.@footnote 2@ W. Drube, T. M. Grehk,R. Treusch and G. Materlik, J. Electron Spectrosc. Relat. Phenom.,88-91(1998)683. @footnote 3@ L. Kövér, D. Varga,I. Cserny, J. Tóth and K. Tökési, Surf. Interface Anal., 19(1992)9. @foonote 4@ A. Cohen-Simonsen, F. Yubero and S. Tougaard, Phys. Rev. B56(1997)1612.

11:40am **QS-MoM11 Multivariate Analysis for XPS Spectral Imaging@footnote 1@*, D.E. Peebles,*** *J.A. Ohlhausen, P.G. Kotula,* Sandia National Laboratories

The acquisition of complete spectral images for x-ray photoelectron spectroscopy (XPS) is a relatively new approach, although it has been used with other analytical spectroscopy tools for some time. This technique generates full spectral information at every pixel of an image, in order to provide a complete chemical mapping of the imaged surface area. Multivariate statistical analysis techniques applied to the spectral image data provide a way to sort through this large block of data to determine the chemical component species present as well as their distribution and concentrations, with minimal data acquisition and processing times. The benefits of multivariate analysis of the spectral image data include significantly improved signal to noise and improved spatial resolution, which are achieved due to the large number of data points included in the image. In this paper, we will illustrate the signal to noise and spatial resolution obtained from a Magnification Reference Standard at a series of spectral image acquisition times, with a direct comparison of the raw images to the multivariate processed data. We will demonstrate the elemental separation and chemical discrimination possible with Sandia's novel multivariate statistical analysis approach for both limited spectral region acquisition as well as more complete spectral imaging data sets. It will be shown that Sandia's techniques provide efficient methods for deriving physically realistic chemical components without user input other than the spectral data matrix itself. @FootnoteText@ @footnote 1@ This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Semiconductors
Room 321/322 - Session SC-MoM
Heteroepitaxy of Wide Bandgap Semiconductors

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

8:20am **SC-MoM1 III-Nitride Epitaxy on Oxide Substrates: New Understanding and Novel Device Alternatives***, **W.A. Doolittle**,* Georgia Institute of Technology **INVITED**

Despite the maturity of III-Nitride molecular beam epitaxy and the successful commercialization of III-Nitride products, many important details of the epitaxy of III-Nitrides remain unexplained. Effects of strain on growth kinetics, interface chemistry and electrostatics, polarization, and doping remain incompletely explained. This paper attempts to clarify some of the uncertain issues remaining in III-Nitride MBE while detailing new concepts such as polarization-engineered structures using polarization domains written into ferroelectric substrates. Topics to be addressed include the role of interface chemistry between oxide substrates (sapphire, zinc oxide, lithium gallate and lithium niobate) and III-Nitrides. The common role that oxygen plays in determining the structure of III-Nitrides near the interface will be examined as will the chemical dependence of and temperatures where oxygen is liberated from sapphire substrates. FET mobility can be varied from 46-1587cm@super 2@/V-sec in identical structures by varying the buffer layer nitridation temperature, buffer layer composition-either GaN or AlN at high or low temperatures, and buffer layer thickness. This variation is correlated to inversion domain, and to a lesser degree dislocation density as measured by electrostatic force microscopy. The use of near lattice-matched substrates supplies insight into the growth of GaN in the elastic strain regime. The surface reconstruction and surface smoothness in this regime differs from mismatched substrates and varies little with III/V ratio. Once the critical thickness is reached (~9 to 10 nm), the surface briefly roughens and further growth proceeds as with all other mismatched substrates. Finally, a new influence on film polarity is described, the control of polarity via electrostatic boundary conditions using ferroelectric substrates. Both potential applications and limitations of this approach for polarization-engineered structures is described.

9:20am **SC-MoM4 Ion-Beam-Assisted Molecular Beam Epitaxy of GaN***, **B. Cui**, I.P. Steinke, P.I. Cohen,* University of Minnesota

Energetic particles, such as photons and ion beams have been widely used to assist semiconductor thin film deposition.@footnote 1,2@ High quality GaN can only be obtained in high growth temperature both for MOCVD and MBE. IBAD provides us with a powerful tool to control the growth kinetics and to grow GaN at relatively low temperatures. In this study, sub-keV ion beams from a 3-cm Kaufman source have been applied at a glancing angle to assist the growth of GaN in a MBE system. Basal plane sapphire and MOCVD GaN templates were used as the substrates. Ga was provided by a thermal effusion cell. Ammonia was used as the nitrogen source. Before growing GaN, the sapphire substrates were pretreated in an ion flux and then annealed for cleaning. The sapphire surface was then nitrided in ammonia at 1100K for about 10 min. After nitridation, a thin GaN buffer layer was prepared by a sequence of adsorption and annealing steps. During the growth, the surface roughness and film quality were monitored in situ using light scattering and RHEED. The height-height correlation functions were obtained from diffraction pattern to quantitatively analyze the surface roughness during growth. The results were compared with that obtained by AFM images. Different ion species, including hydrogen, nitrogen, and argon, were used to study the roles of momentum transfer, energy transfer, and ion reactivity on the evolution of surface morphology. A simplified ion-adatom energy transfer model was used to interpret the results. Partially supported by the National Science Foundation and the Air Force Office of Scientific Research. @FootnoteText@ @footnote 1@R. L. Headrick, et al. Phys. Rev. B 58, 8 4818 (1998) @footnote 2@J. Erlebacher, et al. Phys. Rev. Lett. 84, 25 5800 (2000).

9:40am **SC-MoM5 Optimizing AlGaN-GaN Heterostructures by MOCVD for Microwave Electronics***, **M.E. Aumer**, D.B. Thomson, D.P. Partlow, R.C. Clarke,* Northrop Grumman*; S. Cho, G.W. Rubloff, R.A. Adomaitis,* University of Maryland

GaN-based monolithic microwave integrated circuits (MMICs) for high power, high frequency applications have been reported. Despite impressive initial results, it is clear that realization of the full potential of GaN requires improvement of both the material quality and heterostructure design. To achieve the desired improvements, a set of experiments was performed to uncover material-related factors limiting device performance. Epitaxial films were grown by metalorganic chemical vapor deposition (MOCVD) and characterized by photoluminescence (PL), x-ray diffraction (XRD), x-ray reflectance, reciprocal space mapping, Hall effect, and contactless resistivity mapping. Wafer maps of the data illustrate correlations such as a relationship between substrate rocking curve linewidth and AlGaN-GaN interface roughness. Also, it was found that nucleation layer microstructure has a large effect on GaN crystallinity and HFET performance. Optimization of the nucleation layer resulted in a reduction of the screw and edge dislocation density from over 5x10@super8@ cm@super-2@ to less than 5x10@super7@ cm@super-2@. The defect reduction was not accompanied by a significant improvement in the sheet resistance of the channel region, suggesting that neither the electron density nor the low-field mobility were directly affected; however, devices fabricated on such wafers exhibited improved breakdown voltage and output resistance, both of which are important for MMICs. Results from short-loop fabrication of HFETs will be presented to illustrate the impact of material properties as well as heterostructure design on device properties such as I@subDSS@, transconductance, and breakdown voltage.

10:00am **SC-MoM6 Improvement of Optical and Electrical Properties in Blue Light-Emitting Diodes with InGaN-based Triangular-Shaped Quantum Wells***, R.J. Choi, H.-W. Ra, **Y.B. Hahn**, H.J. Lee, E.K. Suh,* Chonbuk National University, Korea

Improvement of optical and electrical properties in blue light-emitting diodes with InGaN-based triangular shaped quantum wells We report the electrical and optical properties of blue light-emitting diodes (LEDs) fabricated by using InGaN-based multiple triangular quantum wells (QWs). The triangular-shaped band structure in the QW was obtained by modulating the In composition in the InGaN well. LEDs with the triangular QWs were compared with rectangular ones in terms of current-voltage (I-V) characteristics, output power, and electroluminescence (EL) spectrum. Compared to the LEDs with conventional rectangular QW structures, the triangular QW LEDs showed a higher intensity and a narrower linewidth of electrical luminescence (EL), a lower operation voltage, and a stronger light-output power. EL spectra of the triangular-QW-based LEDs also showed that the peak energy is nearly independent of the injection current and temperature, indicating that the triangular QW LED is more efficient and stable than rectangular one.

10:20am **SC-MoM7 Optical Studies on the Incorporation of Carbon as a Dopant in Cubic GaN***, **J.A.N.T. Soares**,* Universidade de São Paulo, Brazil*; J.R.L. Fernandez, F. Cerdeira, E.A. Meneses, M.J.S.P. Brasil,* Universidade Estadual de Campinas, Brazil*; A.M. Santos, O.C. Noriega, J.R. Leite,* Universidade de São Paulo, Brazil*; D.J. As, U. Köhler, S. Potthast, D.G. Pacheco-Salazar,* Universität Paderborn, Germany

The metastable cubic phase of GaN (c-GaN) has attracted a lot of attention for its potential optoelectronic applications, especially since the successful fabrication of light-emitting diodes based on this material. In contrast to the wurtzite variety, no spontaneous polarization or strain-induced piezoelectric field exists in the cubic polytype grown on (001) planes. Hence, a greater optical recombination efficiency in c-GaN is expected, due to a greater overlap between electrons and holes wave functions. For the fabrication of devices it is essential to be able to introduce p- and n-type doping in a controlled manner. Among the possible acceptor impurities, carbon (C) has been regarded as an interesting candidate due to its similarity with nitrogen, both in atomic radius and electronegativity. Recently, D.J.As@footnote 1@ reported p-type doping with C during c-GaN plasma-assisted molecular beam epitaxy (PA-MBE) achieving concentrations of the order of 3x10@super 20@cm@super -3@. In order to render this impurity concentration into a high concentration of mobile holes, the details of C incorporation in the GaN lattice must be understood. In this work we performed Raman, photoluminescence, photoluminescence excitation, and photoreflectance spectroscopies on C doped c-GaN samples, deposited by PA-MBE on (001) GaAs substrates, for various C concentrations. The evolution of all four types of spectra is consistent with C atoms initially entering into N-vacancies producing a marked improvement in the crystalline properties of the material. At higher concentrations they also begin to enter interstitially and form C complexes, with a consequent decrease of crystalline quality. A model calculation of the localized vibrations of the C-atom in the GaN lattice allows for the interpretation of a feature in the Raman spectrum of samples with an "optimum" C concentration, which reinforces this view. @FootnoteText@@footnote 1@D.J.As et al., J.Phys.:Condens.Matter 13, 8923 (2001).

10:40am **SC-MoM8 Effect of Substrate Temperature on Crystal Orientation and Residual Stress in RF Sputtered Gallium Nitride Films***, T. Hanabusa, **K. Kusaka**, K. Tominaga,* Tokushima University, Japan

The crystal orientation and residual stress in gallium nitride (GaN) films deposited on a single-crystal (0001) sapphire substrate using a new sputtering system are examined through x-ray diffraction measurements as part of a study of low-temperature sputtering techniques for GaN. The new rf sputtering system has an isolated deposition chamber to prevent contamination with impurities, and is expected to produce high-purity nitride films. GaN films are deposited at various substrate temperatures and constant gas pressure and input power. This new system is found to produce GaN films with good crystal orientation, with the c-axes of GaN crystals oriented normal to the substrate surface. The crystal size of films deposited at high temperature is larger than that deposited at low Ts. All films except that deposited at 973 K exhibit compressive residual stress, and this residual stress is found to decrease with increasing temperature. Finally, the film deposited at 973 K was tinged with white, and the surface contained numerous micro-cracks.

11:00am **SC-MoM9 Formation of Zinc-blende-structure GaN Thin Films on Si Substrates by Radio Frequency Planar Magnetron Sputter Deposition***, **J.H. Kim**, P.H. Holloway,* University of Florida

GaN thin films were grown on silicon (100) and (111) wafers with no intentional substrate heating by radio frequency (RF) planar magnetron sputtering of a bulk-GaN-crystal target in a pure nitrogen atmosphere. The N@sub2@ gas pressure during the film growth was varied from 7 to 50 mTorr to investigate the influence of energetic particle bombardment on the phase evolution in the deposited GaN films. The GaN films grown at pressures higher than 20 mTorr exhibited a randomly-oriented polycrystalline wurtzite structure. For pressures between 10 and 20 mTorr, both zinc-blende and wurtzite phases were observed and the relative fraction of the zinc-blende phase increased at lower pressure. Below 10 mTorr, the deposited GaN films had a predominant zinc-blende structure with a preferred orientation in the [111] direction perpendicular to the film surface. As the N@sub2@ gas pressure was reduced from 50 to 7 mTorr, the internal stress of GaN films became increasingly compressive as a result of atomic peening effects and reached a value of about 3.2 x 10@super10@ dyne/cm@super2@ at 7 mTorr. The mechanism responsible for the formation of metastable zinc-blende GaN will be discussed in relation to the energetic particle bombardment of GaN films during growth.

Advanced Surface Engineering
Room 323 - Session SE-MoM
Modern Challenges in Surface Engineering

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

8:20am **SE-MoM1 Nanomechanical Testing of Films and Coatings***, **I. Robertson**,* University of Illinois **INVITED**

The fundamental deformation and fracture processes of thin metallic films with a nanograined microstructure and of thin hard coatings with a composite nanocrystalline- amorphous structure will be investigated by using the in situ TEM straining technique. For the nanograined materials, a novel uniaxial tensile test device has been fabricated using microelectronic fabrication processes to integrate MEMS force sensors with metallic films on a silicon wafer. The device permits direct correlation of the measured mechanical properties with the observed deformation mechanisms. The importance of grain boundaries as sources and sinks for dislocations will be demonstrated for a 200-nanometer thick freestanding aluminum film. For the hard coatings, a TiC coating supported on a stainless steel substrate was fabricated. Preliminary results suggest that the failure mode for coatings with the same C/Ti ratio is dependent on the percentage of crystalline TiC and the oxygen content, demonstrating the importance optimizing the composition and structure. Results from these studies will be compared with model predictions.

9:00am **SE-MoM3 Molecular-Scale Tribology in Model SAMs and Amorphous Carbon Films***, **J.A. Harrison**, G.M. Chateauneuf, P.T. Mikulski, G.T. Gao,* US Naval Academy **INVITED**

With the rapid development of MEMs and NEMs, protection of the surfaces of these devices has become an urgent issue. In recent years, much effort has been devoted to methods for passivating the surfaces of MEMs. Amorphous carbon films (a-C) and self-assembled monolayers (SAMs) are both possible candidates for the passivation and lubrication of MEMs. The fundamental problem associated with minimizing friction and wear mechanisms is to gain a better understanding of the underlying chemical and physical processes at the atomic scale. Over the past several years, we have done extensive molecular dynamics (MD) simulations that examine the compression and friction of model hydrocarbon SAMs attached to diamond and amorphous carbon films attached to diamond. Recently, compression and shear-induced polymerization have been modeled in unsaturated hydrocarbon films. The effects of polymerization on friction will be discussed. In addition, we have also done extensive simulations that analyze the structure and friction of a-C and a-CH films. These results will also be discussed. @FootnoteText@ **Supported by The Office of Naval Research & The Air Force Office of Scientific Research.

10:20am **SE-MoM7 Thin Film Growth by PVD in the Presence of Residual Gas***, **J.M. Schneider**,* RWTH-Aachen, Germany **INVITED**

Vacuum based synthesis techniques are characterized by the presence of residual gas. It is well known that the residual gas in high vacuum mainly consists of water. Depending on the affinity of the residual gas to the growing film material, incorporation during thin film growth has recently been reported.@footnote 1@ Here, a review on residual gas - growing film interactions is presented. Sources@footnote 2@ for residual gas incorporation as well as incorporation mechanisms@footnote 1@ are described. Furthermore the effect of impurity incorporation on the film structure and film properties is discussed.@footnote 3@ @FootnoteText@ @footnote 1@ J. M. Schneider, A. Anders, I. G. Brown, B. Hjorvarsson, and L. Hultman, Applied Physics Letters 75, 612 (1999). @footnote 2@J. M. Schneider, A. Anders, G. Yushkov, Applied Physics Letters 78, 150 (2001). @footnote 3@J.M. Schneider, K. Larsson, J. Lu, E. Olsson and B. Hjorvarsson, Applied Physics Letters 80, (2002) 1144.

11:00am **SE-MoM9 John A. Thornton Memorial Award Address: Advances in Reactive Sputtering Processing Technology***, **W.D. Sproul**[1],* Advanced Energy Industries **INVITED**

Reactive sputtering is the sputtering of an elemental target in the presence of a gas that is purposely added to the system to react with the sputtered species to form a compound film. Although simple in theory, reactive sputtering can be difficult to carry out if one wants to obtain high deposition rates and good properties in the deposited films. The classic problem with reactive sputtering when the flow control of the reactive gas is used to regulate the inlet of the reactive gas into the chamber is that the surface of the target will suddenly change from the elemental state to a compound state when the flow of the gas is increased beyond a certain point. When this happens, the target becomes covered with the compound ("poisoned state"), and the sputtering rate drops precipitously while the composition and properties of the deposited film change. To avoid the problems associated with flow control of the reactive gas, it is possible to increase the pumping speed of the system, which will prevent avalanching from the metallic state to the poisoned state for most materials. However, this technique will not prevent the loss in deposition rate. To avoid the loss of rate from target poisoning and a degradation of film properties, it is necessary to control the partial pressure of the reactive gas. Partial pressure control is more involved than flow control of the reactive gas, but it does provide high deposition rates, good composition control, and excellent film properties. For partial pressure control to be effective, a feedback signal that varies as the partial pressure changes is required. Common feedback signals are the cathode voltage, a partial pressure signal from a mass spectrometer, or an optical emission signal from the sputtering plasma. Each has its advantages and disadvantages. Signal acquisition, processing, and response times are all very important for partial pressure control. If the update time of the feedback signal or if the response to a change in the control signal are too long, it may not be possible to maintain a stable reactive gas partial pressure. The feedback signal must be obtained and processed quickly, and the response to any change must also be quick. If this is done, it is possible to operate at any point along the transition from the metallic state to the poisoned state of the target, which means that it is now possible to achieve both high

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

deposition rates and good film properties. Reactive sputtering of insulating films presents special problems because arcing can occur on the target surface, which leads to instabilities in the process. Fortunately, arcing can be eliminated by using a power supply that can suppress or prevent arcing. For deposition of insulating films, it is necessary to combine the correct type of power and with partial pressure control of the reactive gas to generate a stable, high-rate reactive sputtering process. One without the other will not produce the optimum results

Surface Science
Room 326 - Session SS1-MoM
Gas-Surface Dynamics

Moderator: K.W. Kolasinski, Queen Mary, University of London, UK

8:20am **SS1-MoM1 Angular Distribution of Cl Atom Products from Direct and Precursor-Mediated Hyperthermal Abstractive Chemisorption of Cl2/Al(111)***, **G.C. Poon**, A.C. Kummel,* University of California, San Diego

Resonantly Enhanced Multiphoton Ionization (REMPI) and Time-of-Flight Mass Spectroscopy (TOF-MS) have been used to demonstrate that the reaction of Cl@sub 2@ on the low work function Al(111) surface proceeds via a prompt vertical electron harpooning process. Sticking measurements were performed showing that Cl@sub 2@ adsorbs via a direct chemisorption process at either high incident translation energy or high surface temperature. However, at glancing incident angles and low surface temperatures (100 K), a precursor-mediated channel predominates. REMPI studies show that fast abstracted Cl was produced via both channels: direct, remotely-dissociated incident Cl@sub 2@, and indirect, physisorption-mediated Cl@sub 2@. An abstraction reaction results in one Cl atom bound to the surface and one Cl atom ejected back into the gas phase. For incident Cl@sub 2@ of 0.11 and 0.27 eV at 40° incident angle and 100 K surface temperature, only the precursor-mediated channel was observed with atomic Cl abstracted product energies of 0.09 to 0.14 eV. At high surface temperature, 500 K, all incident translational energies and angles yield only the direct channel, with abstracted product energies of 0.19 to 0.26 eV. Currently, angular distributions of the ejected Cl atom products are being determined for both direct and precursor-mediated channels. End-on impinging Cl@sub 2@ on the Al surface is expected to promote harpooning and subsequent abstraction products should be directed along the surface normal. Side-on physisorbed Cl@sub 2@ precursor would yield more broadly distributed abstraction products.

8:40am **SS1-MoM2 Photoinduced Electron Transfer Chemistry and Dissociation of Adsorbed CO@sub 2@: Harnessing Å-Scale Molecular Acceleration Towards a Surface***, **R. Zehr**,* University of Virginia*; T. Wagner,* University of Essen, Germany*; I. Samanta, I. Harrison,* University of Virginia

Activated dissociation of molecules on a metal surface is essential to many catalytic syntheses (e.g. N@sub 2@ dissociation in NH@sub 3@ synthesis) and a firm scientific understanding of this process is important to advancing the field of heterogeneous catalysis. In commercial catalysis, activation energy barriers are invariably surmounted by random thermal energy and not through a more directed use of the energy in light, despite the ubiquitous example of photosynthesis in nature. Potential advantages of using light to overcome a rate-limiting dissociative adsorption step in catalysis include better selectivity towards a chosen reaction pathway, the ability to work at much reduced reaction temperatures, and the opportunity to exploit solar energy. Here, we present evidence that photoinduced electron transfer from a low temperature Pt(111) surface to physically adsorbed CO@sub 2@ leads to rapid acceleration of the newly formed negative ion towards the surface, neutralization, and a high energy collision with the surface that efficiently dissociates (ca. 30%) and desorbs CO@sub 2@. Importantly, this photochemical activation mechanism constitutes an Å-scale molecular accelerator that may be applicable to other hard-to-activate adsorbates. The ability to photochemically induce an adsorbate/surface collision at chemically significant energies (up to ~2.5 eV), after an acceleration over a distance of no more than a few Å from an initial configuration prescribed by the physisorption binding potential, provides novel opportunities to drive energetic dissociation and desorption processes at low temperatures and to examine the reaction dynamics of catalysis.

9:00am **SS1-MoM3 Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100)***, **B.D. Kay**, Z. Dohnalek, G.K. Schenter, L.R. Corrales, R.S. Smith,* Pacific Northwest National Laboratory **INVITED**

The adsorption dynamics and desorption kinetics of Ar and CH4 on MgO(100) are studied using a combination of molecular beam scattering and temperature programmed desorption (TPD). Both Ar and CH4 exhibit an initial trapping probability that decreases dramatically with increasing kinetic energy and is independent of incident angle indicating adsorption is a barrier-less process obeying total energy scaling. The trapping probability for both adsorbates increases roughly linearly with the increasing coverage in the first layer. Such behavior can be described by a simple model involving constant but different trapping probabilities on clean and adsorbate covered MgO(100) with fast intra-layer diffusion leading to preferential filling of the bare MgO(100). An analogous behavior is observed for trapping on the second and third layers and indicates layer-by-layer growth of the adsorbate overlayer with layer dependent trapping probabilities. Analysis of the TPD spectra yields desorption energies of 8.5 and 13 kJ/mole for Ar and CH4, respectively in agreement with previous measurements and theoretical calculations. The total energy scaling observed for the initial trapping of Ar and CH4 on MgO(100) is in sharp contrast with the normal energy scaling previously observed for these species on Pt(111). These differences indicate that the adsorbate-substrate interaction is laterally smooth on Pt(111) and highly-corrugated on MgO(100). Theoretical scattering calculations based on the classical trajectory method are used to complement and interpret the experimental data. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

9:40am **SS1-MoM5 Adsorption of CO on Rutile (1x1)-TiO@sub 2@(110): A Molecular Beam Study***, M. Kunat,* Ruhr-University in Bochum, Germany*; **U. Burghaus**,* North Dakota State University

Presented are initial, S@sub 0@, and coverage dependent, S(@THETA@), adsorption probability measurements, respectively, of CO on the rutile (1x1)-TiO@sub 2@(110) surface obtained along both high symmetry azimuth directions (i.e. along the [1-10] and [100] azimuth) and parametric in the impact energy, E@sub i@, the angle of incidence, and the surface temperature, T@sub s@. Whereas along the [001] azimuth approx. a Kisliuk shape of S(@THETA@) has been observed, for glancing angle of incidence and E@sub i@ @>=@ 0.52 eV a turnover from the Kisliuk shape of S(@THETA@) to an auto-catalytic adsorption (increase in S with @THETA@) could be detected along the [1-10] direction. Along both azimuth directions S@sub 0@ obeys for E@sub i@ @>=@ 0.52 eV normal energy scaling and below that impact energy total energy scaling. The effect of an intrinsic precursor state is tentatively concluded. A decrease in the heat of adsorption with coverage indicates repulsive lateral interactions of the CO. The results will be discussed in comparison with Monte Carlo Simulations.

10:00am **SS1-MoM6 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl@sub 2@ on Al(111)***, **T.G. Grassman**, G.C. Poon, A.C. Kummel,* University of California, San Diego

Non-resonant multiphoton ionization (MPI) and time-of-flight mass spectrometry (TOF-MS) have been used to monitor the desorption of aluminum chloride (Al@sub x@Cl@sub y@) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (<5% monolayer) monoenergetic Cl@sub 2@ dosing. Three pulsed molecular beams of Cl@sub 2@ were prepared with translational energies ranging from 0.11 eV to 0.65 eV. The desorption products showed predominantly hyperthermal exit velocities under all dosing conditions, regardless of etch product species assignment (AlCl, AlCl@sub 3@, or Al@sub 2@Cl@sub 6@). For example, with an incident beam of Cl@sub 2@ seeded in neon (0.27 eV) at normal incidence dosing and normal detection, the etch product was found to have a most probable velocity of 532 ± 29 m/s at an Al(111) surface temperature of 100 K. This corresponds to nearly 7 times the expected thermal kinetic energy even if one assumes that the etch product is AlCl, and 30 times expected if one considers the more likely etch product, Al@sub 2@Cl@sub 6@. Sticking probability and transient etch rate profile measurements show etching even at Cl@sub 2@ coverages of less than 5% monolayer at all surface temperatures. High-temperature (500 K) etch rate profiles reach steady-state etching at equally small doses. These experimental results seem to indicate a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides, and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

10:20am **SS1-MoM7 Probing the Vibrational State-Resolved Gas-Surface Dynamics of Polyatomic Molecules Without the Laser***, D. Killelea, D. DelSesto, R. Smith,* ***A.L. Utz,*** Tufts University

We describe an experimental approach that yields vibrational-state-resolved reaction probabilities for polyatomic molecules without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study and its vibrational energy transfer dynamics in a supersonic expansion. In the case of methane, non-equilibrium cooling of vibrational states within polyads leads to the population of a single vibrationally excited state under easily obtained expansion conditions, even though several excited vibrational states would contain significant population under the nominal thermal conditions of the nozzle source. We apply this approach to extract state-resolved reaction probabilities for methane in its ground vibrational state (v=0) and @nu@@sub 4@ vibrational fundamental incident on clean, low-index nickel surfaces. State-resolved reaction probabilities obtained in this way are free from the vibrational-state averaging that clouds interpretation of beam-surface reactivity measurements and permit a more direct test of theoretical models of gas-surface reactivity.

10:40am **SS1-MoM8 Kinetics of H Atom Adsorption on Si(100) at 325 - 600 K***,* ***A. Kutana****, B. Makarenko, I.L. Bolotin, J.W. Rabalais,* University of Houston

The kinetics of atomic hydrogen isothermal adsorption on a Si(100) surface has been studied by the time-of-flight scattering and recoiling spectrometry (TOF-SARS) technique. A continuous decrease in saturation coverage with temperature under constant atomic hydrogen exposure has been observed for temperatures in the range 325 - 650 K. It is suggested that the obtained coverages are a result of a kinetic equilibrium between competing adsorption, abstraction, and migration reactions occurring at the surface. This approach explains how the coverages corresponding to the well-known phases of hydrogen on Si(100) at different temperatures are obtained. Introducing two types of adsorption sites into the model for the Si sticking probability, the coverage decrease is shown to be due to depletion of the surface concentration of atoms in the secondary adsorption sites. For lower temperatures, there is a significant concentration of hydrogen atoms in the precursor states that saturate the monohydride dangling bonds after hydrogen source shut-off and discontinuation of Eley-Rideal abstraction. The time for this transition is on the order of @kappa@(1 - n@sub sat@), where n@sub sat@ is the saturation coverage for a given temperature. Increasing the temperature leads to an increase in the migration rate from secondary to primary sites, where more efficient Eley-Rideal abstraction causes a decrease in total concentration. The migration constant @kappa@ obeys the Arrhenius equation with a low activation energy of 0.29 eV. It follows from the model, and has been proven experimentally, that the saturation coverage depends not only on temperature, but also on the incoming hydrogen flux, i.e. the ambient H@sub 2@ pressure at which adsorption is performed.

11:00am **SS1-MoM9 Charge Exchange between Metal Ions and Surfaces***,* ***X. Chen****, J. Doan,* University of California, Riverside*; Z. Sroubek,* Czech Academy of Science, Czech Republic*; J.A. Yarmoff,* University of California, Riverside

Ion-surface charge exchange is important in surface analytical methods that employ ion beams, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). In earlier work, we showed that the probability for neutralization of an alkali ion scattered from a metal surface is determined by the local electrostatic potential (LEP) a few Å's above the scattering site. We are now extending this work to investigate homogeneous charge exchange between metal ions and identical metal surfaces. In the first set of experiments, Ar@sup +@ and Kr@sup +@ ions are used to induce direct recoil of fast Al from Al(100). The neutral fraction of the recoils is then measured with time-of-flight as a function of emission angle and energy. From this data, and with the aid of Monte-Carlo simulations using scattering and recoiling imaging code (SARIC),@footnote 1@ we can obtain information on homogeneous charge exchange processes. Adsorbates, such as Cs and O, will be used to modify the surface work function so that measured changes in neutralization can be used to further reveal the charge transfer process. In the next set of experiments, we are producing metal ion beams for scattering. Al ions are being produced in an Al(CH@sub 3@)@sub 3@ plasma, and Ga ions from a liquid metal ion source. Such pure metal ion beams will allow for simple scattering experiments in which a clear correlation between can be made neutralization and trajectory. @FootnoteText@ @footnote 1@ V. Bykov, C. Kim, M. M. Sung, K. J. Boyd, S. S. Todorov and J. W. Rabalais, Nucl. Instrum. Meth. B 114 (1996) 371.

Surface Science
Room 327 - Session SS2-MoM
Catalysis I: Adsorption and Reactions of Small Molecules at Surfaces

Moderator: J.E. Reutt-Robey, University of Maryland

8:20am **SS2-MoM1 Atomic Level Explanation of the Compensation Effect in Heterogeneous Catalysis***,* ***T. Bligaard****, K. Honkala, A. Logadottir,* Center for Atomic-scale Materials Physics, Denmark*; J.K. Norskov,* Technical University of Denmark, Denmark*; S. Dahl, C.J.H. Jacobsen,* Haldor Topsoe A/S, Denmark

For a class of heterogeneously catalyzed reactions, we explain the compensation effect in terms of a switching of kinetic regimes leading to a concomitant change in the apparent activation energy and in the prefactor for the overall rate of the reaction. We first use the ammonia synthesis to illustrate the effect. Both experiments and a detailed kinetic model show a compensation effect. Secondly, we use density functional theory calculations to show that the compensation effect is not only due to changes in the activation barrier and prefactor of the rate-determining step, N@sub 2@ dissociation. We compare N@sub 2@ dissociation on Ru and Pd. The barrier for dissociation differs by more than 2 eV (200 kJ/mol), but calculations of the prefactor based on harmonic transition state theory shows a difference of less than 10%. In order to analyze the origin of the compensation effect we construct a general kinetic model for a surface catalyzed reaction, and show that the effect can be related to a shift in kinetic regime, from one dominated by the rate of activation of the reactants to a regime where the stability of the reaction products on the surface becomes increasingly important. Finally, we present arguments, why this should be a general effect for a broad class of reactions. We will show that the compensation effect in the rate is intimately linked to the underlying linear relationships between activation energy and stability of intermediates, which have been found to hold for a number of surface reactions.

9:00am **SS2-MoM3 Formation of Surface Cyanide through Carbon-Nitrogen Coupling Reactions on Pt(111)***,* ***E. Herceg****, M. Trenary,* University of Illinois at Chicago

The C-N coupling reaction to form CN on the Pt(111) surface has been studied with temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). This reaction underlies the industrially important synthesis of HCN from NH@sub 3@ and CH@sub 4@ over platinum catalysts. In the absence of oxygen, the catalytic reaction is endothermic and occurs at 1200 °C. In previous kinetic studies using model reactors, it has been inferred that the C-N coupling reaction occurs through surface C and N atoms.@footnote 1@ The surface CN formed is then hydrogenated to HCN. However, direct support for this mechanism has been lacking. Alternatively, surface CH@sub x@ and NH@sub y@ with x = 1, 2, or 3 and y = 1 or 2, may react to form a CNH@sub z@ species with z@>=@2, which is then dehydrogenated to HCN. Therefore characterization of the possible CH@sub x@ and NH@sub y@ surface species is important. Although NH@sub 3@ and CH@sub 4@ do not react on Pt(111) under ultrahigh vacuum conditions, the present study shows that the C-N coupling reaction is readily achieved in UHV in various ways, such as from coadsorbed CH@sub 3@, produced from thermal decomposition of CH@sub 3@I, and NH, produced from electron beam induced dissociation of adsorbed NH@sub 3@. The conversion of adsorbed NH@sub 3@ to NH@sub 2@, NH, and N was monitored with RAIRS and TPD. The surface N atoms readily react with hydrogen to reform surface NH, which is identified by its intense NH stretch peak at 3317 cm@super -1@. The presence of surface CN is detected through its reaction with hydrogen to form a surface CNH@sub 2@ (aminocarbyne) species, which has characteristic RAIRS peaks, as well as by HCN desorption. From the fact that C-N bond formation occurs at a temperature above where all CH@sub x@ and NH@sub y@ species have dehydrogenated indicates that the reacting species are in fact surface C and N atoms. @FootnoteText@@footnote 1@ D. Hassenberg and L. D. Schmidt, J. Catal. 97, 156 (1986).

9:20am **SS2-MoM4 The Effect of Atomic Steps on the Adsorption and Desorption of CO on Ru(109)**, ***G.A. Morgan, Jr.,*** *T. Zubkov, J.T. Yates, Jr.,* University of Pittsburgh*; O. Kühlert, M. Lisowski, R. Schillinger, D. Fick, H.J. Jänsch,* Philipps University, Germany

Ru is well known as an effective catalyst for the hydrogenation of CO to produce hydrocarbons. CO hydrogenation likely occurs after CO dissociation on Ru. We have shown that the dissociation of CO occurs preferentially on the atomic step sites of the Ru(109) surface, which exposes 9-atom wide terraces of (001) orientation, separated by double-atom height steps. This was demonstrated by isotopic mixing studies where @super 12@C@super 16@O and @super 13@C@super 18@O were shown to extensively mix above 480 K, a temperature where the C-O bond has just disappeared in the reflection IR spectrum. The isotopically mixed CO desorbs in a distinct recombination process at about 500 K, a kinetic process which is absent on the planar Ru(001) surface. Carbon atoms deposited from the decomposition of ethlylene can poison the step sites, which are responsible for CO dissociation. Thus the well known activity of Ru as a Fischer-Tropsch catalyst may be due to the special activity of defect sites with low Ru-Ru coordination numbers compared to Ru(001) sites.@footnote *@ @FootnoteText@ @footnote *@ Work Supported by DOE-BES.

9:40am **SS2-MoM5 Medard W. Welch Award Address: Get Real ! --- The Importance of Complexity for Understanding the Function of Surfaces*, M. Scheffler*** [1] *,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

Knowledge of the surface composition and atomic geometry is a prerequisite for understanding the physical and chemical properties of (most) modern materials as for example hardness, electronic and magnetic properties, and chemical activity. In this talk I will emphasize that to understand the function of surfaces it is important to "get real !", i.e. to go out of the vacuum and to take into account the influence of environmental gas and liquid phases at finite (possibly high) temperature and pressure.@footnote 1@ We employ ab initio, atomistic thermodynamics to construct a phase diagram of surface structures in the (T, p)-space from ultra-high vacuum to technically-relevant pressures and temperatures.@footnote 2-4@ The value of such phase diagrams as well as the importance of the reaction kinetics that may be crucial e.g. close to phase boundaries will be emphasized. -- We also calculated reaction pathways and energy barriers and use this information for a long time-scale modeling of surface diffusion, island nucleation, crystal growth, and oxidation catalysis. Examples in this talk are: semiconductor quantum-dot formation,@footnote 5@ the function of transition metals and transition-metal oxides, and heterogeneous catalysis.@footnote 6@ @FootnoteText@ @footnote 1@ C. Stampfl, et al., Catalysis and Corrosion: The Theoretical Surface-Science Context, Surf. Sci. 500, 368 (2002). @footnote 2@ X.-G. Wang, et al., Phys. Rev. Lett. 81, 1038 (1998). @footnote 3@ K. Reuter and M. Scheffler, Phys. Rev. Lett. 90, 046193 (2003); and Phys. Rev. B, in print. @footnote 4@ W. X. Li, C. Stampfl, and M. Scheffler, Phys. Rev. Lett., in print (June 2003); and Phys. Rev. B, in print. @footnote 5@ P. Kratzer and M. Scheffler, Surface Knowledge: Toward a Predictive Theory of Materials, Computing in Science & Engineering 3, 16 (2001); and Phys. Rev. Lett. 88, 036102 (2002). @footnote 6@ K. Reuter and M. Scheffler, to be published.

10:20am **SS2-MoM7 CO and Ethylene Dissociation on Ni(111): Influence of Steps*, R.T. Vang*,** *E.K. Vestergaard, F. Besenbacher,* University of Aarhus, Denmark

Steps on metal surfaces are well known to be more reactive than terraces and often provide the important active sites for catalytic processes. From high-resolution STM experiments we have found direct atomic-scale evidence that CO and C@sub 2@H@sub 4@ (ethylene) dissociate on the step edges of Ni(111) with a much higher rate than on the terraces. When CO is dosed at 400 K onto a clean Ni(111) surface small carbon islands are nucleated at the step edges. The coverage of these carbon islands saturates as soon as a thin brim of carbon is formed along the steps, indicating that adsorbed carbon prevents further CO dissociation, thus blocking the step sites. Concerning ethylene adsorption we observe the same mechanism of carbon growth at steps saturating after the formation of a thin carbon brim, when the dosing is performed at room temperature (RT). At higher temperatures (above 350 K), however, ethylene dosing leads to a continuous growth of carbon islands, which is interpreted as dissociation on terrace sites. When the step sites are blocked by small amounts of Ag, Au or S, we find that the dissociation rate of the two molecules is dramatically changed. No carbon is seen along the modified step edges after exposure to CO at 400 K or ethylene at RT. It is, however, still possible to form carbon islands by dosing ethylene at elevated temperatures owing to dissociation at terrace sites. These findings exemplify the concept of active sites in catalytic reactions and provide new directions for designing selective catalysts from fundamental surface science studies.

10:40am **SS2-MoM8 From Atomic Scale Reactant Ordering to Mesoscale Pattern Formation: CO Oxidation on Pd(100)*, D.-J. Liu,*** *J.W. Evans,* Iowa State University

We successfully connect-the-length-scales from the realistic modeling of reactant ordering in CO+O/Pd(100) to the prediction of mesoscale reaction front propagation. Description of ordering of CO on bridges sites, and O on four-fold hollow sites requires atomistic lattice-gas modeling. Repulsive CO-CO and O-O interactions beyond nearest-neighbor in range must be carefully selected to match experimentally observed ordering. Precise description of reaction-diffusion fronts also requires sophisticated analysis of chemical diffusion of CO which reflects CO-CO interactions and the presence of the coadsorbate. Numerical techniques are developed to analyse both reaction kinetics and diffusion under inhomogenous conditions using realistic lattice gas modeling. The results are then incorporated into a continuous reaction-diffusion equation. Pattern formation problems on the mesoscale, e.g., chemical wave profiles, can then be studied efficiently.

11:00am **SS2-MoM9 The Correlation between the Electronic Structure and the Energetics of CO Chemisorption on Pd/Re (0001) Surfaces*, B.S. Mun,*** *C.M. Lee, V. Stamenkovic, N.M. Markovic, P.N. Ross,* Lawrence Berkeley National Laboratory

We explored the nature of CO chemisorption on a Pd thin film electrode by utilizing ex-situ x-ray photoelectron spectroscopy (XPS) and in-situ Fourier transform infrared (FTIR) spectroscopy. The Pd film was deposited on Re (0001) single crystal by evaporation in UHV. Upon the deposition of the Pd thin film, the valence band (VB) photoemission spectrum shows a significant change from the bulk Re VB spectrum, yet also unlike the VB of bulk Pd(111). The morphology of the Pd thin film on the Re surface is discussed from LEED measurements. Careful analysis and comparison of lineshape and peak positions of the VB spectrum of the monolayer Pd film revealed a valence band spectrum similar to that of Ag(111), implying a filling of the Pd d-band from the intermetallic bonding with the Re substrate. Analysis of FTIR spectrum on this same sample transferred from UHV to the in-situ electrochemical cell indicated direct evidence of a modified (unlike Pd) CO bonding state consistent with reduced back-bonding from the Pd d-band to the CO Ï€* antibonding orbitals. It is also found that this "weakly bonded" CO is oxidized to CO2 at a much lower (ca. 0.2 V) electrode potential than on the Pd multilayer film.

11:20am **SS2-MoM10 Chemisorption Bond Weakening on Finite Size Terraces: CO on the Stepped Ru(109) Surface Compared to Ru(001)*, T. Zubkov*,** *G.A. Morgan, Jr., J.T. Yates, Jr.,* University of Pittsburgh

We have compared the bonding energy, compressional LEED structures, and vibrational frequency of chemisorbed CO on the 10 atom wide (001) oriented terrace sites of Ru(109) with chemisorbed CO on the Ru(001) surface as a function of CO coverage. The measurements indicate that the Ru-CO bond energy is significantly smaller on the 22 Å wide (001) terrace sites than on the Ru(001) surface, except at the zero coverage limit where equal bond energies are observed. This results in lower saturation coverage and in a less dense saturated CO overlayer on the terraced surface with finite-width (001) planes. The results are explained by compressive relaxation of the (001) Ru terrace sites, leading to a decrease of the average d-band energy and to weaker chemical bonding of the CO. The implication of a finite-size substrate effect on chemical bonding to transition metal catalyst crystallites is important since, within the framework of this finding, smaller facets will exhibit weaker chemisorptive bonding than larger facets.@footnote *@ @FootnoteText@@footnote *@Work supported by DOE-BES.

11:40am **SS2-MoM11 Orientation of N@sub 2@O on Pd (110) and Rh(110) at Low Temperatures*, H. Horino*,** *I. Rzeznicka, K. Imamura, T. Matsushima,* Hokkaido University, Japan*; K. Takahashi, E. Nakamura,* Institute for Molecular Science, Japan

Catalytic N@sub 2@O decomposition on Pd(110) and Rh(110) has attracted much attention because N@sub 2@O is a major by-product in catalytic NO decomposition and also the intermediate emitting N@sub 2@ in an inclined way along the [001] direction. To understand this peculiar desorption, the orientation of adsorbed N@sub 2@O was examined at 60 K

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[1] **Medard W. Welch Award Winner**

on Pd(110) and Rh(110) by near-edge X-ray absorption fine structure (NEXAFS). On Pd(110), N@sub 2@O adsorbs in a molecular form. Remarkable anisotropy was found in the X-ray incidence angle dependence of two @pi@ resonance NEXAFS peaks at 401 and 405 eV of the photon energy, i.e., with increasing shift of the x-ray incidence from the surface normal up to grazing angles, their intensities increased about 70% when the x-ray polarization was in a plane along the [001] direction, and for the polarization in a plane along the [11-0] direction, the intensities decreased about 25 %. It is derived that major N@sub 2@O is lying along the [001] direction and minor species is standing. This is consistent with DFT calculations. On Rh(110), at small exposures, only one @pi@ resonance at 401 eV was observed and its polarization dependence was very similar to that of N@sub 2@ (a), indicating dissociation of N@sub 2@O. N@sub 2@ (a) stands on the surface. At saturation, N@sub 2@O is partly standing, and lying either along the [001] or the [11-0] direction with similar populations, since with increasing shift of the x-ray incidence from the surface normal, the @pi@ resonance at 405 eV decreased only slightly when the polarization was in a plane in either the [001] or [11-0] direction. No anisotropy was found in NEXAFS peaks. The signal at 401 eV is affected by the contribution from co-adsorbed N@sub 2@ (a).

Surface Science

Room 328 - Session SS3-MoM

Surface Diffusion and Wetting

Moderator: J.B. Hannon, IBM Research Division

8:20am **SS3-MoM1 Determining Diffusion Mechanisms Using STM***, **B.S. Swartzentruber,*** Sandia National Laboratories **INVITED**

Determining a diffusion path is not a simple task; for it is the nature of kinetic processes that atomic configurations are arranged in low energy states most of the time. The move from one low energy state to another occurs on timescales usually not accessible to experimental observation. Although the transition path is inaccessible to direct measurement, in some cases it is possible to infer how motion occurs through indirect means. Using atom-tracking STM, in which the tip is "locked" onto the diffusing species using lateral feedback, the diffusion statistics are measured explicitly. >From the diffusion statistics of a dilute surface alloy of palladium or lead impurity atoms embedded in the outermost layer of Cu(001), we determine that the mass transport occurs predominantly via exchange with surface vacancies. Furthermore, the nature of the vacancy-impurity interaction has a dramatic effect on the overall diffusivity. For the case of Pb embedded in the Cu(111) surface, measurements of diffusion on two length scales are necessary to determine the active mechanisms. Short-range motion is predominantly vacancy mediated, while long-range diffusion occurs through exchange with surface adatoms and subsequent transport on top of the surface. Comparison of measurements with first-principles calculations yields valuable insight into diffusion processes, because the energetics of arbitrary diffusion paths can be calculated. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. .

9:00am **SS3-MoM3 Surface Characterization and Inter-diffusion Study of Copper on Ruthenium Thin Film Deposited on Silicon Substrate***, O. Chyan,* ***T. Arunagiri,*** *R. Chan, R.M. Wallace, M.J. Kim,* University of North Texas*; T.G. Hurd,* Texas Instruments

The dual-damascene patterning processing, coupled with the bottom-up Cu electrofill of damascene features and chemical-mechanical planarization, will continue to be the key for the future success of advanced IC chips. Recent advances in physical vapor deposition development allow highly engineered Ta/TaN diffusion barrier to be extended through 90 nm node. However, the tri-layer Cu-seed/Ta/TaN will likely encounter scaling difficulties in the Cu damascene trench/via features of advanced 65 and 45 nm nodes. We recently reported, J. Electrochem. Soc., 150, C347(2003), that Ruthenium (Ru) metal can function as a directly plate-able, seedless barrier materials. In this presentation, we report new findings centered on the interfacial and inter-diffusion studies of Cu/Ru system. Specifically, comparative study of wetting properties between electroplated-Cu and PVD-Cu on Ru barrier film (~ 10 nm) was carried out by XPS, SEM and AFM. Both electroplated and PVD Cu were found to wet well on Ru, based on SEM, AFM imaging and the scribe/peeled test, before and after thermal annealing over 450C. A strong adhesion between Cu/Ru interconnect microstructures is critical in order to withstand the demanding chemical-mechanical planarization process. Interfacial profiling was performed on Cu/Ru/Si samples using secondary ions mass spectroscopy (SIMS) depth profiling. To avoid knock-in ion-mixing interference, SIMS profiling was directed through the silicon back substrate. The backside SIMS profiling through Cu/Ru/Si samples show distinct interfaces without Cu inter-diffusion after annealed at 450C. TEM was further used to provide detailed cross-sectional imaging of Cu/Ru/Si interfaces. The wetting and inter-diffusion data of Cu/Ru systems will be discussed in the context of Cu diffusion barrier application.

9:20am **SS3-MoM4 Dynamics of Surface Alloys: Decay of 2D Islands on Pb/Cu(111)***, **M.L. Anderson**, N.C. Bartelt, G.L. Kellogg, B.S. Swartzentruber,* Sandia National Laboratories

To achieve control of nanostructure formation via self-assembly or growth processes, it is critical to gain an understanding of the complex physics governing mass transport. Observing thermal decay of 2D islands has proven useful to quantify atomic mechanisms of surface diffusion in single component systems. In this work we use this method to study more complicated issues of diffusion in multi-component systems. Using both STM and LEEM, we studied thermal decay of Pb-overlayer and Pb-Cu alloy islands on Pb/Cu(111). By combining techniques we extend the length scale from nanometers to microns and measure decay rates over 4 orders of magnitude. When Pb atoms are deposited on Cu(111), they place exchange with surface Cu atoms, forming a 2D surface-alloy phase. At Pb coverages above 0.22 ML, the surface alloy is saturated and further deposition causes Pb to de-alloy and form overlayer (pure Pb) islands. Despite large differences in structure, measured decay rates of both overlayer and alloy islands as a function of temperature follow an Arrhenius form with the same activation barrier (~0.8 eV). Equivalent barriers indicate that the same rate-limiting process is effective for both types of islands. The measured energy is comparable to DFT calculations of Cu adatom formation plus diffusion energies@footnote 1@ suggesting that transport of Cu is the rate-limiting process. Although the barriers are the same, the absolute rate at a given temperature is ~20 times slower for the alloy than for the overlayer islands. The rate difference is partially accounted for by the fact that, for equal size islands, there are 5 times more Cu atoms to transport in the coarsening of alloy islands. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. @FootnoteText@@footnote 1@ P. J. Feibelman, private communication.

9:40am **SS3-MoM5 Edge Diffusion on Spiral Steps on Pb(111) Microfacets****, **D.B. Dougherty**, W.G. Cullen, J.E. Reutt-Robey, E.D. Williams,* University of Maryland at College Park

A classic source of steps on solid surfaces is a screw dislocation intersecting the surface.@footnote 1@ From the intersection a spiral step emerges that can provide active sites for mass transport. To investigate the local kinetics associated with spiral steps, we have employed highly pure micron-size Pb crystallites grown on Ru(0001) with spiral steps on flat Pb(111) facets. Spiral step fluctuations have been observed with STM from 300-390 K and analyzed using the temporal correlation function and the persistence probability.@footnote 2@ The scaling of both functions points to a rate-limiting relaxation mechanism of step edge diffusion, exactly as observed for steps on single-crystal Pb(111).@footnote 3@ The kinetic parameter governing edge diffusion, the hopping mobility, has been extracted from the temporal correlation function and an activation energy has been extracted from the temperature dependence of the mobility. To investigate step fluctuations away from equilibrium, we have made fluctuation measurements on slowly rotating spiral steps on Pb crystallites in the process of thermal equilibration. The continuous unwinding due to the presence of the dislocation is distinct from the previously observed layer peeling process.@footnote 4@ The magnitude of the temporal correlation function for the fluctuations of a rotating spiral was observed to increase with the spiral curvature. The dynamic scaling was unaffected, showing that edge diffusion is still the rate-limiting transport mechanism. * Supported by UMD-NSF-MRSEC DMR-00-80008. @FootnoteText@ @footnote 1@ W.K. Burton, N. Cabrera, F.C. Frank, Proc. R. Soc. London, Ser. A 243 (1951) 299.@footnote 2@ D.B. Dougherty, O. Bondarchuk, M. Degawa, E.D. Williams, Surf. Sci. 527 (2003) L213. @footnote 3@ S. Speller, et al., Surf. Sci. 331-333 (1995) 1056; L. Kuipers et al., Phys. Rev. B 52 (1995) 11387.@footnote 4@ K. Thurmer, et al., Phys. Rev. Lett. 87 (2001) 186102.

10:00am **SS3-MoM6 Sb-mediated Ge and Si Growth on Ge(001)**, ***J. Wang***, *M. Li, E.I. Altman,* Yale University

Antimony-mediated Ge and Si growth on Ge(001) were studied using scanning tunneling microscopy and other surface characterization techniques. For the homoepitaxial growth on intermixed SbGe(001) with submonolayer Sb incorporated into the surface and below the Sb-Ge exchange temperature (470 K), Sb decreased the Ge island size with isolated ad-dimers seen on intermixed surfaces but not on pure Ge. The islands were found on top of Ge not Sb indicating that diffusion was not significantly inhibited on the Sb-passivated surface. The islands were always seen near Sb-Ge substrate domain boundaries. STM movies recorded at elevated temperatures showed that Ge dimers rapidly moved along Ge substrate dimer rows but could not pass or move onto Sb dimers embedded in the surface. These results can be explained by a repulsive barrier at Sb-Ge domain boundaries that inhibits Ge dimer diffusion from Ge to Sb domains but not from Sb to Ge domains. For Si heteroepitaxial growth at 520 K where Sb-Si and Sb-Ge exchange happens, a high density of small clusters were observed when Si was pre-deposited at 520 K and then 0.3 ML Sb was deposited at room temperature. The observed enhanced nucleation was attributed to zero-order nucleation due to both surface defects and adatom-surfactant exchange. The surface becomes smoother than Si deposition on bare Ge(001), with a much lower density of deep trenches on the terraces. Further annealing up to 590 K caused the small clusters to disappear producing a surface with square-shaped islands with typical sizes of 6 x 6 nm2. The isotropic island shape suggests that the anisotropic surface diffusion was disrupted due to the existence of domain boundary barriers between Sb and Si or Ge. Growth with different Sb coverages will also be discussed.

10:20am **SS3-MoM7 The Frustrated Alloying of Ge on Ultra-Flat Si(001)**, ***J.B. Hannon***, *M. Copel, M.C. Reuter, R.M. Tromp,* IBM

Using low-energy electron microscopy and atomic-force microscopy, we have investigated the alloying of Ge at the Si(001) surface during growth at elevated temperature (750 to 900 C). We show that alloying occurs primarily via step flow during growth. However, on large terraces, where step flow does not occur, complex and coordinated step structures ("stripes") spontaneously form and migrate over the surface. The stripes consist of a string of alternating adatom and vacancy islands, and move at speeds approaching 1 micron per sec. As these structures traverse the large terraces, they leave alloyed regions in their wake.

10:40am **SS3-MoM8 New Diffusion Mechanisms on Amorphous Surfaces**, ***A.S. Dalton***, *D. Llera-Hurlburt, E.G. Seebauer,* University of Illinois at Urbana Champaign; *K.R. Bray, G.N. Parsons,* North Carolina State University

The structural and energetic heterogeneity of amorphous surfaces should lead to effective values of the diffusivity that differ significantly from those on crystalline surfaces. However, little work has been done to investigate this possibility. The present work employs a combination of molecular dynamics simulations and experiments involving fractal analysis of surface topography to examine diffusion mechanisms on amorphous silicon (a-Si). Simulations indicate that surface diffusion on a-Si involves substantial exchange with the underlying bulk, but is dominated primarily by short-lived atoms generated from strained three-membered ring structures. The total effective activation energy for mass transport is 2.3 eV, and the formation energy for the most mobile species is about 0.8 eV. Experiments probed crystalline grains grown on a-Si surfaces by simple annealing at 635 to 665°C. Atomic force microscopy images were examined using dimensional fractal analysis to extract the static scaling coefficient and lateral correlation length. The transport rate varied with the length scale over which it was measured--a new result that represents the first experimental measurement of this theoretically predicted phenomenon. At short length scales near 50 nm on amorphous fields, surface diffusion was found to obey an Arrhenius law with an activation energy of 0.9 eV. Measurements over larger length scales including multiple crystal grains exhibited a larger activation energy of 2.4 eV. The significance of the correspondence between the computational and experimental values is discussed.

11:00am **SS3-MoM9 Mobility of Nanostructures on the Surface of a Desorbing Solid: Friction at the Nanoscale**, ***V.N. Antonov***, *J.S. Palmer, A.S. Bhatti, J.H. Weaver,* University of Illinois at Urbana-Champaign

Physical vapor deposition of Au (or other atoms) on rare gas solids leads to spontaneous formation of clusters. The thermal desorption of the buffer causes the clusters to move and aggregate into larger structures, a process known as buffer-layer-assisted growth (BLAG) and desorption assisted coalescence. Our results demonstrate that the initial nucleation density is independent of the buffer thickness. We have studied the extent of aggregation and the size distribution of Au nanostructures as a function of the buffer composition (Xe, Kr, or Ar) and thickness. In the limit of large Au nanostructures (>20 nm), the diffusivity scales as the inverse of the contact area, in agreement with molecular dynamics simulations of fast slip-diffusion of nanocrystals on incommensurate surfaces. A model for BLAG is proposed, based on the concept that nanostructure growth kinetics is controlled by competition between the rate of diffusion and the rate of buffer depletion. From this model, the effective activation energy for Au cluster diffusion is found to be within a few times the single atom binding energy on the surface. For small Au nanostructures (

11:20am **SS3-MoM10 Time-space Height Correlations of Thermally Fluctuating 2-d Systems; Application to Vicinal Surfaces and Analysis of STM Images**, ***L. Barbier***, *B. Salanon, E. Le Goff,* CEA Saclay, France

For thermally fluctuating 2-d systems, like solid surfaces, time and space correlation of the local surface height diverge logarithmically in the rough phase, whereas saturation is obtained below the roughening transition (at T@sub R@). A 2-d Langevin formalism with matter conservation within the surface plane is presented. An overall expression for correlation functions is obtained that are related to atom hopping rates and surface stiffnesses@footnote 1@. In contrast with previous 1-d approaches of step dynamics on vicinal surfaces,@footnote 2-4@ solution of the 2-d Langevin equation for anisotropic systems gives time correlation functions G(t) depending on energetic and hopping rates in the two main directions and the influence of surface stiffnesses on surface dynamics can be emphasized. At finite times, G(t) cross over to power laws ~t^(1/n) (n = 1, 2 or 4), within limited time ranges as it was observed for isolated fluctuating steps. Limits of time ranges are related to stiffnesses and diffusion anisotropies. For long times, logarithmic divergence (T > T@sub R@) or saturation (T < T@sub R@) of G(t) are recovered. Applications to the analysis of STM images of vicinal surfaces are given.@footnote 1@ @FootnoteText@ @footnote 1@E. Le Goff, L. Barbier and B. Salanon, Surface Science 531(3) (2003) 337. @footnote 2@M. Giesen, Progress in Surface Science 68 (2001) p 1, and references therein. @footnote 3@A. Pimpinelli, J. Villain, D.E. Wolf, J.J. Métois, J.C. Heyraud, I. Elkinani, G. Uimin Surf. Sci. 295 (1993) 143. 4 -T. Ihle, C. Misbah, O. Pierre-Louis, Phys Rev. B 58 (1998) 2289.

11:40am **SS3-MoM11 STM Tip-induced Translation through Excitations of the H@sub 2@O and D@sub 2@O Bending Modes on Pd(111)**, ***E. Fomin,*** University of California at Berkeley; *T. Mitsui,* Lawrence Berkeley National Laboratory; *M.K. Rose,* University of California at Berkeley; *D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We have studied the adsorption and manipulation of H@sub 2@O and D@sub 2@O molecules on Pd(111) using low temperature (~40 K) scanning tunneling microscopy (STM). We investigated the temperature dependence of molecular diffusion using two different approaches: tracking of individual molecules with the STM tip sitting on top of the molecules; and a "movie" technique - a series of consecutive scans showing hopping for an ensemble of molecules. In the course of this work it became clear that under certain conditions the STM tip had a strong influence on molecular motion. We found that the tip-induced hopping rate starts to grow exponentially as the bias reaches 200 meV for H@sub 2@O or 160 meV for D@sub 2@O, which corresponds to the molecular bending-mode excitation energy. This allows us to propose a coupling between vibrational excitation and molecular translation for water on Pd(111).

Thin Films
Room 329 - Session TF-MoM
Atomic Layer Deposition

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

8:40am **TF-MoM2 Advancements in ALD Chemistry**, ***M. Ritala,*** University of Helsinki, Finland **INVITED**

The atomic layer deposition (ALD) method has gained continuously increasing interest as a future manufacturing technology for microelectronics, and also several other potential application areas have been pointed out. This interest arises from the excellent conformality and large area uniformity and the atomic level composition and thickness control offered by ALD through its self-limiting film growth mechanism. While the ALD method is currently widely examined worldwide, a majority of the research is still largely focused on rather limited number of processes. A wider application of ALD in microelectronics and elsewhere is directly dependent on the availability of appropriate processes. There is thus a continuous need for developing cost-effective ALD processes for materials of an interest, like metals, metal nitrides, and high-k and ferroelectric oxides. In this presentation, recent advancements in ALD process development will be presented, mostly focusing on metals. Challenges for the future research will be discussed too.

9:20am **TF-MoM4 Incorporation and Control of Silica in Hafnium Silicates using Atomic Layer Deposition Techniques***, **M.N. Rocklein**, F.H. Fabreguette, S.M. George,* University of Colorado

HfO@sub 2@ and hafnium silicates are leading high-k candidates for replacing SiO@sub 2@ as the gate dielectric in MOSFETs. Advantages of incorporating silica in HfO@sub 2@ are to reduce the interfacial oxide and to prevent crystallization. Very few studies have reported incorporation of silica in HfO@sub 2@ by atomic layer deposition (ALD). We have investigated a new silicon precursor for hafnium silicate ALD. Although sequential exposures of this Si-precursor and H@sub 2@O will not lead to continuous SiO@sub 2@ ALD, growth of hafnium silicates is possible by mixing this Si-precursor and H@sub 2@O exposures together with HfO@sub 2@ ALD from 200 - 260 °C. HfO@sub 2@ ALD is conducted using tetrakis-diethylamidohafnium (TDEAH). Compositional control of the hafnium silicate Hf@sub x@Si@sub (1-x)@O@sub 2@ is achieved by controlling the relative number of Si-precursor/H@sub 2@O and TDEAH/H@sub 2@O reaction cycles. Silica incorporation and control is demonstrated using quartz crystal microbalance (QCM), transmission Fourier tranform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) investigations. Various reactant exposure sequences yield SiO@sub 2@ content ranging from 0 - 70 %. Hafnium silicate growth rates are also measured and confirmed using a variety of techniques including QCM, spectroscopic ellipsometry, and x-ray reflectance (XRR). Growth rates decrease with increasing SiO@sub 2@ content and vary from 0.65 Å/cycle at 21% SiO@sub 2@ to 0.18 Å/cycle at 67% SiO@sub 2@.

9:40am **TF-MoM5 In-situ Infrared Analysis of Atomic Layer Deposition Half-Reactions: Hafnium Diethyl- Amide Adsorption and Dissociation on SiO@sub2@ and HfO@sub2@***, **M.J. Kelly**, T.D. Abatemarco, G.N. Parsons,* North Carolina State University

A critical challenge in ALD is to control bond structure at the initial heterostructure interface. For example, the deposition of metal oxide dielectric materials on silicon results in unwanted substrate oxidation and uncontrolled interface structure. To better understand elementary ALD half reactions, we have built an in-situ attenuated total internal reflection infrared spectrometry system, and used it to observe adsorption, desorption and decomposition of Hf diethlyamide [Hf(N(CH@sub 2@CH@sub 3@)@sub 2@)@sub 4@] (HDA) on oxidized silicon and on deposited HfO@sub 2@ at substrate temperatures from 50 to 300°C. The effect of water exposure on adsorbed HDA was also characterized under some conditions. We find that for adsorption on thin HfO@sub 2@ at 50 and 175°C, the C-H stretching modes indicate adsorption and saturation of the molecular precursor at typical dosing pressures (10-40mTorr), followed by desorption upon pumping, consistent with molecular physisorption at low temperature. At 300°C, minimal CH stretching mode adsorption is observed, consistent with rapid decomposition of the precursor upon adsorption. At intermediate temperatures (250°C), non-self-limiting adsorption and decomposition are observed, and Si-O-H bond formation indicates silicon oxidation. Analyzing the precursor uptake curves as a function of temperature, we find that the rate of adsorption on HfO@sub 2@ is thermally activated with an effective barrier of ~0.1eV, consistent with a reduction in entropy upon adsorption. Results will be discussed in terms of the inter-relation of precursor structure and surface pretreatment on the energetics and kinetics of precursor reaction and substrate oxidation.

10:00am **TF-MoM6 Characteristics of Hafnium Aluminate Films for Gate Dielectric Applications Deposited by Atomic Layer Deposition Method***, **J. Lee**, J. Koo,* Hanyang University, Korea*; Y. Kim,* Pusan National University, Korea*; H. Jeon,* Hanyang University, Korea

The decrease of SiO@sub 2@ gate oxide thickness in sub-100nm metal-oxide-semiconductor (MOS) technology causes high leakage current and serious device reliability problems. To avoid these problems, high-k materials such as HfO@sub 2@ and Al@sub 2@O@sub 3@ have been mainly investigated as a potential candidate to substitute SiO@sub 2@ gate dielectric. However, these high-k materials have some supplement to be solved for applying to MOS device. Hafnium aluminate films would solve relatively high leakage current and low dielectric constant problems of HfO@sub 2@ and Al@sub 2@O@sub 3@, respectively. Hafnium aluminate films were expected to have amorphous structure of Al@sub 2@O@sub 3@ while maintaining high dielectric constant of HfO@sub 2@. Hafnium aluminate films were deposited on p-type Si substrates by atomic layer deposition (ALD) method using HfCl@sub 4@ and trimethylaluminium (TMA) as Hf and Al precursors, respectively, with H@sub 2@O as reaction gas. All samples were rapid thermal annealed at 800°C for 10 seconds in N@sub 2@ ambient. Forming gas anneal was performed in an H@sub 2@+N@sub 2@ atmosphere at 450°C for 30 minutes after Pt gate electrode deposition. The physical and chemical properties were analyzed by cross sectional transmission electron microscope (XTEM), Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). The electrical and reliability characteristics including equivalent oxide thickness (EOT), hysteresis, leakage current and interface defects were analyzed by I-V and C-V measurements. In this study, the characteristics of hafnium aluminate films for gate dielectric applications deposited by atomic layer deposition method were investigated. The chemical compositions and heat-treatments effects on the electrical and reliability characteristics of hafnium aluminate films for gate dielectric applications will be mainly presented. @FootnoteText@ @footnote 1@M. Leskela, M. Ritala, Thin Solid Films, 409(2002), 138, 146.

10:20am **TF-MoM7 Atomic Layer Deposition of Transition Metal Films***, **R.G. Gordon**,* Harvard University **INVITED**

Effective reactions have been discovered for ALD of many metal compounds, including oxides, nitrides, sulfides and fluorides. However, ALD of pure metals has proven to be more difficult. Tungsten and ruthenium are the only metals previously deposited from molecular precursors by self-limiting, complementary ALD reactions. ALD of titanium, tantalum, copper and aluminum used atomic hydrogen as a reactant, which limits the step coverage attainable in deep trenches because of the rapid recombination of hydrogen atoms. It is also difficult to design ALD apparatus to distribute hydrogen atoms over large areas, and to avoid plasma damage to substrates. We synthesized many new metal acetamidinates, a class of metal precursors that we designed to have the properties needed for ALD of metals. These compounds have the required high thermal stability because two metal-nitrogen bonds hold each ligand onto the metal (chelate stabilization). Nevertheless, each metal-nitrogen bond is individually weak (formally a bond order of only one half) and highly reactive. The high volatility of these metal compounds (vaporization temperatures less than 100 C) arises from the outer surfaces of the molecules being entirely saturated hydrocarbons. For example, homoleptic N,N'-diisopropylacetamidinato metal compounds and molecular hydrogen gas were used as ALD reactants to form highly uniform and conformal thin films of transition metals including iron, cobalt, nickel and copper. We propose that these ALD layers grow by a catalytic hydrogenation mechanism that should also operate during the ALD of many other metals. The process should allow improved production of many devices, such as copper interconnections in microelectronics, magnetic information storage, micro-electromechanical structures and catalysts. Use of water vapor in place of hydrogen gives highly uniform, conformal films of metal oxides, while ammonia gives metal nitrides.

11:00am **TF-MoM9 Demonstration of AlN ALD Using Hydrazine as the Nitrogen Precursor***, **F.H. Fabreguette**,* University of Colorado*; T.E. Seidel,* Genus, Inc.*; S.M. George,* University of Colorado

Aluminum nitride (AlN) has attracted widespread attention due to its remarkable thermal, electronic and mechanical properties leading to numerous applications. AlN growth by chemical vapor deposition (CVD) is accomplished using trimethylaluminum (TMA) and ammonia (NH@sub 3@) precursors. AlN atomic layer deposition (ALD) has also been attempted using TMA and NH@sub 3@. Unfortunately, high ALD temperatures are required where TMA pyrolysis is a problem. Lower ALD reaction temperatures where TMA will not decompose can be obtained using hydrazine, N@sub 2@H@sub 4@ , as the nitrogen precursor. This study presents the use of hydrazine as a new route for AlN ALD at temperatures as low as 177°C. AlN ALD using both ammonia and hydrazine was monitored and compared using an in-situ quartz crystal microbalance (QCM). ALD uptake curves showed 'soft' saturation behavior for the TMA half-reaction and 'hard' saturation for the hydrazine half-reaction. The AlN growth rate using hydrazine was found to be about 1.0 Å/cycle at 177°C. The ammonia reactant produced a growth rate < 0.1 Å/cycle. Different characterizations were performed on the AlN ALD films grown at 177°C. Ellipsometry and x-ray reflectivity confirmed a growth rate of about 1 Å/cycle. The AlN ALD films were determined to be amorphous by x-ray diffraction and smooth when measured by atomic force microscopy. X-ray photoelectron spectroscopy showed aluminum and nitrogen in the films and an oxide surface layer. Electrical measurements for the dielectric constant and the leakage current density were in good agreement with results from AlN CVD films. This study demonstrates the potential of hydrazine as a suitable nitrogen precursor for low temperature AlN ALD.

11:20am **TF-MoM10 Low Temperature Deposition of SiN using Sequential Exposures of Si@sub 2@Cl@sub 6@ and NH@sub 3@**, *J.Y. Ahn, J.G. Kim,* ***J.W. Lim****, H.S. Kim, U. Chung, J.T. Moon,* Samsung Electronics, Korea

Low temperature deposition of SiN is required in many applications for fabrication of high performance MOSFET devices. SiN films were deposited by atomic layer deposition (ALD) and cyclic chemical vapor deposition (CVD) using sequential exposures of Si@sub 2@Cl@sub 6@ and NH@sub 3@ at temperatures ranging from 400 to 600°C. The films were deposited in a mini-batch reactor employing cross-wafer gas flow scheme for rapid delivery of precursors and rapid evacuation of reactants. The saturated growth rate of ALD-SiN was 2.2Å/cycle. The films were characterized by AES, AFM, FTIR, RBS, SIMS, SEM, spectroscopic ellipsometry and TEM. The wet etch and reactive ion etch (RIE) characteristics were also investigated. ALD-SiN films are smooth, highly conformal and stoichiometric. In addition, they contain less hydrogen than the conventional LPCVD-SiN films deposited at equivalent temperatures, and exhibit high etch selectivity to SiO@sub 2@. The RIE selectivity to SiO@sub 2@ was determined to be nearly constant within the temperature range of 400-600°C. The properties of the films deposited by cyclic CVD method, in which self-limited surface saturation is not obtained, were comparable to ALD-SiN, and the Si:N ratio of cyclic CVD-SiN is controllable in the range of 0.7 - 1.0 by varying the Si source exposure and dilution. The electrical properties of the ALD and cyclic CVD films were evaluated by performing I-V and C-V measurements with MIS (Metal Insulator Silicon) capacitor structures. The physical and electrical properties of cyclic CVD films deposited at 590°C were as good as the conventional LPCVD films deposited at 700°C using DCS/NH@sub 3@ chemistry, and therefore the thermal budget for device fabrication can be reduced using cyclic CVD-SiN. The suitability of ALD-SiN films deposited at 450°C was reviewed for fabrication of high performance CMOS devices employing NiSi module process.

11:40am **TF-MoM11 Atomic Layer Deposition on Fine Particles***, J.D. Ferguson, A.W. Weimer,* ***S.M. George,*** University of Colorado

Because of the self-limiting nature of the sequential surface reactions in atomic layer deposition (ALD), atomic layer controlled and conformal films can be deposited on fine particles. Our recent work has investigated coatings on BaTiO@sub 3@ particles that are used to fabricate multilayer capacitors. SiO@sub 2@ has been coated on BaTiO@sub 3@ particles using NH@sub 3@-catalyzed SiO@sub 2@ ALD with tetraethoxysilane (TEOS) and H@sub 2@O as the reactants. ZnO has been coated on BaTiO@sub 3@ particles using ZnO ALD with diethylzinc (DEZ) and H@sub 2@O as the reactants. The ALD surface chemistry has been investigated using Fourier transform infrared (FTIR) spectroscopy. The FTIR studies observe the exchange of surface species as expected from the surface chemistry. In addition, the growth of the bulk SiO@sub 2@ and ZnO films versus number of reactant cycles is also observed in the FTIR spectra. Further confirmation of the SiO@sub 2@ ALD and ZnO ALD is obtained from transmission electron microscopy (TEM) analysis of the BaTiO@sub 3@ particles. The TEM analysis reveals conformal SiO@sub 2@ films with a SiO@sub 2@ growth rate of 0.7 Å per TEOS/H@sub 2@O reaction cycle at 300 K. TEM measurements also observe conformal ZnO films with a ZnO growth rate of 2.2 Å per DEZ/H@sub 2@O reaction cycle at 450 K. Additional FTIR and TEM studies have explored Al@sub 2@O@sub 3@ ALD on polyethylene (PE) particles at 350 K using trimethylaluminum (TMA) and H@sub 2@O as the reactants. The deposition of inorganic oxides on polymers may be important as gas diffusion barriers for packaging applications. The FTIR investigations observe the exchange of surface species during Al@sub 2@O@sub 3@ ALD and the growth of Al@sub 2@O@sub 3@ bulk features. The TEM measurements reveal a conformal Al@sub 2@O@sub 3@ film on the surface of the PE particles. ALD on large quantities of fine particles will be demonstrated using fluidized particle bed ALD reactors.

Vacuum Technology
Room 310 - Session VT-MoM
Looking Back: Fifty Years of Vacuum Science and Technology

Moderator: B.R.F. Kendall, Elvac Laboratories

8:40am **VT-MoM2 Fifty Years of Vacuum Science***,* ***E.V. Kornelsen,*** Unaffiliated, Canada **INVITED**

A selection is presented of problems in the physics and chemistry of vacuum systems and devices which has attracted considerable research during the past 50 years. These include examples where the limiting gas sources are water vapor, hydrogen, or helium. Also considered are self-sustained crossed-field discharges and the interaction of molecules, electrons, ions, and photons with the "technical" surfaces found in most vacuum systems.@footnote 1@ @FootnoteText@ This manuscript was prepared by J.P.Hobson shortly before his death.

9:20am **VT-MoM4 The Measurement of Vacuum;1950-2003***,* ***P.A. Redhead,*** National Research Council, Canada **INVITED**

The major developments in the measurement of vacuum since the Bayard-Alpert gauge was invented in 1950 are reviewed.These include a) improvements in understanding the processes limiting the lowest measurable pressure (both total and partial), b) development of new gauges, residual gas analysers,and optical methods to reduce these limitations, c) introduction of room temperature electron sources to replace thermionic cathodes,and d) development of the spinning rotor gauge as a secondary standard.

10:00am **VT-MoM6 Major Advances in Capture Pumps in the Last 50 Years***,* ***K.M. Welch,*** Consultant **INVITED**

Capture pumps either temporarily or permanently remove and store gases from a vacuum system by pumping mechanisms including chemisorption, physisorption and particle implantation on pumping surfaces. All or only some of these pumping mechanisms might come into play depending on the type of capture pump. Momentum transfer pumps, having no inherent capacity limitation, whisk gases through their innards, compressing the gases for removal at a pump outlet. Because capture pumps retain pumped gases, they have inherent capacity limitations. Developments of capture pumps focused on improving both the capacity and throughput of these pumps. Some of the major advances in the development and use of capture pumps in the last fifty years are given. Specifically, comments are included on the developments of nonevaporable getters, sputter-ion pumps, titanium sublimation pumps and cryopumps during this period.

10:40am **VT-MoM8 Major Advances in Transfer Pumps; 1953-2003***,* ***M.H. Hablanian,*** Varian Inc. **INVITED**

The major advances made in the design and operation of transfer pumps (i.e. vacuum pumps that transfer gas from a vacuum system to the atmosphere) during the lifetime of the American Vacuum Society (1953-2003) are reviewed. Included are vapor-jet, turbomolecular, and oil-free mechanical pumps. In addition to engineering development of pump designs, the basic understanding of pumping mechanisms of various pumps and their performance parameters has been greatly improved during this period.

11:20am **VT-MoM10 The Development of Ultrahigh and Extreme High Vacuum Technology for Physics Research@footnote 1@***,* ***H.F. Dylla,*** Jefferson Lab **INVITED**

Over the last 50 years, increasingly large and more sophisticated devices have been designed and put into operation for the study of particle and nuclear physics, magnetic confinement of high temperature plasmas for thermonuclear fusion research, and gravity wave observatories based on laser interferometers. The evolution of these devices has generated many developments in ultrahigh and extreme high vacuum technology that were required for these devices to meet their operational goals. The technologies that were developed included unique ultrahigh vacuum vessel structures, ultrahigh vacuum compatible materials, surface conditioning techniques, specialized vacuum pumps and vacuum diagnostics. Associated with these technological developments are scientific advancements in the understanding of outgassing limits of UHV-compatible materials and particle-induced desorption effects. @FootnoteText@@footnote 1@ This work supported by the U.S. DOE Contract No. DE-AC05-84ER40150.

AVS 50th Anniversary Plenary Session
Room 310 - Session AP-MoA

Where Next for Nanotechnology?

Moderator: R.J. Colton, Naval Research Laboratory

2:00pm **AP-MoA1 Nanotechnology: A Policy Perspective*, S. Hays,*** National Science and Technology Council **INVITED**

Nanotechnology research and development is a top priority of the current Administration. Scientific and technological breakthroughs in the ability to measure, manipulate and understand matter on the atomic and molecular scale are enabling the development of novel structures, systems, and devices. Realizing the full potential of the discoveries requires multidisciplinary efforts among researchers as well as truly interdisciplinary work by those who can bridge the "languages" and cultures of biology, physics, chemistry and engineering. The National Nanotechnology Initiative is a coordinated multi-agency federal research program that supports not only fundamental and applied research but also development of necessary tools and infrastructure, education and workforce development, and the study of societal issues. The future of nanotechnology rests in particular on advances in instrumentation and materials processing capabilities, two areas that are central to the interests of the AVS and the expertise of its members.

2:40pm **AP-MoA3 Nanotechnology: Future Challenges and Opportunities*, E. Hu,*** University of California, Santa Barbara **INVITED**

The launching of the National Nanotechnology Initiative nearly 4 years ago has captured the scientific and popular imagination and has catalyzed tremendous scientific discovery at an international level. Working with building blocks at the nanometer scale (molecules, nanoclusters, quantum dots, etc.), nanoscale science and engineering promises to alter not only what complex systems we can make, but also how we can make or manufacture systems. Substantial advancements have been made in (1) designing new instrumentation to image and characterize structures at the nanoscale, in (2) computational power and architectures that will allow modeling and simulation of nanostructure properties and performance, in (3) integrating diverse nanoscale building blocks (e.g. biological and electronic materials), and in (4) assembling modest-level nanosystems. The next 'giant steps' in the realization of multifunctional, manufacturable, higher-complexity nanosystems will require substantial improvements in all the areas mentioned above. Complex assembly of new materials will require designing in redundancy and repair into the processes. As more biological/molecular-electronic composite systems are utilized, we will need much a better understanding of information transfer and coherence across biological-electronic material interfaces. The richness of the work done thus far in creating a new Nanotechnology reveals a multitude of outstanding challenges and at the same time opens many avenues for further exploration and applications.

3:20pm **AP-MoA5 Self-Assembly Processing for Nanomanufacturing*, M. Tirrell,*** University of California, Santa Barbara **INVITED**

Self-assembly is a route to processing of chemical products that relies on information content built into the process precursors. The bonding mechanisms of self-assembled products are weaker than the electronic bonds of molecules; the complexity built into self-assembled products is at the level of supermolecular structure. Self-assembly processes may be spontaneous or directed by the influence of templates or fields. Self-assembly occurs frequently in biology but translating that bioinspiration to controllable chemical processing presents many interesting problems. A challenge for chemical engineers is to develop the practical routes to technologically important self-assembly processes. Applications will be to biomaterials, porous materials, molecular electronics and many other areas. Hurdles that must be overcome include the precision synthesis of precursors, mastering the kinetics and dynamics of such processes, scale-up, and the characterization and control of self-assembly products and processes. Prospects for success and current efforts in these areas will be discussed.

4:00pm **AP-MoA7 Nanotechnology: Constructing a Computer from Molecular Components*, J.M. Tour,*** Rice University **INVITED**

Research efforts directed toward constructing a molecular computer will be described in the context of recent developments in nanotechnology. Routes will be outlined from the synthesis of the basic building blocks such as wires and alligator clips, to the assembly of the processing functional blocks. Specific achievements include: (1) isolation of single molecules in alkane thiolate self-assembled monolayers and addressing them with an STM probe, (2) single molecule conductance measurements using a mechanically controllable break junction, (3) 30 nm bundles, approximately 1000 molecules, of precisely tailored molecular structures showing negative differential resistance with peak-to-valley responses far exceeding those for solid state devices, (4) dynamic random access memories (DRAMs) constructed from 1000 molecule units that possess 15 minute information hold times at room temperature, (5) demonstration of single-molecule switching events and (6) initial assemblies and programming of molecular CPUs in a Nanocell configuration that show room temperature electronic memory for days.

4:40pm **AP-MoA9 Massively Parallel Assembly*, J.N. Randall,*** *G.D. Skidmore, M. Ellis, A. Geisberger, K. Tsui, M. Nolan, R. Saini, C. Baur, K. Bray, M. Chiew, R. Folaron, R. Gupta, J. Hochberg, J.F. Liu, R. Stallcup, P.G. Yu,* Zyvex Corp. **INVITED**

Assembly is generally considered a low-tech, tedious, and expensive undertaking that must be dealt with to manufacture useful systems. Monolithic integration and system-on-a-chip efforts minimize the required assembly, but even the IC industry is economically driven to separate memory and logic chips that are assembled into systems. Where assembly has been automated, the results are expensive primarily because the assembly is serial. This talk will update the ongoing efforts to take assembly manufacturing through the same transition made when Kilby and Noyce revolutionized electronics by going parallel and providing a path for downscaling. We are developing technology for the parallel assembly of Microsystems supported by a NIST-ATP award.@footnote 1@ This technology involves both Micro-Electro Mechanical Systems (MEMS) and high precision robotic stages. By using novel MEMS components that we refer to as "Silicon Snap Connectors" and MEMS grippers, we can do automated, parallel, pick-and-place assembly that achieves higher precision assembly than the precision of the robot that did the pick and place. This is made possible through a self-centering mechanism in the connectors and the sub-micron CD control of the MEMS components. Videos of various microscale automated assembly construction projects will be shown. While the assembly being demonstrated so far is being done with MEMS components and is only modestly parallel, the general strategy for parallel assembly is not restricted to MEMS parts and, as the parts are downscaled, the level of parallelism can grow exponentially. The paper will close with some recent developments towards both massively parallel and nanoscale assembly. @FootnoteText@ @footnote 1@ NIST ATP Award #70NANB1H3021

Applied Surface Science
Room 324/325 - Session AS-MoA

Nanotube and Nanoparticle Characterization

Moderator: M.C. Burrell, GE Global Research

2:00pm **AS-MoA1 Vibrational Behavior of Adsorbed CO@sub 2@ on the Interior and Exterior Surfaces of Carbon Nanotubes: An Experimental and First Principles Study*, W.-L. Yim,*** *O. Byl, P. Kondratyuk, J.K. Johnson, J.T. Yates, Jr.,* University of Pittsburgh

We have used CO@sub 2@ as a probe for the adsorption sites on single-walled carbon nanotubes (SWNTs). CO@sub 2@(g) shows an intense infrared band at 2349 cm@super -1@, due to the asymmetric CO@sub 2@ stretching mode. When CO@sub 2@ is adsorbed on (10,10) nanotube surfaces, this mode should be red shifted to a lower vibrational frequency. We measured the infrared spectrum of CO@sub 2@ adsorbed on SWNTs and have observed absorption peaks at 2341 cm@super -1@ and 2329 cm@super -1@. After ozone treatment and annealing in vacuum to 823 K, CO@sub 2@ adsorption causes the mode at 2329 cm@super -1@ to increase dramatically in intensity, with the peak at 2341 cm@super -1@ less affected. We have performed density functional calculations using the local density approximation on (10,10) SWNTs, with CO@sub 2@ adsorbed on interior, exterior, groove, and interstitial sites of bundles of the nanotubes. The CO@sub 2@ in the groove site and in the nanotube interior exhibit vibrational red shifts of 20.9 cm@super -1@ and 23.2 cm@super -1@, respectively, for the asymmetric stretching mode. This agrees very well with the experimental results for the larger shift. The CO@sub 2@ on the nanotube exterior has a theoretical red shift of 14.8 cm@super -1@ from the gas phase CO@sub 2@ mode, which may contribute to the peak at 2341 cm@super -1@ in the experiments. We have monitored the replacement of CO@sub 2@ by Xe through a series of co-adsorption experiments. Xe selectively replaces the CO@sub 2@ species giving the mode at 2329 cm@super -1@ and assigned to CO@sub 2@

bound inside the nanotubes. Thus, both experiments and simulations indicate that the more red-shifted absorption peak is due to CO@sub 2@ adsorbed on the inside and possibly the groove sites of the SWNT bundles. This work was supported by the Army Research Office.

2:20pm **AS-MoA2 Adsorption and Dimerization of NO Inside of Single Walled Carbon Nanotubes - An Infrared Spectroscopic Study***, **P. Kondratyuk**, O. Byl, J.T. Yates, Jr.,* University of Pittsburgh

The physical adsorption of NO on purified (10,10) single walled carbon nanotubes was investigated at low temperatures by means of transmission infrared spectroscopy. Ozone treatment followed by annealing was used as a method of opening the entry ports for adsorption into the interior of the nanotubes. The IR spectra show that NO which is adsorbed inside of nanotubes exists exclusively in its dimer form, with no infrared bands of the monomer visible at a sensitivity level of 5 mole % NO. The internally adsorbed NO dimer species observed is cis-(NO)@sub 2@ with v@sub 1@(symmetric) = 1853 cm@super -1@ and v@sub 5@ (asymmetric) = 1754 cm@super -1@. Introduction of Xe into the system leads to selective displacement of the internally-bound cis-(NO)@sub 2@ dimer. A large spectroscopic red shift of the symmetric [-0.80%] and the asymmetric [-1.96%] modes for cis-(NO)@sub 2@ adsorbed inside of nanotubes (relative to gas phase cis-(NO)@sub 2@) points to the strong interaction of the dimer with the nanotube interior. The enthalpy of dissociation of the adsorbed dimer molecule is 15.1±0.7 kJ/mol.

2:40pm **AS-MoA3 Adsorption of CF@sub 4@ on Opened Single Walled Carbon Nanotubes***, **O. Byl**, P. Kondratyuk, L. Chen, J.K. Johnson, J.T. Yates, Jr.,* University of Pittsburgh

Single walled carbon nanotubes are currently the subject of intensive studies because of their potential application as sorbents. This is due to the deep potential energy well for adsorption inside of the nanotube. To make accessible the interior of the nanotube O@sub 3@ was used as an oxidizer to attack the strained endcaps and also defect sites, causing local oxidation of carbon atoms there. The ozonolysis was followed by annealing in vacuum to decompose carbonyl functionalities formed during the ozone treatment. Infrared spectroscopy has been used to make the first experimental discrimination between molecules bound by physisorption on the exterior surface of carbon single walled nanotubes (SWNTs) and molecules bound in the interior. In addition, the selective displacement of the internally-bound molecules has been observed as a second adsorbate is added. SWNTs were opened by oxidative treatment with O@sub 3@ at room temperature, followed by heating in vacuum to 873 K. It was found that at 133 K and 0.033 Torr, CF@sub 4@ adsorbs on closed SWNTs exhibiting its v@sub 3@ asymmetric stretching mode at 1267 cm@super -1@ (redshift = -15cm@super -1@). Adsorption on the nanotube exterior is accompanied by adsorption in the interior in the case of opened SWNTs. Internally-bound CF@sub 4@ exhibits its v@sub 3@ mode at 1247 cm@super -1@ (redshift = -35cm@super -1@). It was shown that at 133 K, Xe preferentially displaces internally-bound CF@sub 4@ species, and this counter-intuitive observation was confirmed by molecular simulations. The pseudo-one-dimensional confinement of CF@sub 4@ inside of (10,10) single walled carbon nanotubes does not result in the production of the splitting caused by transition dipole - transition dipole interaction which is observed in 3D ensembles of CF@sub 4@.

3:00pm **AS-MoA4 Sidewall Chemistry of Carbon Nanotubes Investigated by STM***, **K.F. Kelly**,* Rice University

There is a great deal of interest in understanding and controlling the chemistry of carbon nanotube sidewall functionalization. Enhanced solubility, improved formation of composite materials, controlled modification of the electronic structure, and increased hydrogen storage capacity are a few of the applications that this technology may impact. In this talk we will present scanning tunneling microscope studies of partially and fully fluorinated single-walled carbon nanotubes. In addition, we have imaged carbon nanotube sidewalls modified by various solution chemistry methods. Differences in electronic structure and surface coverage produced by each method will be discussed.

3:20pm **AS-MoA5 Iron-Oxide Nanoparticle Stability in an Ion Beam***, K.H. Pecher, **D.R. Baer**, M.H. Engelhard,* Pacific Northwest National Laboratory

The immense interest in nano-structured materials necessarily leads to application of various methods of surface analysis to examine the composition, chemical state and other properties of such materials. There are a variety of reasons why the chemical properties of nanoparticles may differ from bulk versions of similar material. We have been examining various types of iron metal and oxide nanoparticles to understand their chemical behavior. During the course of study 30 nm diameter iron oxide particles distributed on a silicon wafer or a gold coated wafer were exposed to 2 kV ions. In comparison to a 30 nm think iron oxide film, the nanoparticles were significantly altered. Particles suspended on Au were significantly reduced while particles distributed on the uncoated wafer rapidly formed an iron silicide. Further studies show that aggregates of nanoparticles do not show the same reduction. The stability of nanostructures when subjected to various types of analysis may be a significant complication to the study of these interesting materials.

3:40pm **AS-MoA6 Scanning Tunneling Spectroscopy of Boron Nitride Nanotubes; Evidence for a Giant Stark Effect***, **S. Aloni**,* University of California at Berkeley and Lawrence Berkeley National Laboratory*; M. Ishigami,* University of California at Berkeley*; A. Zettl,* University of California at Berkeley and Lawrence Berkeley National Laboratory

The Electronic properties of double-walled boron nitride nanotubes BNNT's were studied by scanning tunneling microscopy and spectroscopy at 7K. High resolution topographs of the tubes reveal information about the hexagonal boron nitride lattice as well as information about interlayer coupling between inner and outer tube. Tunneling spectra are also strongly dependent on the electronic coupling between the tube and the substrate. When the tube is well coupled to the substrate the spectra clearly show manifestation of a one dimensionality of the electronic structure and band gaps of 3.5eV. However, weakly coupled tubes display significantly higher apparent band gaps of 7-9.5 eV, indicating that the applied electric field is not fully applied across the tunneling gap between the STM tip and the tube. Simple analysis of the current-distance spectra shows that the actual BNNT bandgap is significantly smaller (3-5 eV) and is attributed to a second tunneling junction present between the tube and the under-laying substrate. Unlike their carbon analogues, BNNT are expected to be semiconducting with a chirality independent band gap of 5-5.5eV. We explain the low measured band gap values by a tip induced giant Stark effect, where the band gap is narrowed due to the high electric field as predicted in recent theoretical calculations by S.Louie et.al.

4:00pm **AS-MoA7 Size Dependency of Structural, Optical, and Photocatalytical Properties of TiO@sub 2@ Nanoparticles***, **W. Li**, S.I. Shah, S. Lin, C. Ni, C.-P. Huang,* University of Delaware

Polycrystalline TiO2 anatase nanoparticles with different average sizes (12, 17, 23 nm) were synthesized by metallorganic chemical vapor deposition (MOCVD). The particle sizes were determined by x-ray diffraction and transmission electron microscopy. The specific surface areas varied between 50 and 150 m2/gm, as measured by Brunauer-Emmett-Teller (BET) method. The size effects on the thermodynamic stability of TiO2 was analyzed by annealing samples in the temperature range of 700 to 800 oC. Only anatase to rutile phase transformation occurred. The transformation rate was accelerated with the decrease of initial particle size. The activation energy was calculated from the XRD data. The activation energy decreased from 298.85 to 180.28 kJ/mol as the initial anatase particle size decreased from 23 to 12 nm. Photoabsorption measurements showed a red shift of the absorption edges with the decrease in the particle size down to 17 nm. Below this particle size, a blue shift was observed. Photodegradation of 2-chlorophenol solutions under ultraviolet irradiation showed 17 nm sample had the highest photoreactivity. This result will be discussed on the basis of size related difference of light absorption efficiency, active surface area, and lifetime of charge carriers.

4:20pm **AS-MoA8 Determination of the Fermi Level of Isolated Single-Walled Carbon Nanotubes in Solution***, **K. Murakoshi**,* Hokkaido University, Japan

Single-walled carbon nanotubes (SWNT) should be among the best candidates for ultra-small functional units in ultra-sensitive, low-energy consumption nano-devices. Several characteristics of the electronic band structure of individual SWNT have been obtained successfully employing recently developed experimental techniques in confocal micro Raman spectroscopy, scanning tunneling microscopy and fluorescence methodology. In addition to band profiles, information regarding absolute potential of energy levels of the states is known to be essential to nano-device fabrication. Several estimations of energy levels from measurements of work function were attempted in vacuums and in electrolyte solution; however, all of these measurements utilized bulk bundle SWNT, which display certain distributions with respect to size. The diameter-dependent absolute potential of individual tubes has never been observed experimentally. The present report reveals that the energy position of the Fermi level of individual SWNT relative to the vacuum level depends on tube diameter based on measurements of resonance Raman intensity of individual SWNT under electrochemical potential control. Absolute potential of the Fermi level was found to be extremely sensitive to tube diameter. Structural dependence of metallic tubes is larger than that of semiconducting tubes. The values obtained can provide absolute potential maps of single SWNT at interface.

4:40pm **AS-MoA9 Band Modulation in Various Nanopeapods and Its Origin***, **J. Lee**, H. Kim,* Seoul National University, Korea*; S.-J. Kahng,* Korea University, Korea*; J. Ihm,* Seoul National University, Korea*; H. Shinohara,* Nagoya University, Japan*; Y. Kuk,* Seoul National University, Korea

Recent studies show interesting electronic properties of carbon nanotubes with various metallofullerenes. We have performed scanning tunnelling microscopy and spectroscopy study on these peopods.@footnote 1@ Two surprising characters were found: 1) large magnitude of the bandgap modulation (as large as ~1eV in Gd@sub 2@C@sub 92@ peapods and ~0.3eV in GdC@sub 82@ peapods) and 2) multiple oscillation of the conduction band edge in the position dependent spectroscopy near a defect. Our theoretical simulation results partly describe the main features in the experimental data. The modulation of band is caused by derived states from states of nanotube and metallofullerene. The conduction band oscillation was explained by many body screening effect around a defect. The observation of multiple fringe patterns near a potential barrier was predicted in the STM theory of Luttinger liquid near a perfect reflecting boundary,@footnote 2@ which expected a set of infinitely extending hyperbolars in the dI/dV(X,V) spectra. In the case of metallofullerene peapod, however, the finite barrier potential can result in curvilinear sub-bands surrounding the scattering potential. The current results imply that the transport properties of peapods may be dominated by the extent and strength of the scattering potential associated with the electronic structure of the inserted metallofullerenes. The recent transport measurement@footnote 3@ also supports our observation and calculation. A more detailed understanding of the phenomenon may require a many-body electron screening theory with e the pseudo-2D geometry and external potential. @FootnoteText@ @footnote 1@ Jhinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara, and Young Kuk, Nature 415, 1005 (2002).@footnote 2@ Sebastian Eggert, Phys. Rev. Lett. 84, 4413 (2000)@footnote 3@ P.-W. Chiu, G. Gu, G.-T. Kim, G. Philipp, S. Roth, S.F. Fang, and S. Yang, Appl. Phys. Lett. 79(23), 3845-3847 (2001).

Biomaterial Interfaces

Room 307 - Session BI-MoA

Non-fouling Surfaces and Biolubrication

Moderator: D.G. Castner, University of Washington

2:00pm **BI-MoA1 Towards the Prevention of Protein Adsorption, and Bacterial and Cell Adhesion by Optimised Surface Modification***, **P. Kingshott**, J. Wei,* Risoe National Lab, Denmark*; H. Thissen,* CSIRO Molecular Science, Australia*; N. Gadegaard,* Univ. of Glasgow, UK*; D. Selmeczi,* Risoe National Lab, Denmark*; L. Gram, D. Bagge-Ravn,* Technical Univ. of Denmark, Denmark*; N.B. Larsen,* Risoe National Lab, Denmark*; H.J. Griesser,* University of South Australia, Australia **INVITED**

A non-fouling surface is still elusive since problems such as bacterial colonisation on medical devices and food processing equipment, and failure of implants caused by clotting and foreign body reactions are still existent. Surface modification with PEG or PEO is the most effective way of reducing protein adsorption, and bacterial and cell adhesion (also called bio-adhesion). The best reports show that protein adsorption can be reduced to a fraction of the uncoated surface or even prevented. However, so far reductions in bacterial adhesion by PEG surfaces have only been marginally successful (up to 1 or 2 orders of magnitude). Why is this the case? Can surfaces that prevent protein adsorption also prevent bacterial and cell attachment? Can theoretical predictions of a non-fouling surface ever be put into practice by design of the perfect surface? In order to answer these questions it is necessary to be able to generate stable PEG layers with sufficiently high graft density and uniformity to provide the optimal steric repulsive barrier against bio-adhesion. In addition, to make the claim that a surface is non-fouling depends on one being able to detect protein adsorption below the threshold where no subsequent events can occur (such as bacterial adhesion). In this presentation some of these issues will be discussed. Surface modification based on plasma polymerisation and wet chemical methods are used to provide reactive groups for PEG grafting, confirmed by surface derivatisation reactions and surface analysis including XPS and ToF-SIMS. PEGs are grafted at their lower critical solution temperature (LCST) for maximal surface coverage. In addition, highly sensitive and specific surface mass spectrometry analysis (i.e. ToF-SIMS and surface-MALDI) is shown to be both very useful at detecting ultra-low levels of protein on the best PEG surfaces. Furthermore, the ability of PEG surfaces to prevent protein adsorption is heavily dependent on the size and type of protein.

2:40pm **BI-MoA3 Factors that Determine the Protein Resistance of Oligoether Self-assembled Monolayers - Internal Hydrophilicity, Terminal Hydrophilicity and Lateral Packing Density***, S. Herrwerth, W. Eck, **M. Grunze**,* University of Heidelberg, Germany

Protein resistance of oligoether self-assembled monolayers (SAMs) on gold and silver surfaces has been investigated systematically in order to elucidate structural factors that determine whether a SAM will be able to resist protein adsorption. Oligo(ethylene glycol) (OEG), oligo(propylene glycol) and oligo(trimethylene glycol) terminated alkanethiols with different chain length and alkyl termination were synthesized as monolayer constituents. The packing density and chemical composition of the SAMs were examined by XPS spectroscopy; the terminal hydrophilicity was characterized by contact angle measurements. IRRAS spectroscopy gave information about the chain conformation of specific monolayers; the amount of adsorbed protein compared to alkanethiol monolayers was determined by ellipsometry. We found several factors that can suppress the protein resistance of oligoether monolayers. Monolayers with a hydrophobic interior such as those containing oligo(propylene glycol) show no protein resistance. The lateral compression of oligo(ethylene glycol) monolayers on silver generates more highly ordered monolayers and may cause decreased protein resistance, but does not necessarily lead to an all-trans chain conformation of the OEG moieties. Water contact angles higher than 70Â° on gold or 65Â° on silver reduce full protein resistance. We conclude that both internal and terminal hydrophilicity favor the protein resistance of an oligoether monolayer. It is suggested that the penetration of water molecules in the interior of the SAM is a necessary prerequisite for protein resistance. We discuss and summarize the various factors and the balance of forces which are critical for the functionality of "inert" organic films.

3:00pm **BI-MoA4 Use of QCM-D to Analyze Thin Polymer Films at Interfaces***, **E.F. Irwin**, J Ho, K.E. Healy,* University of California, Berkeley

An interpenetrating polymer network (IPN) of acrylamide (AAm) and poly(ethylene glycol) (pEG) was designed that can be covalently bound directly onto metal oxide and polymer surfaces via photoinitiated free radical polymerization. A p(AAm-co-EG) with acrylic acid (AA) was also designed to allow further functionalization of the IPN surface with a diamino pEG spacer arm (pEG-NH@sub 2@).@footnote 1@ In this study, we are employing a quartz crystal microbalance with dissipation (QCM-D) (qsense) to monitor the IPN swelling and protein adsorption behavior in phosphate buffered saline (PBS), pH 7.4. QCM-D crystals coated with SiO@sub 2@ and TiO@sub 2@/Ti were modified with IPNs of p(AAm-co-EG), p(AAm-co-EG/AA), and p(AAm-co-EG/AA) + pEG-NH@sub 2@. The Sauerbrey relationship was used to calculate a thickness of 48nm for a dry film of p(AAm-co-EG/AA). QCM-D thickness data can be compared to a dry IPN thickness of 17nm determined previously by spectroscopic ellipsometry.@footnote 1@ A Kelvin-Voight model of viscoelasticity was used to interpret frequency and dissipation data of the hydrated films over the swelling period. Modeling the swelling data of a p(AAm-co-EG/AAc) IPN gave an initial hydrated thickness of 101nm (after 2 minutes) and a final swollen thickness of 150nm. The shear modulus of the film ranged from 285 to 365kPa and the viscosity ranged from 6.7E-3 to 8.6E-3kg/ms according to the model. One limitation of this model is that one single density of the IPN surface is assumed (in this case a density of 1.1g/cm@super 3@) over the entire swelling period. These IPN surfaces minimize the adsorption of the protein fibrinogen that has a role in thrombosis. The QCM-D provides unique and complementary information to other surface analytical techniques (i.e. AFM, XPS) for understanding the behavior of thin polymer films at interfaces. @FootnoteText@ @footnote 1@ Bearinger, JP, et al., J. Biomat. Sci. Polym. Ed., 9 (7) 1998.

3:20pm **BI-MoA5 Non-Fouling Surfaces: Their Use and Study by Matrix-Assisted Laser Desorption / Ionization Mass Spectrometry***, G.R. Kinsel, **J. Zhang**, R.B. Timmons,* The University of Texas at Arlington

Matrix-Assisted Laser Desorption / Ionization mass spectrometry (MALDI MS) has emerged in recent years as a powerful method for the mass spectrometric analysis of a wide range of biomolecules including proteins, oligonucleotides, polysaccharides, etc. Advantages of this analytical approach include simplicity of sample preparation, high analysis speed and high sensitivity. Recently MALDI-MS has been used in the characterization of non-fouling surfaces and related mechanistic studies in our group. Specifically, non-fouling coatings are applied to MALDI sample targets using a variety of published approaches including PEO chemical modification of polyurethane and pulsed plasma deposition of tetraethylene glycol dimethylether. From a practical standpoint these surfaces are shown to significantly lower the limit of detection (to sub-femtomolar quantities) in a MALDI experiment, presumably by reducing the amount of protein lost to surface-binding interactions. This influence is revealed by the acquisition of MALDI standard curves for a variety of peptides and proteins using methods previously established in our group. Additional studies of the influence of various MALDI parameters, including matrix solvent, pH, and ionic strength and various surface properties, primarily contact angle, have been performed to reveal relationships between, for example, surface hydrophilicity and protein binding, peptide/protein size and protein binding and elution solvent properties and protein binding. These studies offer useful experimental insights into various proposed mechanisms of non-fouling behavior.

3:40pm **BI-MoA6 Comparison of Immunoassay Blocking Strategies on Metal Oxide Substrates***, **A.N. Scribner**, C.L. Cole, R.J. Colton, L.J. Whitman,* Naval Research Laboratory

We have developed an alumina filter-based immunosensor that is 10 times faster and ~3 orders of magnitude more sensitive than an analogous microtiter well-based format. The assay is based on a standard sandwich immunoassay but uses magnetic microbeads and magnetic forces to differentiate between specific and nonspecific interactions. The combined use of magnetic force discrimination with PEG-based surface chemistries that minimize nonspecific binding forces result in a demonstrated specificity of >98%. Additionally, a more traditional blocking agent can also be added to compensate for lot-to-lot variability in the surface chemistry of commercially available alumina membranes. However, immunoassays on metal oxide supports not based on electrochemical detection are uncommon, so comparatively little is known about the effectiveness of different blocking agents for such surfaces. We examine agents typically used to block polystyrene plates for their relative effectiveness at blocking PEGylated and non-PEGylated alumina membranes, including detergents, proteins, hydrophobic, and hydrophilic molecules. The effectiveness of each substance as a blocker is determined quantitatively by measuring the amount of IgG-HRP remaining after incubation on a pre-blocked surface. Our results suggest that traditional reagents such as gelatin or BSA do not have the same ability to block nonspecific binding on PEGylated alumina as on polystyrene, and that casein and charged reagents such as SDS may be more appropriate choices for the blocking of modified metal oxide surfaces. Supported by ONR and the DoD JSTPCBD. ANS and CLC are employees of Nova Research, Inc., Alexandria, VA.

4:00pm **BI-MoA7 Lubricating with Water: Biomimetic Additives***, M. Müller, S. Lee,* ETH-Zürich, Switzerland*; X. Yan, S.S. Perry,* University of Houston*; **N.D. Spencer**,* ETH-Zürich, Switzerland **INVITED**

Nature often relies on surface-bound, brush-like structures to impart lubricity to natural surfaces (joints, G.I. tract, lungs) in an aqueous environment. These generally consist of polysaccharides, which are frequently charged and coordinate a large amount of water. We have found that another heavily hydrated brush-forming system: poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), can impart lubricity to inorganic surfaces, such as silicon, glass and steel, in an aqueous environment. A clear dependence on polymer architecture can be observed, which is manifested on both nano- and macro-scales, as determined by AFM and tribometer measurements, respectively.

4:40pm **BI-MoA9 Boundary Lubrication Properties of Bio- and Synthetic Polymers Containing Poly- and Oligosaccharides***, **S. Lee**, G. Kilcher, N.D. Spencer,* ETH-Zürich, Switzerland

In this study, we have investigated the boundary-lubrication properties of aqueous solutions of natural and synthetic polymers possessing poly- and/or oligosaccarides as an additive to reduce interfacial friction forces. As natural polymers containing poly- and oligosaccarides, we have chosen porcine gastric mucin (PGM) as a standard material responsible for bio-lubrication. Mucins are large and complex glycoproteins composed of a linear polypeptide and polysaccarides side-chains. Due to their aggregation or polymerization, often involving gel formation, mucins are known to form a protective layer between the lumen and the cell surface. Mucins possess a structure involving a combination of hydrophilic and hydrophobic domains with high molecular weight. The boundary lubrication properties of PGM-containing aqueous solutions have been investigated on hydrophobic tribo-pairs, such as self-mated poly(dimethylsiloxane) (PDMS). To more systematically investigate the role of poly- and/or oligosaccharides for water-based lubrication, we have synthesized block copolymers consisting of a polypeptide backbone, e.g. poly(L-lysine), and oligosaccarides with well-defined structure and chemistry. For this model system, we have selected various oxide surfaces as a tribo-pair. Both macroscopic- and molecular-scale sliding contact have been investigated employing pin-on-disk tribometry and atomic force microscopy respectively. The frictional properties of the selected tribosystem have been measured as a function of pH and ionic strength/type of the aqueous lubricant solution. The observed changes of the lubrication properties of both bio- and synthetic polymers as a function of pH and ionic strength are discussed in terms of the corresponding changes of conformation and adsorption behavior.

5:00pm **BI-MoA10 The Role of Polysaccharides in Bacterial Adsorption: A Chemical Perspective***, **K.T. Queeney**, J.W. Clemens, C. Royce,* Smith College

While it is well known that extracellular polysaccharides influence the adhesion properties of a range of encapsulated bacteria, studies of the adsorption properties of these polysaccharides have been largely limited to investigations of their conformational and/or mechanical properties.@footnote 1@ Xanthan, a model bacterial polysaccharide, has been well studied in the solution phase and therefore provides a useful starting point for understanding, at a molecular level, what influences the adsorption properties of these large and complex molecules. We have used surface infrared spectroscopy to investigate the adsorption of xanthan on a variety of surfaces that exhibit both varying hydrophobicity and a range of chemical terminations. While a previous study of polysaccharide adsorption on oxide surfaces focused only on hydrogen-bonding behavior as evidenced by the OH-stretching region,@footnote 2@ we find that the carbonyl stretching region shows marked changes in the local chemical environment of these moieties, suggesting that they interact strongly with the surface. Furthermore, xanthan's similar affinity for hydrophobic and hydrophilic surfaces provides evidence that polysaccharide/surface interactions must include non-hydrogen bonding effects. @FootnoteText@ @footnote 1@See for example T. A. Camesano and K. J. Wilkinson, Biomacromolecules 2, 2001, 1184-1191.@footnote 2@B. A. Jucker, H. Harms, S. J. Hug and A. J. B. Zehnder, Coll. Surf. B 9, 1997, 331-343.

High-k Gate Dielectrics and Devices Topical Conference
Room 317 - Session DI-MoA

High-k Dielectric Stability

Moderator: Y.J. Chabal, Agere Systems

2:00pm **DI-MoA1 Etching and Thermal Stability of Zirconium and Hafnium Oxide High-k Dielectrics***, **J.P. Chang**,* University of California, Los Angeles **INVITED**

The aggressive down-scaling of the silicon based metal-oxide-semiconductor field effect transistor (MOSFET) replies strongly on the materials and the resultant electrical properties associated with the dielectric material employed to isolate the transistor gate from the silicon. Currently, the major challenges in integrating high-k materials include a thorough understanding of the thermal stability of these materials on silicon and an effective etching chemistry in patterning these materials. In this talk, I will discuss current research progress in atomic layer controlled deposition of high-k dielectric films on silicon with tailored electronic, chemical, interfacial, thermal, and mechanical properties, followed by discussions on plasma patterning of the high-k materials. Specifically, research work on ZrO@sub 2@ and HfO@sub 2@ thin films and their thermal stability, dielectric function, and integration on silicon surfaces will be presented. The talk will focus on linking the molecular coordination and film morphology to the electronic properties of the high-k dielectrics, and elucidating the reaction pathways leading to the deposition of thermally stable, stoichiometric, amorphous, smooth, uniform, and highly conformal high-k dielectrics. Plasma enhanced etching of metal oxides in halogen based chemistries will be presented, including the effect of ion energy and ion type on etching rate and etching selectivity. I will also highlight some new research directions that aim at enabling the predictive engineering of a superior high-k/silicon interface and its associated device performance through ab initio calculations.

2:40pm **DI-MoA3 Structure and Stability of Alternative High-K Gate Dielectrics*, S. Stemmer,*** University of California, Santa Barbara **INVITED**

This talk will present an overview of extrinsic and intrinsic stability issues of high-k dielectrics, such as ZrO@sub 2@, HfO@sub 2@, Y@sub 2@O@sub 3@, their alloys with SiO@sub 2@ or Al@sub 2@O@sub 3@, and their interfaces with electrodes and Si. While thermodynamics predicts that all high-k gate dielectrics currently under investigation are stable in contact with Si, interfacial reactions have been reported. We show that gate oxide stoichiometry and processing conditions, such as oxygen excess or reducing conditions, can explain reactions and are consistent with predictions from thermodynamics. Intrinsic stability issues include phase separation of silicates and aluminates, and will be discussed in the context of equilibrium as well as metastable phase diagrams, respectively. A combination of experimental methods is needed to experimentally analyze the stability of these ultrathin layers. We have used electron energy-loss spectroscopy (EELS), atomic resolution Z-contrast imaging, high-resolution transmission electron microscopy, small angle x-ray scattering (SAXS) and x-ray absorption spectroscopy fine structure analysis (XANES) to dielectric layers after high temperature anneals necessary for CMOS device processing. For example, phase separated microstructures of Hf-silicate films with different compositions show different morphologies and kinetics, due to mechanisms of microstructural evolution by nucleation and growth, and spinodal decomposition, respectively, consistent with the predictions from metastable phase diagrams. SAXS is used to study the kinetics of phase separation. Oxygen deficiency can lead to silicide reactions, whereas oxygen excess in the films is responsible for interfacial silicate reactions in rare earth oxide films on Si. This research was performed in collaboration with J.-P. Maria, A. Kingon, G. Parsons, P. Lysaght, P. C. McIntyre, S. Ramanathan, and T.P. Ma.

3:20pm **DI-MoA5 Hafnium Silicate High-K Dielectric Etch with High Selectivity to Si at Low Wafer Temperatures***, S. Ramalingam,* Lam Research Corporation*;* ***C.B. Labelle***, Advanced Micro Devices*; S.D. Lee, G.P. Kota, C. Lee, V. Vahedi,* Lam Research Corporation

Advanced microprocessors require the use of increasingly thin gate oxide materials to achieve the highest performance. To date, these materials have consisted primarily of SiO2 and nitridized SiO2, but the leakage current behavior of these materials becomes undesirable as they are successively thinned (=12Å). A potential solution to this problem is replacement of SiO2 by an insulator with a higher dielectric constant (high k). Keeping with current integration schemes, gate etching would then require etching through the polysilicon and high-k materials, stopping on the underlying silicon. However, high-k materials have proven very challenging to etch, specifically due to the low volatility of etch products, which typically require an aggressive approach to the etch, most notably including high temperatures. Key etch issues include selectivity to polysilicon/bulk silicon and masking material, redeposition of high k materials on the poly gate sidewalls, and altering of the poly gate profile and/or CD. A Lam 2300 SeriesTM silicon etch reactor has been used to etch photoresist-masked polysilicon gate wafers with HfSiOx gate dielectric. A BCl3-based process has been developed that provides excellent selectivity to polysilicon, no high k redeposition, and <10Å silicon recess. Selectivity to Si is attained at low ion energy and through passivation of the surface by formation of Si-B bonds. A key advantage of this process over those currently in practice is that wafer temperatures higher than those in typical gate etch processes are not necessary. Key etch results will be presented, including analysis of the impact of a boron-based etch process on gate doping.

3:40pm **DI-MoA6 Post Deposition Stability of High-k Dielectrics to Air Exposure and its Implications to Interface Reactivity*, T. Gougousi,*** *D. Niu, R.W. Ashcraft, G.N. Parsons,* North Carolina State University

Post-deposition stability of the gate oxide is an important issue for advanced gate stacks. For this study, group III and IV high-k dielectrics films are deposited on Si by PECVD or by metal sputtering and ex-situ oxidation in N@sub 2@O. After deposition the dielectrics are permitted to react with ambient H@sub 2@O and CO@sub 2@ for extended periods and their stability is monitored as a function of time using FTIR. We find that group III (Y and La) based-films are generally susceptible to reactions with H@sub 2@O and CO@sub 2@ forming hydride and carbonate species. For PVD La films, the oxidation temperature affects the film stability significantly. Films oxidized at 600°C show signs of reaction within minutes of air exposure while films oxidized at 900°C are stable for exposures up to two weeks. Y@sub 2@O@sub 3@ CVD films deposited at 400°C also show high reactivity with H@sub 2@O. Post deposition inert anneals at 900°C in N@sub 2@ improves the film stability significantly. In-situ capping of the Y@sub 2@O@sub 3@ films with 500Å of a-Si reduces greatly the amount of OH detected in the films. Group IV (Hf and Zr) based film exhibit superior stability as compared to the group III films, however. Carbonate formation is verified for both HfO@sub 2@ and ZrO@sub 2@ films. OH is practically undetectable in the films even after ambient exposure for six months. The effect of the OH incorporation on the interface stability will be discussed, and examples of OH promoted reactions between the dielectric film and the Si substrate or polysilicon gate metal will be presented.

4:00pm **DI-MoA7 Growth, Characterization and Thermal Stability of High-K Gate Stacks*, E.L. Garfunkel,*** *T. Gustafsson, D.G. Starodub, S. Sayan, L.V. Goncharova, D. Vanderbilt, X. Zhao, R.A. Bartynski,* Rutgers University*; T. Nishimura,* Murai Project, Japan*; Y.J. Chabal,* Rutgers University **INVITED**

We describe recent results using medium energy ion scattering (MEIS), soft x-ray photoemission (SXPS), inverse photoemission (IPES), electron microscopy (TEM), infrared spectroscopy (FTIR), electrical methods and first-principles calculations to examine high-K gate dielectrics and their interfaces with silicon and metal layers. MEIS has proven extremely helpful in presenting accurate elemental depth profiles of high-K films on Si, Ge and GaAs, especially related to the problem of interface composition. Our isotopic labeling results give new insight on oxygen incorporation and diffusion in high-K films. In selecting an alternative (to SiO2) gate insulators, many parameters in addition to dielectric constant and thermal stability must be considered, including the barrier heights for tunneling. Our SXPS and IPES experimental results are complemented by first-principles density functional calculations to study the properties of the different crystalline phases of HfO2 and ZrO2. It is found that the band gap, barrier height and dielectric response of these two materials are phase dependent. The densities of states are calculated and compared to various experimental measurements. The thickness, layered structure, and crystal phase of the as-deposited and annealed films have been studied by diffraction (XRD), x-ray adsorption (XAS), MEIS and TEM. Critical electrical and materials changes occur during post-processing at elevated temperature. We discuss these changes, including the decomposition of the films in reducing environments in the 900-1100Â°C range. Finally, FTIR results on initial surface reactivity and ALD/CVD film growth are presented. The authors would like to acknowledge productive interactions with colleagues at Agere, IBM, NCSU and Stanford. We also acknowledge the SRC/Sematech FEP Center and the NSF for financial support.

4:40pm **DI-MoA9 Hafnium Germanosilicate Thin Films for Gate and Capacitor Dielectric Applications: Thermal Stability Studies*, S. Addepalli,*** *P. Sivasubramani, P. Zhao, M.J. Kim, M. El-Bouanani, B.E. Gnade, R.M. Wallace,* University of North Texas

The use of SiO@sub 2@-GeO@sub 2@ mixtures in gate and capacitor dielectric applications is hampered by the inherent thermodynamic instability of germanium oxide. Studies to date have confirmed that germanium oxide is readily converted to elemental germanium.@footnote 1,2@ In sharp contrast, germanium oxide is known to form stable compounds with transition metal oxides such as hafnium oxide (hafnium germanate, HfGeO@sub 4@).@footnote 3@ Thus, the incorporation of hafnium in SiO@sub 2@-GeO@sub 2@ may be expected to enhance the thermal stability of germanium oxide via Hf-O-Ge bond formation. In addition, the introduction of transition metal would simultaneously enhance the capacitance of dielectric thereby permitting a thicker dielectric, which reduces leakage current.@footnote 4@ In this study, the thermal stability and electrical properties of PVD-grown hafnium germanosilicate (HfSiGeO) films on Si(100) substrate were investigated. XPS, RBS, HR-TEM, C-V and I-V results for germanosilicate films after deposition and subsequent annealing treatments will be presented. Our results indicate that the thermal stability of the hafnium germanosilicate films is drastically affected not only by the presence or formation of elemental germanium during annealing, but also by the germanium content in the film. This work is supported by DARPA through SPAWAR Grant No. N66001-00-1-8928, and the Texas Advanced Technology Program. @FootnoteText@ @footnote 1@ W. S. Liu, J .S. Chen, M.-A. Nicolet, V. Arbet-Engels, K. L. Wang, J. Appl. Phys. 72, 4444 (1992), and, Appl. Phys. Lett. 62, 3321 (1993).@footnote 2@ W. S. Liu, M.-A. Nicolet, H.-H. Park, B.-H. Koak, J.-W. Lee, J. Appl. Phys. 78, 2631 (1995). @footnote 3@ P. M. Lambert, Inorg. Chem. 37, 1352 (1998).@footnote 4@ G. D. Wilk, R. M. Wallace and J. M. Anthony, J. Appl. Phys. 89, 5243 (2001).

Electronic Materials and Devices
Room 321/322 - Session EM+SC-MoA

Defects and Interfaces in Electronic Materials and Devices

Moderator: C.G. Van de Walle, Palo Alto Research Center

2:00pm **EM+SC-MoA1 Localized Defect States, Impurities, and Doping in Al@sub x@Ga@sub 1-x@N Epilayers***, **S.T. Bradley**,* Ohio State University **INVITED**

AlGaN and its heterojunction alloys are used in some of the most advanced micro- and optoelectronic devices today and rely on precise control of electronic properties in multilayer film structures on a nanometer scale. Deep level defects in these materials and at their interfaces can alter transport, recombination, contact formation, and doping, yet measuring such small structures is a challenge for conventional techniques. Al-rich AlGaN layers can enable many new applications but little is known of their deep level properties. Also, doping of AlGaN with high Al content is difficult and may be restricted by non-intentional impurities (such as oxygen) and their associated deep levels. We have used a near-surface version of cathodoluminescence spectroscopy (CLS), termed low energy electron-excited nanoluminescence (LEEN), to probe the electronic properties of thin HFET films as a function of lateral position and depth. LEEN spectroscopy can provide electronic properties of states that are localized at the surface, buried interface, and near the middle of these nanometer-scale films. For AlGaN/GaN structures, correlations have been made between deep level defects and the sheet charge density, AlGaN/GaN intermixing, surface roughness, and Ga/N ratio. We have also used LEEN with secondary ion mass spectrometry (SIMS) to correlate deep levels across the AlGaN alloy series with chemical impurities and spatial location at surfaces, interfaces, and in the bulk. Al-rich AlGaN exhibits deep level optical emissions that correlate with O and C impurities. Temperature-dependent CL of the Si-doped films reveal donor energy increases but activation energy decreases with Al content. Coupled with the appearance of an O deep level at mid-gap at highest Al concentrations, these changes can be seen to compensate the intentional Si doping. These results demonstrate how spatially-resolved CL combined with SIMS can provide new understanding of macroscopic III-nitride properties.

2:40pm **EM+SC-MoA3 Contactless Characterization of High Electron Mobility Transistor Structures using Surface Photovoltage Spectroscopy***, **S. Solodky**,* Tel Aviv University, Israel*; A. Khramtsov,* Ben-Gurion University, Israel*; T. Baksht,* Tel Aviv University, Israel*; M. Leibovitch,* Gal-El (MMIC), Israel*; Hava,* Ben-Gurion University, Israel*; Y. Shapira,* Tel Aviv University, Israel

GaN/AlGaN High Electron Mobility Transistor (HEMT), AlGaAs/InGAs/GaAs pseudomorphic HEMT (PHEMT), and InAlAs/InGaAs metamorphic HEMT (MHEMT) epitaxial structures have been characterized using surface photovoltage spectroscopy (SPS). The interplay between two opposite direction signals coming from the regions with opposite direction of electric fields define the shape of the spectra. The shape of the spectra is interpreted using self-consistent numerical simulations. The effects of the transistor delta-doping levels dtop, dbot and surface charge Qsur on the spectrum features have been studied using numerical simulations. Based on the latter, an empirical model has been developed, which allows extraction and comparison of dtop, dbot and Qsur and is applicable for both double-sided and single sided delta-doped structures. Effect of SiN passivation on GaN/AlGaN HEMT surface is shown. Applying of the model to passivated structure shows reduced Qsur. Prediction of the final device performance by the model is shown for two MHEMT structures. Applying of the model shows sensitivity of the methodology to 7.5% difference of dtop. Devices produced on these structures show relative difference of 8.2% in maximum drain currents, which correlate well with dtop values calculated using the model.

3:00pm **EM+SC-MoA4 Atomic Bonding and Electronic Changes at InGaAs/InP Heterojunctions***, **P.E. Smith**, S.H. Goss, S.T. Bradley, L.J. Brillson, M.K. Hudait, Y. Lin, S.A. Ringel,* The Ohio State University*; S.W. Johnson,* Sandia National Laboratories

Lattice-matched In@sub 0.53@Ga@sub 0.47@As/InP heterojunctions have attracted considerable interest for many opto- and microelectronic applications. Achieving abrupt interfaces is difficult since both group III and V elements must be switched at the interface during MBE growth. To minimize structural defects, growers often employ a sequence of source switching such that new group V elements are switched on for brief exposure times before growth of subsequent layers. Interface-specific atomic bonding and diffusion can occur that can alter local electronic properties. We combined secondary ion mass spectrometry (SIMS) depth profiling with micro-cathodoluminescence spectroscopy (CLS) in cross section to measure atomic bonding and compositional changes and their effect on electronic properties. SIMS and CLS measurements of InGaAs-on-InP interfaces subjected to exposure times of 40, 80, 110, 140, and 170 sec reveal: (1) interface broadening (both As and P) that increases from < 5 to 15 nm with the length of time the InP surface is exposed to As prior to InGaAs growth, (2) InGaAs near band edge (NBE) emissions at ~0.79 and 0.80 eV, whose intensities shift to higher energies with proximity to the heterojunction on a submicron scale and become more evident with increasing As exposure time. These electronic changes suggest either lower In interface concentration and/or local defect formation - the latter consistent with increasing trap densities with As exposure measured via photoconductivity decay. Overall, local electronic structure at a lattice-matched III-V compound heterojunction depends sensitively on the competition of atomic species in the transition region during growth.

3:20pm **EM+SC-MoA5 Nanoscale Electronic Characterization of Semiconductors: from Operating Devices to Atomic Scale Defects***, **Y. Rosenwaks**, R. Shikler,* Tel-Aviv University, Israel*; Th. Glatzel, S. Sadewasser,* Hahn-Meitner Institut, Germany **INVITED**

Scanning probe microscopy has opened new opportunities to image semiconductors electronic properties with unprecedented spatial resolution. The recently developed Kelvin probe force microscopy (KPFM) technique has already been demonstrated as a powerful tool for measuring nanoscale electronic properties and has found many diverse applications in recent years. In this talk several novel applications of the KPFM technique recently developed and demonstrated by our group will be presented. The long-range electrostatic force between the AFM tip and the semiconductor surface deteriorates drastically the KPFM spatial resolution, and poses the problem whether surface atomic scale defects can be quantitatively measured. In addition, the physical understanding of the observed contrast in atomic resolution images is still under discussion. We show that by combining ultrahigh vacuum (UHV) KPFM measurements with rigorous modelling of the tip-semiconductor electrostatic interaction it is possible to extract the surface charge density at the atomic steps of a GaP (110) surface. The third part of the talk will be devoted to the use of KPFM for direct measurement of surface states parameters in semiconductors. The method is based on the measurement of very asymmetric cleaved p++n or n++p junctions. The absolute surface band bending, Us, and the surface charge density, Nss, can can be extracted because one side of the junction is degenerate, and all the band bending is taking place in the low doped semiconductor. Methods to obtain the surface states energy distribution are also discussed.

4:00pm **EM+SC-MoA7 STM Observation of Subsurface Boron Dopants on the Si(001)-2x1 Clean Surface***, **M. Nishizawa**, L. Bolotov, T. Kanayama,* National Institute of Advanced Industrial Science and Technology, Japan

As the feature size of integrated circuits approaches nanometer dimensions, dopant distribution in device regions plays an increasingly larger role in determining device performance. This has motivated research in recent years to identify a suitable technique to profile dopant distribution with atomic scale resolution. Among the more promising technologies is Scanning Tunneling Microscopy (STM). While a number of studies have been made to measure individual dopants on cleaved compound-semiconductor surfaces and cleaved or hydrogen-terminated Si surfaces using STM, no studies have been made on the Si(001)-2x1 clean surface. From a surface science perspective, the Si(001)-2x1 is one of the most widely studied and documented surfaces. However, it has not received attention in dopant measurement studies, as it is believed that surface states in the band gap obscure observation of dopant features. In this report, we show that Boron-dopant features can be successfully observed on the Si(001)-2x1 surface using STM. On the Boron-doped Si(001)-2x1 surface (sheet resistance is 0.01 @ohm@ cm) we have observed a number of specific features which are a few nanometers in size and appear as round-shaped protrusions superimposed on the corrugation of surface reconstruction in the filled-state image. The appearance of these features is quite similar to the dopant images observed previously on the other surfaces. These features can be recognized starting at a sample bias voltage (V@sub s@) of -1.0 V and tunneling current (I@sub t@) of 0.2 nA, can be enhanced by increasing V@sub s@ to -0.4 V and I@sub t@ to 2.0 nA. Area density of these features changes with dopant concentration of the substrate. From these results, we conclude that the specific features observed here are related to the Boron dopant located in a subsurface layer. This study was supported by NEDO.

4:20pm **EM+SC-MoA8 Surface Defects After the Growth of Highly P and Sb Doped Si**, ***G.G. Jernigan***, *P.E. Thompson,* US Naval Research Laboratory

Doping in semiconductors is crucial to the formation of electronic devices, but our knowledge of the physical characteristics of electrical interfaces, as they are formed during device fabrication, is limited. We will present a unique study of Si doping with P and Sb during MBE growth on Si (100) wafers using an in vacuuo STM. The process of doping affects the surface morphology, as compared to an undoped film, leading to surface defects. Under dopant flux conditions of ~10@super 12@ atoms/cm@super 2@/s and Si growth rates ~0.10 nm/s, we will report the changes to the Si surface morphology and the production of defects at growth temperatures of 500 °C. The segregation of the n-type dopants, P and Sb, is observed to affect Si adatom attachment at step-edges resulting in an increase in island formation. For thin films of P less than 50 nm, where less than 0.1 monolayers (ML) of P has segregated, the surface roughness is not increased significantly but line defects parallel to dimer rows can be observed. At high P surface coverages observed on films greater than 50 nm, there are blockages at step-edge sites to form pothole-like defects with a density of 2x10@super 10@ /cm@super 2@. For all Sb films grown, there is an increase in surface roughness with increasing film thickness (>2.0 nm) and Sb surface coverage (>0.01 ML). At high Sb surface coverages (0.8 ML), Si islands form into pyramid-like defects with a density of 8x10@super 10@ /cm@super 2@, and this casts concern for the use of Sb in surfactant assisted growth. The evolution of the surface morphology and defect appearance with film growth and dopant segregation will be discussed.

4:40pm **EM+SC-MoA9 The Effect of Strain on Impurity States in Si and Methods of Calculation Thereof**, ***A. Rockett***, *D.D. Johnson,* University of Illinois*; B.R. Tuttle,* University of Pennsylvania*; S.V. Khare,* University of Illinois

We propose a simple model for estimating the contribution of strain to the ionization energy of defect states in semiconductors. The model is illustrated for group III and V impurities in Si. The approach uses an extrapolation technique to determine the ionization energies from the results of density functional theory (DFT) calculations. The method is shown to produce reliable results for a range of dopants with no parameters and none of the usual corrections requried in DFT. The results are generalized through an analysis of the resulting energies based on a screened electrostatic interaction, strain, and a bonding localization term.

5:00pm **EM+SC-MoA10 New Mechanism for Coupling between Properties of Interfaces and Bulk Semiconductors**, ***K. Dev***, *E.G. Seebauer,* University of Illinois at Urbana Champaign

A new mechanism is described by which interface electronic properties can affect bulk semiconductor behavior. In particular, experimental measurements by photoreflectance of Si(100)-SiO2 interfaces show how a controllable degree of band bending can be introduced near the interface by ion bombardment and annealing. The resulting electric field near the interface can affect dopant concentration profiles deep within the semiconductor bulk by drastically changing the effective interfacial boundary condition for annihilation of charged interstitial atoms formed during bombardment. Kinetic measurements of band bending evolution during annealing show that the bending persists for substantial periods even above 1000 C. Unusually low activation energies for the evolution point to a distribution of energies for healing of bombardment-generated interface defects. The transformations take place at temperatures higher than those characterizing other defects known to exist at the Si-SiO2 interface. The findings have significant implications for pn junction formation during CMOS device processing.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI-MoA

Magnetic Recording and Magnetoresistive Structures

Moderator: M.C. Tondra, NVE Corp.

2:00pm **MI-MoA1 Materials/Structures for High Areal Density Write Poles**, ***M.K. Minor***, *T.J. Klemmer, M.A. Seigler, O. Mryasov,* Seagate Technology*; M. Kim, A.J. Freeman,* Northwestern University **INVITED**

The maximum effective write field of a head is related to head geometry and the saturation magnetization (4@pi@M@sub S@) of the pole material. Typically, head designs require a pole material at the air bearing surface (ABS) which exhibits a large 4@pi@M@sub S@, low coercivity, and a well-defined uniaxial anisotropy. The material with the largest known 4@pi@M@sub S@ at room temperature is exhibited by Fe@sub 65@Co@sub 35@ which has a value of ~2.4T. One of the problems with FeCo that prevents it from being used as a pole material is that the material is not uniaxial, therefore, it has nearly zero permeability which results in an inefficient write head. This lack of uniaxiality or magnetic "softness" is a direct result of the relatively large value of magnetocrystalline anisotropy exhibited by the high moment FeCo alloys. This talk will review some of the methods employed to induce magnetic softness in the high moment FeCo alloys. These methods include the effects of various processing conditions, the use of buffer layers, and laminated structures which are magnetostatically coupled. For each of these methods magnetic properties and film microstructure will be reviewed. A large portion of this talk will focus on FeCo multilayered structures fabricated via dc magnetron sputtering. Some modeling and experimental results will be presented. These results include enhanced moment prediction and effect of multilayering on anisotropy. The modeling results are compared to experimental results where we will show structural and magnetic properties of the FeCo multilayers.

2:40pm **MI-MoA3 Influence of Pd and Pt Buffers on the Soft Magnetic Properties of Fe@sub 70@Co@sub 30@ Thin Films**, ***C.L. Platt***, *J.K. Howard,* Seagate Technology*; D.J. Smith,* Arizona State University

Writer pole materials with large saturation magnetization are desired to maximize the available writing field for magnetic recording. A 5 nm thick Pd or Pt buffer layer is sufficient to significantly alter the magnetic and structural properties of sputtered high moment (2.4 T) Fe@sub 70@Co@sub 30@ thin films. A 50 nm thick FeCo film with no buffer grown on an amorphous SiO@sub 2@ substrate had a coercivity of 40 Oe and showed no evidence of an induced easy axis, although the film was grown in an applied field of 50 Oe. This is typical of high moment FeCo alloys which usually do not exhibit soft magnetic properties due to large magnetostriction and difficulty controlling magnetic ripple structure. Use of 5 nm Pd or Pt buffer reduced the coercivity of 50 nm FeCo films to about 15 Oe with a definable easy axis. Structurally, the primary influence of the Pd or Pt buffer was a reduction in the average FeCo grain size and more clearly defined columnar grain boundaries. This is similar to what has been observed using other fcc buffers.@footnote 1,2@ Growing thicker FeCo films (200 nm) resulted in a significant increase in average column width and a loss of soft magnetic properties regardless of the buffer. @FootnoteText@ @footnote 1@H. S. Jung, W. D. Doyle, J. E. Wittig, J. F. Al-Sharab, and J. Bentley, Appl. Phys. Lett. 81, 2415 (2002).@footnote 2@C. L. Platt, A. E. Berkowitz, D. J. Smith, and M. R. McCartney, J. Appl. Phys. 88, 2058 (2000).

3:00pm **MI-MoA4 Atomistic Simulations of Metal/Metal Oxide Heterostructures**, ***X.W. Zhou***, *H.N.G. Wadley,* University of Virginia

A thin aluminum oxide layer sandwiched between a pair of ferromagnetic metal layers forms a spin-dependent tunnel junction that can be used to construct random access memory. Atomistic simulations based upon interatomic potentials provide a way to identify the best conditions to synthesize these structures. However, unlike the approaches that have been successfully used to simulate metal multilayer deposition, atomic simulation methods for metal and metal oxide heterostructures are poorly developed. Metal oxides involve a significant ionic interaction between constituent cations and anions. Traditional fixed charge ionic potentials do not allow the introduction of different oxidation states and cannot ensure charge neutrality during simulation of oxide vapor deposition. They also significantly overestimate the cohesive energy of oxides. Because their charges are designated (for a given bulk oxide), they are not applicable to metal oxide heterostructures and cannot address metal/oxide interfaces. A charge transfer ionic potential (CTIP) model proposed by Streitz and Mintmire has attempted to overcome these deficiencies. However, we found that this charge transfer model is unstable and can only be applied to single metal-oxygen binary systems. By incorporation of the physical principle of elemental valency we have found an expedient solution to the limitations of the original CTIP model. The improved CTIP potential has been combined with an existing embedded atom method (EAM) metal potential to dynamically address both ionic and metallic components of the interatomic interactions in an O-Al-Ni-Co-Fe system during atomistic simulations. Application of this novel approach in the oxidation of aluminum layer in Ni65Co20Fe15/Al2O3/Ni65Co20Fe15 spin-dependent tunnel junction multilayer is reported and the roles of processing conditions used to synthesis the aluminum oxide layer are discussed.

3:20pm **MI-MoA5 Quantum-size Effect of Tunneling Magnetoresistance in Magnetic Tunnel Junctions***, **S. Yuasa,*** AIST and PREST-JST, Japan*; T. Nagahama, Y. Suzuki,* AIST and CREST-JST, Japan **INVITED**

We fabricated magnetic tunnel junctions (MTJs) with single-crystal bottom electrodes and observed new phenomena such as the crystal-orientation dependence of the tunneling magnetoresistance (TMR) effect,@footnote 1@ the quantum-size effect of TMR,@footnote 2@ and the spin-polarized resonant tunneling.@footnote 3@ Here, we report the results on three types of MTJs with a single-crystal bottom electrode; (i) MTJ with an ultrathin ferromagnetic electrode, (ii) MTJ with an ultrathin nonmagnetic electrode grown on a ferromagnetic layer, and (iii) MTJ with an antiferromagnetic electrode grown on a ferromagnetic layer. The results are discussed in terms of spin lifetime of tunneling electrons. @FootnoteText@@footnote 1@S. Yuasa et al.: Europhys. Lett. 52, 344 (2000). @footnote 2@T. Nagahama, S. Yuasa, Y. Suzuki, E. Tamura: Appl. Phys. Lett. 79, 4381 (2001). @footnote 3@S. Yuasa, T. Nagahama, Y. Suzuki: Science 297, 234 (2002).

4:00pm **MI-MoA7 Magnetization Dynamics and Magneto-transport in Epitaxial Nano-structures***, **R.A. Lukaszew,** D. Pearson, Z. Zhang,* University of Toledo*; A. Zambano,* Michigan State University

Abstract: The latest results on ballistic magneto-resistance (BMR) research have shown surprising ballistic magnetoresistance.@footnote 1@ It has been postulated that the BMR effect arises from non-adiabatic spin scattering across very narrow magnetic domain walls trapped at nano-sized constrictions.@footnote 2@ The reported BMR effect has been observed in nano-contacts electrodeposited between Ni wires. Much of the publish data so far, is still poorly understood. In an attempt to clarify some of the possible processes present in the observed phenomena we applied e-beam lithography to epitaxial Ni films to fabricate nano-bridges with more controlled geometry than the ones made with electrochemical deposition. Epitaxial ferromagnetic thin films exhibit narrow domain walls that may favor ballistic regime provided that the nano-contact is small enough. We have modeled the magnetization reversal in epitaxial films and have established that the unusually high coercive field observed along hard axes is due to a second order type transition prior reversal that induces high density of domain walls at the reversal.@footnote 3@ Thus we expect that a patterned nano-structure with segments parallel to magnetization hard axes will be more likely to experience domain-wall related effects in magneto-transport. Therefore we patterned a similar T geometry to that utilized by Chopra and Garcia.@footnote 1,3@ Our preliminary results indicate that magnetic domains do play a role in the magneto-resistance of these nano-bridges but the order of magnitude of the observed effect is considerably smaller than the reported observations for electrochemically prepared nano-contacts. @FootnoteText@@footnote 1@B. D. Chopra and S. Z. Hua, Phys. Rev. B. 66, 020403(R), 2002. @footnote 2@P. Bruno, Phys. Rev. Lett. 83, 2425 (1999). @footnote 3@Lukaszew, R.A. and Clarke R., unpublished. @footnote 4@N. Garcia, M. Munioz, V. V. Osipov, E. V. Ponizovskaya, G. G. Quian, I.G. Saveliev and Y.-W. Zhao, J. Magn. Magn. Mater. 240, 92 (2002).

4:20pm **MI-MoA8 Artifacts in Ballistic Magnetoresistance Measurements***, **W.F. Egelhoff,** M.D. Stiles, T.P. Moffat, J. Mallett, R.D. McMichael, H. Ettedugi, A.J. Shapiro, C.J. Powell,* National Institute of Standards and Technology*; E.B Svedberg,* Seagate

The Ballistic Magnetoresistance (BMR) effect has attracted much attention in the past year with BMR values as large as 100,000% having been reported in Physical Review@footnote 1@ and 1,000,000% reported at Intermag2003.@footnote 2@. Naturally, such impressive results have led many researchers to attempt to reproduce large BMR values. Unfortunately, these attempts have widely failed. This failure has led to much skepticism over whether BMR is a real effect. In our research, we have found several artifacts caused by magnetostriction and magnetostatics that can produce what appear to be huge BMR values. In this talk, we will illustrate these artifacts, provide an assessment of the implications these artifacts have for the field of BMR, and give guidelines for performing BMR measurements in an artifact-free manner. We will also present results of new BMR measurements in which we follow our recommended procedures. @FootnoteText@@footnote 1@S. Z. Hua and H. D. Chopra Phys. Rev. B 67, 060401 (2003). @footnote 2@Nicolas Garcia, invited talk, Intermag2003.

4:40pm **MI-MoA9 Arrays of Magnetoresistive Sensors for Non-destructive Testing***, **A.V. Nazarov,*** National Institute of Standards and Technology*; F.C.S. da Silva,* National Institute of Standards and Technology, US*; P. Kabos, D.P. Pappas,* National Institute of Standards and Technology

Magnetic field mapping is a powerful tool that can provide high sensitivity and high spatial resolution for current localization.@footnote 1@ In this work, we used magnetic field mapping to non-destructively analyze the current distribution in integrated circuit chips and localize wiring defects. The magnetic field produced by current distributions was simultaneously measured with arrays of magnetoresistive (MR) sensors in order to increase the effective speed of the scan. Arrays of eight permalloy barber-pole type MR sensors were fabricated using a two step lift-off lithography process. The sensors were 40 µm long, 4 µm wide, and separated by 210 µm. The nominal resistance of the sensors was in the 24.9 to 25.2 @ohm@ range and the MR change was 1.8 %. A broadband, simultaneous, 8-channel, computer-based digital lock-in technique was developed for data acquisition and analysis. The measured magnetic field distributions were directly converted to current images using normalized discrete 1-d Fourier transforms. Measurements of test structures show the absence of cross-talk between sensors and that the spatial resolution is approximately z/2 where z is the distance between current plane and the sensor. This work was supported by the National Institute of Standards and Technology Office of Law Enforcement Standards, the Federal Bureau of Investigation, the National Security Agency, the National Institute of Justice, and the Advanced Technology Program. @FootnoteText@ @footnote 1@S. Chatraphorn, E. F. Fleet, F. C. Wellstood, L. A. Knauss, and T. M. Eiles, Appl. Phys. Lett. 76, 2304 (2000).

Manufacturing Science and Technology
Room 309 - Session MS-MoA

Challenges in Advanced Materials and New Processes for Semiconductor Manufacturing

Moderator: A. Testoni, Varian Semiconductor Equipment Associates

2:00pm **MS-MoA1 Research and Challenges in Nano Mechanics and Materials***, **K.P. Chong,*** National Science Foundation **INVITED**

Mechanics at the nano-scale is quite different from continuum mechanics. Nanomechanics is basic and essential in all areas of nano science, materials and engineering. Basic principles and experimental tools, multi-scale simulation, self-assembly as well as nanomechanics in information technology, biotechnology, micro/nano electronics [M/NEM] and other issues are presented. Recent workshops, research issues, research projects, as well as opportunities and challenges in nanomechanics are also discussed.

2:40pm **MS-MoA3 Opportunities and Challenges in the Materials Supply Chain for Semiconductor Manufacturing***, **R.J. Richardson,*** Air Products and Chemicals, Inc. **INVITED**

Over 100 gases and chemicals are used to manufacture semiconductor devices. Many of these materials present formidable challenges in synthesis, purification, analysis, container and distribution system compatibility, contamination control, ESH and regulatory issues. As we near the end of the CMOS roadmap, a large number of new materials and processes are being considered to enable the manufacture of ever-smaller device structures. Although the large number of new candidate materials appears to provide a number of new opportunities, they bring a host of challenges. Only a few of the new alternatives will eventually end up in high volume manufacturing, which poses a dilemma for a full service materials supplier beyond the decisions related to the allocation of scarce R&D resources to multiple solutions to the same problem. How these issues (e.g., purity requirements, materials compatibility studies, ESH impacts) are addressed for some of the new materials under consideration for advanced CMOS manufacturing and the various competing trends (e.g., consistency of supply vs. ever-higher purity) facing the materials supplier will be discussed.

3:20pm **MS-MoA5 New Processes and Materials for Environmentally Benign Semiconductor Manufacturing***, **F. Shadman,*** University of Arizona **INVITED**

The environmental issues are beginning to have significant impact on both the development of new processes and the application of new materials. In this presentation, some of the technical challenges and the potential solutions will be discussed. The specific examples will include: surface preparation, new dielectric materials, gaseous emissions particularly of global warming compounds, environmental bottlenecks in chemical mechanical planarization (CMP), and finally, environmental drivers for process integration in patterning and deposition of dielectrics in copper/low-k dielectric systems.

4:00pm **MS-MoA7 Sub-100 nm Copper Wiring Challenges and Solutions***, M. Xi, M. Yang, W.-F. Yau, J. Dukovic,* ***A. Rosenfeld****, N. Maity,* Applied Materials **INVITED**

With the emergence of sub-100 nm Cu-low k BEOL technology, copper-electroplating faces a new set of challenges. The combination of shrinking dimensions (coupled with an increase in aspect ratio) and increased current density, necessitate innovation in process and hardware development that can provide acceptable process integration results. Furthermore, the ever-shortened development cycle requires proliferation of new innovations into predictable and repeatable production-worthy processes in minimal development and qualification cycle time. The Cu metallization process is performed in two steps. First, thin metallic layers of barrier material (such as TaN or Ta) and Cu seed is deposited into the vias and lines that define the interconnect. Next, Cu electroplating is used to fill the interconnect structures. The function of the barrier material is to prevent Cu diffusion into the surrounding dielectric, while the Cu seed enables the electroplating fill. The key requirement for both barrier & seed layers is conformal step coverage in sub 100nm features. As such, ionized PVD technology is required to achieve the desired step coverage. To address this requirement, a novel magnetron source was developed that enables high metal ionization with a flat target. The flat target design enables low defects and low cost of ownership for the Cu Barrier-Seed process. Moving to 65 nm and below, the PVD films could be substituted by ultra-thin conformal ALD films, particularly for the barrier process. This will enable lower interconnect resistance and further reduce cost of manufacturing, by reducing the cost of consumables for both the barrier deposition and the barrier CMP processes. To address the needs of sub 100nm copper plating, a novel electroplating system featuring a small volume plating bath with individual electrolyte circulation is was developed. Conventional large volume electroplating bath systems is are adequate for 130nm productions needs, but shows limitations in the area of consistent gap fill and defect performance for sub 100nm applications. In addition, a large bath system lacks the flexibility to change chemistry quickly, which slow down the development and optimization of new processes to meet the new requirements. Root cause of the inconsistent gap fill is correlated to organic by-product build up. In one experiment, the total organic content of a large bath system is measured throughout the life of the bath. The result shows that gap fill consistency is compromised when the total organic content is above 550ppm. In contrast, the small volume plating system allows periodic dumping and refilling of the plating bath after processing a small number of wafers, such as 200 wafers. This provides two key advantages. First, incoming wafers are exposed to fresh plating solution. This minimizes the gap fill inconsistency caused by aging and breakdown of the organic additives mentioned above. Second, by dumping and refilling the small bath after a small number of wafers are processed, different chemistry can be introduced and tested efficiently, from one bath to the next. This can provide significant time and chemical savings for process development and optimization. In addition, the individual electrolyte circulation design allows different plating cells within a plating system to process with different chemistries. This design enables sequential processing, or multi-step plating within a single plating system. The advantage of multi-step plating is demonstrated with experimental results showing dramatic reduction in as plated mounding.

4:40pm **MS-MoA9 Nanoporous Organosilicates for On-Chip Applications Using Sacrificial Macromolecular Porogens***,* ***R.D. Miller****, W. Volksen, H.-C. Kim, E. Connor, J.L. Hedrick, C.J. Hawker, T. Magbitang, V. Lee,* IBM Almaden Research Center **INVITED**

Porous organosilicates have many potential applications, including separation media, catalyst supports, high surface area materials for bio-applications and ultralow-k media for on-chip insulator applications. The latter is driven by the need for low-k insulators to minimize signal delays and crosstalk. We have studied the generation of nanoporous thin film organosilicates using sacrificial macromolecular porogens, a process that requires a tailored interaction between the pore generators and the respective matrix resin. Depending on the porogen structure, the pore generating process can be classified either as nucleation and growth or templating. Each technique produces porous materials, but the film morphologies can be quite process specific. The integration of porous organosilicates for copper interconnects puts a premium on matrix mechanical properties. These can be altered by structural variations and/or process variations. The generation, characterization and integration of porous thin organosilicate films will be discussed.

Contacts to Organic Materials Topical Conference
Room 318/319 - Session OM-MoA

Contacts to Molecules and Molecular Films (II)

Moderator: D.R.T. Zahn, Technische Universität Chemnitz, Germany

2:00pm **OM-MoA1 Characterization of Organic-Metal and Organic-Organic Interfaces***,* ***J.L. Bredas****,* Georgia Institute of Technology **INVITED**

In organics-based (opto)electronic devices, organic/metal and organic/organic interfaces play a key role in determining the device performance. Here, we focus first on the interface dipole present at organic-on-metal interfaces. The origin of this dipole is rationalized from the results of a joint experimental and theoretical study based on the interaction between pi-conjugated molecules and transition metal surfaces. It is found that the interface dipole formed at the organic/metal interface can be divided into two contributions: (i) the first corresponds to the "chemical" dipole induced by a partial charge transfer between the organic layers and the metal upon chemisorption of the organic molecules on the metal surface; and (ii) the second relates to the change in metal surface dipole due to the modification of the metal electron density tail that is induced by the presence of the adsorbed organic molecules. In a second part, we investigate the electronic structure of metal-on-oligomer and organic/organic interfaces.

2:40pm **OM-MoA3 The Role of Charge Neutrality Level in Molecular Level Alignment at All-organic Heterojunctions***,* ***W. Gao****, A. Kahn,* Princeton University

Alignment of molecular levels at organic-organic (OO) heterojunctions controls charge injection and transport in multilayer organic devices. Because of weak intermolecular interaction and absence of free charges, vacuum level alignment is often observed at heterojunctions between intrinsic (undoped) molecular films. We present here the first experimental evidence that an alignment mechanism based on the charge neutrality level of the molecular semiconductor becomes important when one of the interface constituents is doped. Our direct and inverse photoemission (UPS, XPS, IPES) investigation focuses on interfaces between hole transport layers (HTL) and electron transport layers (ETL).@footnote 1@ We use the strong electron acceptor F@sub 4@-TCNQ to p-dope the HTLs.@footnote 2@ We show that, unlike at metal-organic (MO) interfaces, molecular levels and energy barriers across the interfaces are not strongly anchored and shift with respect to each other upon doping of the HTL. The shift is accompanied by the formation of an interface dipole, the size of which depends on the constituents of the heterojunction. The key result is that the Fermi level position in the gap of the undoped ETL remains fixed and independent of the HTL when the HTL is doped. This important observation suggests that the introduction of charges and of electronic states at the interface in the gap of the HTL and ETL via doping results in a pinning of the Fermi level at or near a specific energy level, tentatively related to the charge neutrality level of the organic material. @FootnoteText@@footnote 1@W. Gao and A. Kahn, Appl. Phys. Lett., (in press) @footnote 2@W. Gao and A. Kahn, Organic Electronics 3, 53 (2002).

3:00pm **OM-MoA4 Au/CuPc Interface: A Photoemission Investigation***,* ***L. Lozzi****, S. Santucci,* INFM and University of L'Aquila, Italy*; S. La Rosa,* Sincrotrone Trieste SCpa,Trieste, Italy

Copper phthalocyanine (CuPc) are deeply investigated for many different applications as thin films. One of the most promising application is the fabrication of photovoltaic cells, in which the CuPc film is the active part.@footnote 1@ Au is a widely used metal for metallic contact, in particular for organic photovoltaic cells, because of its high work fuction. In this study we will show our results on the investigation of the interface between CuPc and Au by means of photoemission. We have deposited, by means of thermal evaporation in ultra high vacuum conditions, very thin Au films on a 70 nm thick CuPc film and we have investigated both core levels and valence band features as a function of the Au thickness. We have used different photon energies (from X-ray to UV) to investigate surface and in depth properties. Moreover we have performed high spatial resolution photoemission experiments (Spectromicroscopy beamline at Elettra Synchrotron Radiation Center, spatial resolution about 0.5@micron@) to investigate the homogeneity of the Au film on the organic film. The evolution of the Au 4f spectrum, as a function of the Au film thickness shows indicates the formation of gold cluster.@footnote 2@ Comparing the valence band acquired using low photon energy with those using X-ray photons, it is evident that these clusters are dispersed inside the organic film. No evident variations are observed in the core levels of the CuPc elements. The spatially resolved photoemsiion spectra do not show any difference of the valence band spectra as a function of the position and also the images, acquired looking at different energies of the valence band, showed a very high homogeneity of the deposition, althought the CuPc surface is quite rough. @FootnoteText@ @footnote 1@ P. Peumans and S.R. Forrest, Appl.Phys.Lett. 79, 126 (2001) @footnote 2@ S.B. Di Censo, S.D. Berry, and E.H. Hartford Jr., Phys.Rev.B38, 8465 (1988).

3:20pm **OM-MoA5 XPS and HRSEM Studies on the Interfaces of Au/CuPc vs. Au/FCuPc***, **X. Yu**, T.E. Madey,* Rutgers, The State University of New Jersey

Ultrathin films of Au have been grown on both copper phthalocyanine (CuN@sub 8@C@sub 32@H@sub 16@, CuPc) and copper hexadecafluorophthalocyanine (CuN@sub 8@C@sub 32@F@sub 16@, FCuPc) samples at room temperature (RT). These are model systems for metal contacts on organic semiconductors. X-ray photoelectron spectroscopy (XPS) measurements, corresponding to various average Au film thicknesses (from 0.3 to 3.0 Å), show that Au deposited on CuPc does not react, but for Au on FCuPc there is evidence for possible charge transfer from Au atoms to the four aromatic rings of FCuPc. Annealing the films at 125°C for one hour enhances charge transfer at the interfaces of Au/FCuPc, while it does not cause any chemical reactions at the interfaces of Au/CuPc. High-resolution field emission scanning electron microscopy (HRSEM) was employed to examine the nucleation and growth of Au (average thicknesses from 5 to 180 Å) on CuPc and FCuPc films at room temperature. Au grows in an island mode on four types of samples CuPc (RT), CuPc (125), FCuPc (RT), and FCuPc (125) in the initial stages of Au deposition (average thicknesses from 5 to 15 Å). The number in the parentheses is the temperature of substrates (in degrees Celsius) during CuPc or FCuPc deposition. Au atoms tend to form bigger clusters with a lower cluster density on CuPc surfaces than on FCuPc surfaces. This may indicate a lower diffusivity for Au on FCuPc than on CuPc, perhaps because of a stronger interaction between Au and FCuPc. These observations support our results from XPS studies. The onset of percolation occurs at a Au thickness of @>=@90Å for Au/CuPc (RT) and Au/CuPc (125), and 90Å for Au/FCuPc (RT) and Au/FCuPc (125). A continuous and hole-free Au film is formed at a thickness of 180Å.

3:40pm **OM-MoA6 A Combined Photoemission Spectroscopy and Scanning Probe Microscopy Study of Organic Charge Injection Layer / Metal Interfaces***, **A.J. Makinen**, J.P. Long, N.J. Watkins, Z.H. Kafafi,* Naval Research Laboratory

The electronic structure of organic/metal interfaces was investigated using photoemission spectroscopy in combination with scanning probe microscopy. Organic films of copperphthalocyanine (CuPc) and @alpha@-sexithiophene (6T) were vacuum-deposited onto a single-crystal Au(111) substrate step-by-step, and ultraviolet and x-ray photoemission spectroscopies (UPS and XPS) were performed on the sample, together with scanning probe microscopy (SPM), at each step. By correlating different organic film structures revealed by SPM measurements with the corresponding electron energy spectra measured with UPS and XPS, we have been able to gain insights into how the frontier orbital character and position evolve with the organic film growth on the Au substrate. Since CuPc/Au and 6T/Au interfaces serve as model systems for similar structures responsible for charge injection and transport in many organic electronic devices, such as organic light-emitting diodes and photovoltaics, the results of this investigation will be useful for the characterization of such systems.

4:00pm **OM-MoA7 Electronic Structures of Al/Liq/Alq@sub 3@ Interfaces Studied by Photoemission Spectroscopy***, **Y. Park**,* Korea Research Institute of Standards and Science, Korea*; J. Lee,* Samsung Advanced Institute of Technology, Korea*; J.W. Choi,* KRISS, Korea*; M. Han,* University of Seoul, Korea

Lithium quinoate (Liq) has recently been attracting a good deal of attention for a cathode interlayer material in organic light-emitting devices (OLEDs)@footnote 1@ as it showed electron injection performance as good as most commonly used LiF. Using X-ray and UV photoemission spectroscopy (XPS & UPS) techniques, we studied the evolution of the electronic structures at Al/Liq/Alq@sub 3@ interface as it is formed in ultrahigh vacuum condition. The valence region spectra taken with UPS showed that the HOMO peaks move to higher binding energy (relative to Fremi level, E@sub F@) as Liq is deposited on Alq@sub 3@. This indicates that the deposition of Liq caused density of states inside the HOMO-LUMO gap although its intensity is too weak to be observed clearly with UPS. The total amount of the peak movement is ~ 1.8 eV comparable to the value for LiF (~1.9 eV). We believe this shift of Fermi level (relative to vacuum level) toward LUMO level is principal cause of the observed improvement in device performance. The evolution of XPS peaks during the interface formation is very similar to the case of LiF and there is no appreciable direct chemical reaction when Liq was initially deposited on Alq@sub 3@. We further discuss the possible origins of the observed HOMO peak movement.

4:20pm **OM-MoA8 Direct Observation of the Evolution of the Molecular Orbital Energy Levels of a Silole Derivative as a Function of Magnesium Deposition***, **N.J. Watkins**, A.J. Makinen,* Naval Research Laboratory*; Y. Gao,* University of Rochester*; M. Uchida,* Chisso Corporation, Japan*; Z.H. Kafafi,* Naval Research Laboratory

The electronic structure of the interface formed by Mg deposition onto 2,5-bis(6-(2,2-bipyridyl))-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPySPyPy) was investigated using ultraviolet photoemission, inverse photoemission, and X-ray photoemission spectroscopies. PyPySPyPy is of interest due to its high electron mobility. In addition, organic light-emitting diodes (OLEDs) using this silole derivative in the electron injection/transport layer exhibit very low operating voltages. Upon deposition of Mg onto PyPySPyPy a shift of the occupied molecular orbital energy level structure to higher binding energy, away from the Fermi level, was observed and accompanied by the appearance of two new levels within the energy gap of PyPySPyPy. These new levels have been assigned to a charge transfer complex between Mg and PyPySPyPy. At high Mg coverage, the shift in the lowest unoccupied molecular orbital can be correlated with the formation of "metallic-like" Mg clusters. The impact of these results on charge injection at the Mg metal contact in an OLED structure will be discussed.

4:40pm **OM-MoA9 Band Alignment on Patterned Surfaces***, **G. Koller**, F.P. Netzer, M.G. Ramsey,* Karl-Franzens University, Austria

An important parameter for the function of organic electronic devices is the barrier to charge injection which is controlled by the interface dipole. This is determined by the details of the interaction of the first layer of molecules with the contact material. In reality the interface is not perfectly homogeneous and thus local differences in band alignment are to be expected although not necessarily observable with standard area averaging techniques. In this contribution we explore the local variation in band alignment on a nanoscopically patterned substrate surface by investigating the growth of bithiophene films, from sub-monolayer to multilayer coverages, with angle resolved UV-photoemission and workfunction measurements. The substrate used was the oxygen reconstructed Cu(110) surface. This surface reconstructs to form a mesoscopically patterned surface consisting of alternating stripes of clean Cu(110) and passive Cu(110)-(2x1)O, with stripe widths in the range of several nanometers depending on oxygen exposure. The bonding interaction of the probe molecule bithiophene is very different on the two surfaces resulting in band alignment differences of 1 eV for films grown on these surfaces. On the Cu(111)-(2x1)O striped surface for coverages of bithiophene up to two monolayers, the photoemission spectra is a result of the superposition of spectra offset by this difference in band alignment clearly indicating local differences in the charge injection barrier. However, beyond two monolayers the valence band spectra clearly indicate a single emitting species whose energy position is determined by the average interface dipole. The results thus show that inhomogenities of the substrate surfaces will lead to local differences in the charge injection barrier which are invisible to area averaging techniques if the molecular film thickness are greater than the lateral dimensions of the inhomogenities. Acknowledgments: Supported by the Austrian Science Foundation SFB Electroactive Materials

5:00pm **OM-MoA10 A General Soft Contact Evaporation Method for Molecule-Based (Opto) Electronic Devices***, **H. Haick**, J. Ghabboun, D. Cahen,* Weizmann Institute of Science, Israel

Hybrid devices, in which molecular functionality is used to influence the characteristics of established electronic devices, but that do not require electronic charge transfer through the molecules, is an alternative approach to more established ones to molecule-based electronics. It is worth pursuing because of stability issues and the ability to use established technology as much as possible at this stage of molecule-based electronics. One such hybrid approach is based on controlling electronic properties of semiconductor devices by placing molecules, whose dipole can, synthetically, be changed systematically, at the device interface. Because mostly one can not insert molecules into a ready-made device interface, construct-ing such device structures requires device completion by making a sold electrical contact to a surface with the organic molecules on it. This is problematic because a process such as ther-mal evaporation or sputtering easily damages the molecules, especially molecules that have sensitive functional groups exposed. Earlier we overcame this by successful use of soft, al-ternative methods. Still, the clear technological advantages of vacuum evaporation led us to search for ways to adapt this method to meet the challenge. The result, which we will present here is Indirect, Collision-Induced, Cooled Evaporation (ICICE), with which we prepared, among others, GaAs/molecule/Au diodes. ICICE decreases drastically the temperature and, thus, the kinetic energy of the evaporated particles/atoms arriving at the surface and assures that irradiation emitted from the crucible does not reach the modified samples. Based on TOF SIMS, XPS, STM and (I-V) electrical measurements, we find that ICICE provides intimate contacts without damaging the (~ 1-3 nm wide monolayer of) organic ligands and their func-tional groups. This is best expressed by the clear molecular effect on the resulting Au/GaAs barrier heights; they vary with the functionalilty of the adsorbed molecules. To understand the limiting steps for contacting by means of metal evaporation, we com-pared results obtained in our experimental system with ICICE, and another popular one, known as Direct Evaporation Under Cryogenic Cooling (DEUCC). While, indeed use of the DEUCC mode leaves the organic ligands beneath the metal contacts, it does damage their functional groups. This finding, for which we will present an explanation, has very signifi-cant implications as it shows that while the often-used criterion of absence of shorts in metal/molecule/metal junctions is indeed a necessary condition for successful contacting molecules, it is not a sufficient one. We thank the Israel Ministry of Science (Eshkol fellowship to HH and tashtyoth project and the Israel Science Foundation (Jerusalem) for partial support.

Plasma Science and Technology
Room 315 - Session PS+MM-MoA

MEMS Etching

Moderator: F.G. Celii

2:00pm **PS+MM-MoA1 Understanding Deep Silicon Etching: Mechanisms for Formation and Removal of Sidewall Passivation*, M.L. Steen,*** IBM T.J. Watson Research Center*; T.J. Dalton,* IBM Semiconductor Research and Development Center*; C.K. Tsang, R.W. Nunes, J. Vichiconti, E.A. Sullivan, B.N. To, D. Barrett,* IBM T.J. Watson Research Center

One of the interesting aspects of deep silicon etching is the diversity of process requirements. In addition to high throughput, many applications have added demands on profile shape and surface morphology. Supporting such applications hinges on rational control of sidewall passivation. Two fluorine-based methods are used to achieve high silicon etch rates, each with its own variation of sidewall passivation. Most widely used is time-multiplexed deep etching (TMDE), wherein the etching and passivating cycles are performed sequentially. Sidewall passivation is accomplished via polymer deposition at room temperature. Alternately, a second method involves cryogenic cooling of the wafer to reduce lateral etching. However, problematic to both of these processes, the thickness of the sidewall-passivating layer is not uniform with etch depth. In cryogenic etching, the blocking layer is very thin, thereby making it difficult to maintain a consistent thickness over the entire etch depth. In TMDE, the thickness of the polymer covering decreases rapidly at greater depths and lateral etching increases there to form an undesirable bowed or barreled etch profile. This is particularly problematic for applications that have tight specifications for sidewall structure. Our goal is to understand the role the passivating layer plays in the formation of sidewall structure. Toward this goal, a number of process variables were explored using a commercial, inductively-coupled plasma etcher. We report a method that tailors the shape of the profile through better control of the formation and subsequent removal of the passivating layer. A significant increase in the silicon etching rate, minimization of mask undercut, and substantial reduction in bowing will be discussed. Overall, our method demonstrates enhanced process performance and flexibility to meet a broad range of needs in deep silicon etching.

2:20pm **PS+MM-MoA2 Improvement of Anisotropy and Aspect Ratio of a Pattern Etched in Bosch Process by using a Faraday Cage*, J.-H. Min,*** *G.-R. Lee, J.-K. Lee, S.H. Moon,* Seoul National University, Korea*; C.-K. Kim,* Ajou University, Korea

Bosch process, which consists of sequentially alternating etch and deposition steps using SF@sub 6@ and C@sub 4@F@sub 8@ plasmas, has been widely used for deep silicon etching in the fabrication of MEMS due to its advantages for obtaining patterns of high aspect ratio and anisotropy. Because the opening sizes of many MEMS structures are considerably large (about 1~100 µm), the electric field at the convex corner of a micro feature is locally distorted such that ions travel inside the etched pattern with a broad angular distribution. As a result, the flux of ions incident on the bottom surface is decreased with an increase in the etch depth, which eventually limits the maximum aspect ratio obtained in Bosch process. This limiting factor cannot be overcome by optimizing process variables. In this study, a Faraday cage, defined as a box made of conductor walls, was used to overcome this limitation. In the Faraday cage system, ions enter perpendicular to the sheath formed along the top grid plane of the cage and travel inside the cage maintaining the initial incident direction because electric potential in the cage is unaffected by outside voltages and therefore is the same throughout. Accordingly, the trajectory of ions, which has a narrow angular distribution determined by the grid pitch of and the sheath thickness on the top plane, is not changed at the convex corner of the micro feature or inside the pattern located in the cage. It was confirmed by an ion angular-energy distribution analyzer that the angular distribution of ions entering the pin hole of 10-µm-diameter, which is the same as the size of pattern opening, is narrower in the cage system than in the case of no cage. As a result, the aspect ratio and the anisotropy of the etched pattern were improved by using a Faraday cage in Bosch process.

2:40pm **PS+MM-MoA3 Exploring Microdischarges for Manufacturing and Sensing Applications*, Y. Gianchandani,*** University of Michigan **INVITED**

The increasing diversity of applications in microsystems for sensing and actuation motivates a significant amount of research in lithography-based fabrication techniques. The general goals for these processes include the facilitation of structural complexity and material diversity, amongst others. This talk will address how microplasmas (which are ignited between co-planar or stacked thin film metal electrodes patterned on a single wafer surface) can facilitate certain types of structural complexity by permitting materials such as Si to be etched in unique ways; and how micro-arcs (which are ignited between a micromachined electrode array and planar workpiece) can facilitate material diversity by permitting stainless steel and other metals to be micromachined for devices such as cardiac stents. Beyond manufacturing issues, the ability to predict and control microdischarges permits them to be exploited in transduction schemes. Spectroscopic sensing of chemicals in both gas and liquid phase is an obvious application. For example, microdischarges to liquid microchannels have been used to detect inorganic contaminants such as lead and chrome in water. However, the converse application, which is the use of liquids to serve as inexpensive but tunable sources for radiation wavelengths that are otherwise not easy to generate, may also offer value. These issues will be addressed as well.

3:20pm **PS+MM-MoA5 Feature Scale Model of Etching High Aspect Ratio Structures in Silicon using SF@sub 6@/O@sub 2@ Plasma*, J. Belen,*** *S. Gomez,* University of California, Santa Barbara*; M.W. Kiehlbauch, D.J. Cooperberg,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

The need to etch high aspect ratio features (depth-to-width) such as deep holes and trenches in Si arises in manufacturing of microelectromechanical systems and capacitors in memory devices. Anisotropic plasma etching of such features is achieved by taking advantage of energetic ion bombardment of the surface in the normal direction in conjunction with sidewall passivation with a film that is resistant to etching. Feature profile evolves as a result of various ion-assisted etching, passivation and deposition processes that occur on the feature surfaces. A fundamental and quantitative understanding of the balance between these processes is necessary for achieving control over the feature profile shape. We have developed a semi-empirical feature scale model of Si etching in an SF@sub 6@/O@sub 2@ plasma. This model is used to quantify etching kinetics and to identify the important parameters that affect profile evolution. Information from plasma diagnostics and previously published data are used to estimate F, O, and ion fluxes as well as ion energy and angular distributions. These estimates are used as input to the profile simulations in order to reduce the degrees of freedom in the model. Experimentally inaccessible parameters such as the spontaneous chemical etch rate constant, F and O sticking coefficients, ion-enhanced etch yield and ion scattering parameters are determined by matching the experimentally observed and simulated feature profiles under different plasma etching conditions. The mask undercut and the slope of the feature sidewalls are controlled by the F-to-O flux ratio. Two distinct mechanisms for sidewall passivation are identified: (a) surface oxidation, which is thought to be prevalent at high and intermediate F-to-O ratios where the sidewalls are either negatively tapered (bowed out) or vertical, and (b) redeposition of reaction products, which results in positively tapered sidewalls at low F-to-O ratios.

3:40pm **PS+MM-MoA6 Etching of High Aspect Ratio Structures in Si using SF@sub 6@/O@sub 2@ Plasmas***, **S. Gomez**, J. Belen,* University of California, Santa Barbara*; M.W. Kiehlbauch,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Plasma etching of high aspect ratio (depth-to-width) structures in Si is a crucial step in manufacturing trench capacitors for memory devices, and integrated components for microelectromechanical systems (MEMS). We have investigated etching of deep features (~10 µm) with high aspect ratios (~50) using plasmas maintained in mixtures of SF@sub 6@ and O@sub 2@ gases. The etching experiments were conducted in a low pressure (5-80 mTorr), high density, inductively coupled plasma etching reactor with a planar coil to maintain the discharge and with radio frequency (rf) biasing of the substrate electrode to achieve independent control of the ion flux and ion energies. Specifically, we have studied the effects of pressure, rf-bias voltage and SF@sub 6@-to-O@sub 2@ gas ratio on the etch rate, feature profile and selectivity using Si wafers patterned with 0.5-0.35 µm diameter holes in a SiO@sub 2@ mask. Visualization of the profiles using SEM is complimented by plasma diagnostics such as optical emission spectroscopy in conjunction with actinometry and mass spectrometry to understand the key factors that control the anisotropy, selectivity and etch rate. Oxygen ionization and dissociation products (O and O@super +@) oxidize the feature sidewalls and help achieve anisotropic etching through the sidewall passivation mechanism. F-to-ion flux ratio and F-to-O flux ratio are found to be the important internal plasma parameters that determine the etch rate and anisotropy. The mask undercut and the slope of the sidewalls is determined by the F-to-O ratio in the plasma. Increasing the SF@sub 6@-to-O@sub 2@ ratio in the feed gas increases F-to-O ratio and makes mask undercutting worse because passivation by O atoms cannot keep up with chemical etching by F atoms. As F-to-O ratio is decreased, effective sidewall passivation by O atoms results in nearly vertical sidewalls. Further reduction in F-to-O ratio results in sidewalls that slope inwards towards the bottom of the feature.

4:00pm **PS+MM-MoA7 Via Drilling on Silicon Wafers using the Cryogenic Process***, **T. Tillocher**, A. Basillais, X. Mellhaoui, P. Lefaucheux,* GREMI, France*; M. Boufnichel,* ST Microelectronics*; R. Dussart, P. Ranson,* GREMI, France

Plasma etching has an important place in microelectronics and microsystems industries. Some techniques, especially Bosch and cryogenic processes, enable the realization of high aspect ratio structures. The Bosch process is widely used in spite of scalloped profiles whereas the cryogenic process is quicker and presents smooth etched surfaces. Via (12 µm in diameter) drilling on silicon wafers is achieved by cryogenic etching in an industrial ICP reactor (Alcatel 601E). A SF6/O2 plasma is created and expands toward a polarized and cooled silicon wafer. Plasma parameters are optimised so as to obtain vias with an anisotropic profile with a high etch rate. End to end vias were performed with an average etch rate about 7µm/min by etching separately the two sides of the wafer. Yet, all of them did not meet right in the middle of the plate as it should be and their shape is not reproducible in the whole wafer. This seems to be due to a non enough homogeneous cooling system. Moreover, some defects, such as bowing and undercut lead to an increase of the final diameter of the via and hence must be limited. A process including a soft etching step, an over-passivating step, and a standard etching step leads to a significant reduction of these defects. O2/SF6 ratio is adjusted in the two first steps. Additionally, it was shown that bias voltage has a strong influence on the profiles : its increase is not synonym of a deeper etching but a slightly greater volume etched. Crystal orientation dependent etching also appeared at lower temperatures and particularly in the direction what can explain negative slopes in this cases.

4:20pm **PS+MM-MoA8 Si, SiO@sub 2@ Feature Etching for MEMS Fabrication: A Combined Simulator Coupling Local Transport, Surface Etch, and Profile Evolution Models***, **G. Kokkoris,** C. Boukouras, A. Tserepi,* National Center for Scientific Research (NCSR) "Demokritos", Greece*; A.G. Boudouvis,* National Technical University of Athens (NTUA), Greece*; E. Gogolides,* National Center for Scientific Research (NCSR) "Demokritos", Greece

Profile control during feature etching is a central requirement in the manufacturing processes of microelectromechanical systems (MEMS) or microelectronics devices. Simulation of the feature profile evolution can contribute to this challenge. The purpose of this work is a complete simulator for feature etching. The goal is to predict the effect of the bulk plasma phase to the feature profile, and is accomplished through the coupling of the following component modules: 1) a local transport model: local fluxes of neutrals and ions inside features are calculated taking into account shadowing and re-emission phenomena.@footnote 1@ 2) a surface etch model: local etch rates at each elementary surface of the structure are calculated through site balances. Si, SiO@sub 2@ substrate etching models under fluorine or fluorocarbon plasmas have already been developed.@footnote 2@ 3) a profile evolution algorithm: the level set method@footnote 3@ is fed with the local etch rates and moves the feature profile. The complete simulator can be used to a) validate suggested surface models through comparison with experimental data, b) investigate and explain the influence of feature size and surface morphology on etch rates (e.g. reactive ion etching lag phenomenon@footnote 4@, effect of roughness on etch rates) and c) simulate and optimize processes such as the BOSCH process@footnote 5@ for the etching of high aspect ratio Si structures, where pulsed alternating flows of SF@sub 6@ and C@sub 4@F@sub 8@ gases are used. @FootnoteText@ @footnote 1@V. K. Singh, E. S. G. Shaqfeh, and J. P. McVittie, J. Vac. Sci. Technol. B 10, 1091 (1992).@footnote 2@E. Gogolides, P. Vauvert, G. Kokkoris, G. Turban, A. G. Boudouvis, J. Appl. Phys. 88, 5570 (2000).@footnote 3@J. A. Sethian, J. Comp. Phys. 169, 503 (2001).@footnote 4@G. Kokkoris, E. Gogolides, A. G. Boudouvis, J. Appl. Phys. 91, 2697 (2002).@footnote 5@F. Larmer, A. Schilp, German Patent DE 4241045.

4:40pm **PS+MM-MoA9 In-Situ On-wafer Monitoring for Charge Build-up Voltage during Plasma Process***, **T. Shimmura**, S. Soda, M. Koyanagi, K. Hane, S. Samukawa,* Tohoku University, Japan

High-aspect-ratio SiO@sub 2@ contact hole etching is one of the key processes in the fabrication of ULSI devices. However, charge accumulation in contact holes during etching is one of the main causes of serious problems, such as charge-build-up damage, etching-stop, and microloading effects. Therefore, it is very important for realization of the next generation semiconductor devices to understand the mechanism of such electric charge accumulation and to be in control of plasma processes. As a result of our previous research, it was clear that deposited fluorocarbon film in contact holes shows high electric conductivity by ion irradiation.@footnote 1@ This paper reports on in-situ on-wafer monitoring for the build up charging potential during plasma processes. We were developed the device used for measuring charging potential. This device consists of Poly-Si(300 nm)/SiO2(1.7 µmm)/Poly-Si(300 nm) stacked layer structure. The contact hole of 300 nm diameter is formed to top Poly-Si layer and SiO@sub 2@ layer, and the numbers of holes were 6,400,000. The potential of top and bottom Poly-Si electrode were measured during plasma exposure with/without deposited fluorocarbon film. The potential difference between top and bottom Poly-Si electrode without the deposited fluorocarbon film is about 70 volts. On the other hand, in the case that the deposited fluorocarbon film exists on sidewall, the potential difference between top and bottom electrode was hardly observed. This result shows that the sidewall deposited fluorocarbon film has high electric conductivity and mitigates the electric charge accumulation at the contact hole bottom during SiO@sub 2@ etching processes. @FootnoteText@ @footnote 1@ T. Shimmura, S. Soda, S. Samukawa, M. Koyanagi and K. Hane, J. Vac. Sci. Technol. B, 20 2346 (2002).

5:00pm **PS+MM-MoA10 Plasma Etching of Chromium as a Hard Mask for a Complex Metal Stack Etch***, **D. Cruz**,* UCLA/Sandia National Laboratories*; M.G. Blain,* Sandia National Laboratories*; J.P. Chang,* University of California, Los Angeles

We have investigated the etching of chromium in an inductively coupled plasma (ICP) reactor and its etching selectivity to Al and SiO@sub 2@. Chromium is being utilized as a hard mask in etching a three-layer aluminum/silicon dioxide metal stack to form a self-aligned structure of 4µm in depth. The stack comprises the basis for a micro-cylindrical ion trap mass analyzer. The chromium etching chemistry was chlorine based, with the addition of He, Ar, and O@sub 2@. The Cr samples, approximately 2500 Å thick, were e-beam evaporated on two and three layers of Al/SiO@sub 2@ stacks. Chemical vapor deposited silicon dioxide was used as a hard mask to pattern Cr into 2-micron sized features. The selectivity of chromium to silicon dioxide during the He/Cl@sub 2@/Ar/O@sub 2@ chromium etch was 15:1. During the main chromium etch, the etch rate was determined to be approximately 1500 Å/min, at a pressure of 10 mTorr and 250 V DC bias. The He/Cl@sub 2@/Ar/O@sub 2@ discharge provided a fast etch rate with no plasma induced damage. Once the chromium was patterned, the Al/SiO@sub 2@ stack was exposed to an ICP Al etch, utilizing a Cl@sub 2@/BCl@sub 3@ based plasma chemistry, followed by an ICP SiO@sub 2@ etch, utilizing SF@sub 6@/Ar/N@sub 2@/O@sub 2@. These two chemistries were used alternatively until all layers of the stack were etched through in a self-aligned fashion. The etch rate ratios of Al and SiO@sub 2@ to chromium were 70:1 and 25:1, respectively. The overall final stack etch totaled about 22 minutes. No grassing or sputtering was noted on the sample, however profile control of the Al layer is an issue due to the lack of a sidewall forming polymer source. Chromium seems to be a promising hard mask, having high selectivity to the ICP Al etch and ICP SiO@sub 2@ etch. @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.

Plasma Science and Technology
Room 314 - Session PS-MoA

Plasma Sources

Moderator: E.V. Barnat, Sandia National Laboratories

2:00pm **PS-MoA1 Ion-Acoustic Solitons in a High Power Pulsed Magnetron Sputtering Discharge**, *K.B. Gylfason,* University of Iceland, Iceland*; **J. Alami**, U. Helmersson,* Linkoping University, Sweden*; J.T. Gudmundsson,* University of Iceland, Iceland

We report on the formation of ion acoustic solitons in an unipolar pulsed magnetron plasma. A high density plasma > 10@super 18@ cm@super -3@ is created by applying a high power pulse (6-17 J) with pulse length 100 µms and repetition frequency 50 Hz to a planar magnetron discharge. The temporal behaviour of the electron density measured by a Langmuir probe shows oscillations as the plasma density decays. We relate these oscillations to solitons traveling away from the target followed by stationary oscillations. The velocity, width, and amplitude characteristics of the soliton are discussed and compared to the properties of the soliton solutions of the Korteweg-de Vries equation. The speed of the soliton along the axis of the discharge decreases with increased gas pressure. We relate this decrease in travelling speed to the decrease in the fractional density modulation dn/n@sub 0@.

2:20pm **PS-MoA2 Next Generation RF Ion Beam Source for Three-Dimensional and other Critical Etching Applications**, ***A.V. Hayes**, V. Kanarov, R. Yevtukhov, C. Borges, K. Williams, M. Campo, B. Druz,* Veeco Instruments, Inc.

Rf plasma broad ion beam etch technology is used in manufacturing of magnetic, optical, and other types of thin film devices due to its unique capabilities to etch difficult materials and control ion energy and incidence angles. Requirements for increased critical dimension (CD) control and directional "static etch" processes have started to exceed the ion current density and directionality uniformity capabilities of conventional ion sources. "Static etch" processes in which the substrate is tilted at ion incidence angles of up to 70°-80° with no or only partial substrate rotation, are particularly challenging, requiring the ion beam to be very uniform and collimated across a three dimensional space within the beam occupied by the wafer. Development of a novel rf ICP broad ion beam source with dynamic plasma magnetic field configuration designed to achieve these requirements will be described. In addition, the role of the beam divergence angle and other beam dispersion parameters on the CD and static etch uniformity will be discussed. Results will be measured in terms of etch uniformity on silicon oxide coated wafers and etch divergence using a shadow mask type measurement fixture. In an optimum configuration the source is capable of achieving a uniformity of less than 1% sigma/mean on a static wafer (about a 4-5X improvement compared with current technology sources) and less than 0.5% on a rotated wafer (a 2-3X improvement) with excellent repeatability. The full etch divergence angle is less than 3°, and uniform across the substrate within 0.5°. Other applications of this source could include uniform etching of features mounted on 3-dimensional substrates.

2:40pm **PS-MoA3 The Use of Reactive Gases with Broad-beam RF Ion Sources for Industrial Applications**, ***St. Schneider**,* Forschungszentrum Juelich, Germany*; T.W. Jolly,* Oxford Instruments Plasma Technology Ltd.*; H. Kohlstedt, R. Waser,* Forschungszentrum Juelich, Germany

Broad-beam ion sources are used for a number of important industrial etching and deposition applications, and the use of inductively-coupled plasmas has greatly increased the feasibility of using beams of reactive gases, especially of chlorine and oxygen, but also of CO, CO@sub 2@, CF@sub 4@, CHF@sub 3@, SF@sub 6@ etc. In order to gain more understanding of the factors that affect the composition of beams of these gases, we have used a Hiden energy-dispersive quadrupole mass spectrometer to analyze the flux of ions and energetic particles produced by an Oxford Instruments 15cm RF ion source. For all of the above gases, we have analyzed the effects of changing the operating conditions on the composition of the ion beam, and the fractional production of multiply-charged ions; on the plasma potential (and the consequential divergence of the ion beam) and on the spread in energy of the ion beam. We discuss how these factors influence the correct use of the ion source in etching applications with these gases. It is important that the design of the ion source should be optimized for the process gases that are used. The source was originally optimized for use on argon. We discuss the effect of the design on the source's performance with the different gases, and we consider whether design changes could be appropriate for optimum performance on different gases.

3:00pm **PS-MoA4 Reactive Sputter Deposition of Nanocrystalline Compound Thin Films with a Hollow Cathode Source Operated in a Static Mode**, ***A. Pradhan**[1], S.I. Shah,* University of Delaware

Hollow Cathode Sources (HCS) are unique sputtering sources that sputter material from the inner surface of a cylindrical tube. Due to their geometry, HCS offer several advantages such as lack of hysteresis, low consumption of the reactive species, high plasma density and high deposition rates. We have characterized a titanium HCS for reactive deposition of titania films in static mode. In this mode the sputtering is carried out in a static gas volume. Stoichiometric films growth could be sustained even after 3 hours of continuous sputtering. This new method of reactive sputtering offers several advantages over conventional techniques such as ease of operation, lower equipment cost, lower environmental load, etc. Langmuir probe measurements were used to determine the plasma parameters in a static HCS. The plasma density was 2-3 orders of magnitude greater than that obtained in planar sputtering. The high-density plasma can be used to deposit stoichiometric nanocrystalline oxide films by negatively biasing the substrate and allowing the ion bombardment to provide the energy required for crystallization of the growing film. X Ray Diffraction (XRD) of the films grown with a substrate bias of -80V shows the presence of the rutile phase. The particle size was estimated from the XRD peak broadening to be around 20nm. The films were also characterized by X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Films were found to be nanocrystalline only when the sputtering gas was rich in oxygen. Monte Carlo simulations were carried out using SRIM program to determine the energy transferred by the ions to the growing surface. It was found that backscattered ion count was much higher in the case of O2 when compared to Ar, which could be responsible for the formation of nanocrystalline films.

3:20pm **PS-MoA5 Evolution of Radiofrequency Plasma Sources**, ***F.F. Chen**[2],* University of California, Los Angeles **INVITED**

Though this is the 50th AVS Symposium, RF plasma sources have a shorter history. Their development, driven by the explosive growth of the computer industry, did not really start until the 1970s. There are three main types: capacitive discharges called Reactive Ion Etchers (RIEs), Inductively Coupled Plasmas (ICPs), and the newcomer on the block, Helicon Wave Sources (HWS). Development of RIEs and ICPs has progressed mainly by trial and error, but in the last ten years their evolution has been aided by computer modeling, a result of the fast chips that these sources themselves make possible. From a plasma physics standpoint, each of these sources poses interesting problems. RF energy penetrates into ICPs much farther than skin depth theory would predict. Helicon sources produce much higher densities than ICPs at the same

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

[2] **AVS 50th Anniversary Invited Speaker**

power. RIEs, with all their deficiencies, still perform better in many applications. Are we simply lucky, or are there physical reasons for this?

4:00pm **PS-MoA7 Physics of High-pressure Helium and Argon Plasmas*, M. Moravej*,** *S.E. Babayan, X. Yang, G.R. Nowling, R.F. Hicks,* University of California, Los Angeles

The physics of helium and argon plasmas was investigated in the pressure range of 10 to 1000 Torr. The current and voltage waveforms and the current-voltage plots were obtained at varying pressures for both gases. The waveforms indicated that before the plasma was struck the load was purely capacitive for both gases, however, after the discharge was ignited, the argon plasma exhibited a greater resistive nature than the helium. The IV curves at 760 Torr indicate that the breakdown voltage for argon was approximately 500 V higher than that of helium. From these IV measurements, the helium and argon plasma densities were calculated to be 3.48*10@super 11@ and 3.15*10@super 11@ cm@super -3@, respectively and the electron temperatures were determined to be 1.3 and 0.3 eV, respectively. The effect of pressure and of impurities, O@sub 2@ and CF@sub 4@, on the physics of the plasma was investigated by these measurements and will be presented at the meeting.

4:20pm **PS-MoA8 Two-dimensional Self-consistent Modeling of Wave Propagation and Plasma Dynamics in a Helicon Source*, D. Bose*,** Eloret Corp.*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center

Helicon plasma sources are of interest in a variety of applications such as space plasma propulsion, fusion experiments, materials processing reactors, etc. The interest in these devices stems from their ability to generate high density plasmas by efficiently absorbing the applied radio frequency power. In this paper we will present results form a two-dimensional helicon plasma model that enforces self-consistency between wave propagation and plasma dynamics. Plasma fluid equations relevant for plasma generation, heating, and transport with externally applied dc magnetic field are solved self-consistently with Maxwell's equations for rf electric field, Ohm's law for rf plasma current, and space charge waves. The absorption and propagation of Trivelpiece-Gould waves generated due to a finite electron mass are implicitly included. This wave is highly dissipative and is the chief mode of energy transfer to the plasma. A parametric study will be performed to isolate the factors that affect bulk versus peripheral power absorption, downstream plasma density and uniformity. The effect of altering the dc magnetic field on plasma and wave characteristics will be presented. Our current results show that the applied magnetic field profile can be adjusted to move the peak plasma density from the near antenna source region to the process chamber. Comparisons with the available experimental data on plasma density and uniformity will also be presented.

4:40pm **PS-MoA9 Large Area Electron-Beam Generated Plasma Processing System@footnote 1@*, D. Leonhardt*,** *C. Muratore, S.G. Walton,* Naval Research Laboratory*; D.D. Blackwell,* SFA Inc.*; R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

NRL has developed a 'Large Area Plasma Processing System' (LAPPS) using an electron beam (e-beam) to initiate the gas ionization process with the goal being the increased control over the flux of reactive species to the surface and the ability to modify surfaces over large areas. Our system demonstrates that the e-beam ionization process is largely independent of gas composition and capable of producing low temperature plasma electrons in high densities over large areas (square meters). The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2 keV, < 1 mA/cm@super 2@ electrons injected into a neutral gas background (oxygen, nitrogen, sulfur hexafluoride, argon). Typical operating pressures range from 20-200 mtorr with beam-collimating magnetic fields (100-200 Gauss) for plasma localization. This presentation will focus on (1) the production of a large area (> 0.5 m@super 2@) system and (2) applications of these plasma sources for surface modification. Construction, scaling and uniformity at the substrate in the large plasma source will be discussed, including the processing stage configurations and layout. General characteristics of these plasmas will be discussed and illustrated through time-resolved in situ plasma diagnostics (Langmuir probes, microwave transmission and mass spectrometry). @FootnoteText@@footnote 1@ Work supported by the Office of Naval Research@footnote 2@ Muratore, C., NRL/ASEE Postdoctoral Research Associate.

5:00pm **PS-MoA10 Post-etch Wafer Cleaning by a New Dry-cleaning Technique using Both Gas Flow and Plasma*, Y. Momonoi*,** *K. Yokogawa, M. Izawa,* Hitachi Ltd., Japan

Because wafer cleaning ultimately affects yield and reliability, it is one of the crucial issues in fabricating semiconductor devices. Regarding devices, scaling-down and adoption of new materials impose an imminent demand for new developments in particle cleaning. Dry-cleaning techniques have been proposed recently as other approaches for particle removal. Their removal efficiency, however, is less than that of wet cleaning, because it is difficult to balance chemical cleaning and physical cleaning. In light of the above circumstances, the authors have developed a new concept of dry particle cleaning, named dry scrubber.@footnote2@ The dry scrubber utilizes both the mechanical effects of gas flow and the chemical effects of a down-flow plasma. Regarding the gas flow, narrowing the flow space along the wafer increases the viscous friction, which causes particles to remove from the wafer surface, and they are transported away. Regarding the plasma, a gas mixture of CF@sub 4@ and O@sub 2@ is induced in it, which weakens the adhesion force of particles chemically. The basic cleaning capabilities of the dry scrubber were evaluated by using it to remove Al@sub 2@O@sub 3@ particles on 8-inch p-type bare silicon wafers. The evaluation showed that the plasma enhanced the particle removal of the gas flow; namely, the combination of a down-flow plasma and a fast gas flow removed particles at an efficiency of 98% in 60 sec. It was also found that the dry scrubber produces an etching depth for poly-silicon of 0.17 nm. The cleaning capabilities of the sample with etched contact-hole patterns were also evaluated. This sample had residues of photo-resist on its surface and particles in the holes. These results confirm that the new cleaning technique can effectively removes the residues and the particles from a patterned surface. @FootnoteText@@footnote 1@Dr. K. Mosig et al., IITC2001@footnote 2@Y. Momonoi, K. Yokogawa, M. Izawa, Proc. Inter. Sym. Dry Process, (2002), p.113.

QSA-10 Topical Conference
Room 320 - Session QS-MoA

Thin-Film Metrology

Moderator: F.A. Stevie, North Carolina State University

2:00pm **QS-MoA1 Metrology Needs for Ultrathin Films in the Wafer Processing Industry. What is Needed? What is Available?*, C.R. Brundle*,** C.R. Brundle and Associates*; C.A. Evans,* Evans FWA **INVITED**

Single layer films of less than 1nm (eg Si/O/N) or stacks of less than 4nm (eg TaN/Cu) are already in production or under development. The ITRS required metrology for these, however, has been lagging because this presents major instrumentation challenges. Thickness SPC specs across wafers and from wafer to wafer are typically 3% RSD, or better, which implies a measurement precision (at 1 sigma) of at least 1%, ie 0.01nm for a 1nm film. Elemental composition precision may need to be similarly tight (eg for N concentration in a 1nm Si/O/N film). More esoteric parameters, such as depth distribution (elemental or even chemical), interface mixing, roughness, or reaction, or surface contamination, may also have to be under SPC, but even if they do not, these variables must not compromise the metrology used. Finally there may be requirement to make such measurements on restricted areas on production wafers. In this paper we review the capabilities of some of the analytical technologies beginning to find their way into the industry to deal with these issues. They include such methods as VUV spectroscopic ellipsometry, XRR/XRF and XRR/ellipsometry combinations, acoustic sonar methods, non-contact electrical methods, Low Energy X-Ray Emission Spectroscopy (LEXES), and XPS and ARXPS. Examples of their use are presented. It is natural that new measurement instrumentation should penetrate the the "lab" first, where the requirement for throughput and non-expert, recipe driven, automation of both data collection and processing are far less demanding than in "the fab", but even in the lab the instrumentation must must handle full 300mm wafers in a manner where the "time to answer" is acceptable. We discuss what attributes are likely to lead to a transition to fab use.

3:00pm **QS-MoA4 Intercomparison of Silicon Dioxide Thickness Measurements Made by Multiple Techniques - The Route to Accuracy*, M.P. Seah*,** National Physical Laboratory, UK **INVITED**

A pilot project has been launched under the auspices of the Consultative Committee for Amount of Substance (CCQM) to evaluate the measurement issues for the amount of SiO@sub 2@ on (100) and (111) Si in the thickness range 1.5 nm to 8 nm. Wafers and methodologies have been carefully prepared to achieve the best results possible. 44 sets of measurements have been made in different laboratories using 9 different methods (MEIS, NRA, RBS, SIMS, XPS, ellipsometry, GIXRR, NR and TEM). The results have been assessed, against NPL XPS data, using d(respondee) = m d(NPL) + c. All show excellent linearity, except 3 sets with methods more suited to composition depth profiles. The main sets correlate with the NPL data with average rms scatters of 0.15 nm with half being better than 0.1 nm. Each set allows the relative scaling constant, m, and the zero thickness offset, c to be determined. Each method has 0 < c < 1 nm and it is these offsets, measured here for the first time, that have caused many problems in the past. Each technique has a different accuracy for m and consistent results have been achieved. XPS has poor accuracy for m but a high precision and, critically, has zero offset if used correctly. Achieving a consistent scaling constant and zero offset for XPS requires reference conditions and is not trivial. Analysts using these conditions generated dramatically improved data. A combination of XPS and another method allows an accurate determination of the XPS scaling constant. XPS then has a high accuracy, traceable via the other method. Several methods have small offsets which, if they can be controlled, will enable these methods also to show high accuracy.

4:00pm **QS-MoA7 Comparative Thickness Measurements of SiO@sub2@/Si Films for Thicknesses less than 10 nm***, **T. Jach**, J.A. Dura, N.V. Nguyen, J. Swider,* National Institute of Standards and Technology*; G. Cappello,* Institute Curie, France*; C. Richter,* National Institute of Standards and Technology

The metrology of gate dielectric thicknesses using different methods for layers below 10 nm is still subject to uncertainties. We report on a comparative measurement of SiO@sub2@/Si dielectric film thickness (t<10 nm) using grazing incidence x-ray photoelectron spectroscopy, neutron reflectometry, and spectroscopic ellipsometry. Samples with nominal thicknesses of 3 nm - 7 nm were characterized by XPS with grazing incidence x-rays at 1.8 keV, with cold neutron reflectometry (@lambda@=0.475 nm), and with spectroscopic ellipsometry over 1.5 eV<E<6.0 eV. The results show good agreement between the ellipsometry and the grazing incidence XPS, with slightly lower values for the neutron reflectometry. The role of sample preparation and the assumptions regarding surface contamination are discussed.

4:20pm **QS-MoA8 The Thickness and Composition of Ultra-thin SiO@sub 2@ Layers on Si***, **C. Van der Marel**, M.A. Verheijen, Y. Tamminga,* Philips Electronics, The Netherlands*; R.H.W. Pijnenburg,* Technical University Eindhoven, The Netherlands*; N. Tombros,* State University of Groningen, The Netherlands*; F. Cubaynes,* Philips Research, IMEC, Belgium

Ultra-thin SiO2-layers are of importance for the semiconductor industry. One of the techniques that can be used to determine the chemical composition and thickness of this type of layers is XPS (X-ray Photoelectron Spectroscopy). As shown by Seah and Spencer,@footnote 1@ it is not trivial to characterize this type of layers in a reliable way. We carried out a series of systematic investigations on layers of SiO2 on Si (in the range from 0.3 to 3 nm). The samples were analyzed by means of TEM, RBS and XPS. The XPS-results were analyzed using the standard Cumpson formula (equation 2 in@footnote 1@), by means of Quases-Tougaard and using an overlayer-substrate model. We also examined the influence of various experimental parameters upon the results (e.g. irradiation time in RBS, objectivity of layer thickness determination in TEM, measuring time and pass energy in XPS). It was found that the ratio O:Si of the layers always corresponds to that of pure SiO2. Yet, for thickness below 2 nm, small but significant deviations were found between RBS and XPS on the one hand and TEM-results on the other hand. The results suggest that the density of SiO2-layers with a thickness below 2 nm is less than the density of bulk SiO2. @FootnoteText@@footnote 1@ M.P. Seah and S.J. Spencer, Surface and Interface Analysis 33 (2002) 640.

4:40pm **QS-MoA9 Characterization and Metrology for High k Materials using Parallel Angular Resolved XPS (PARXPS)***, **G. Conti**, C.C. Wang, Y. Uritsky,* Applied Materials, Inc.*; C.R. Brundle,* C.R. Brundle and Associates

Owing to the excellent matching of the probing depth of XPS to the current ultrathin film thickness range in use in the wafer processing industry (0.5 to 4 nm), this technique is coming to the forefront for providing composition and chemistry information, both in the film and at the surfaces and interfaces. Ideally one would like a technique where a protocol for measuring thickness, composition, and a chemical concentration depth profile can be measured non-destructively. XPS can do this by exploiting PAR-XPS to obtain a depth profile, as opposed to the traditional sputter profile approach, which is both destructive and often introduces artifacts. In PAR-XPS there is no need to rotate the wafer to get series of angular resolved spectra, since it is collected simultaneously over a wide angular range and binned into user defined smaller angular ranges. We present examples of thickness, N dose, and N depth profile characterization for Si/O/N gate oxide (1nm to 3nm range), and for HfO2 films on SiO2 on Si (3nm to 4nm total range) using the VG Theta Probe 300. For the Si/O/N films we show that high precision (better than 1% RSD) is obtainable for thickness and apparent N dose using an integrated angle (22 to 63 degrees) measurement. To turn the apparent N dose into a true dose requires information on the N depth profile, which is obtained from the angle resolved measurements, using the Maximum Entropy modeling approach. For the HfO2/SiO2/Si films the PAR-XPS shows that the films are intermixed for the particular processing conditions discussed here. Our conclusions on the use of PAR-XPS are that the method can meet the needs for precise film thickness measurements, and depth resolved chemistry, provided the film thickness to be analyzed is less than about 4nm. Beyond that, traditional spattering becomes necessary, since PAR-XPS contains too small a component of information from such depths.

5:00pm **QS-MoA10 Multivariate Statistical Analysis of Spatially Compressed Time-of-Flight Secondary Ion Mass Spectrometry Images@footnote 1@***, **J.A. Ohlhausen**, M.R. Keenan, P.G. Kotula, D.E. Peebles,* Sandia National Laboratories

Owing to the parallel nature of Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), complex and very large datasets can easily be acquired. An example of such a large dataset is a spectral image where a complete spectrum is collected for each pixel. Ideally, the complete spectral image would be used to provide a comprehensive materials characterization. This is difficult to accomplish with traditional techniques. Previously, we have demonstrated the application of multivariate spectrum imaging techniques to TOF-SIMS. This technique, called Automated eXpert Spectral Image (and series) Analysis -- AXSIA, is based on the separation of a complex and very large spectral image dataset into physically realizable and intuitive chemical components, including both spectra and concentrations. The full analysis is performed without outside estimates of spectral shapes, concentrations or the number of components present. In TOF-SIMS, we have shown that spectral series in the form of depth profiles (1D), images (2D), and imaged depth profiles (3D) can be analyzed using AXSIA. Since datasets can be large (5MB-1GB), data compression must be performed in order to process the data on laboratory computers. While providing signal-to-noise and memory storage improvements, data compression can hide or dilute important and small features. In this talk, I will present some statistical advantages of using multivariate techniques directly to spatially compressed data while maintaining full image resolution. In addition, I will explore the trade-offs between spatial and spectral compression and small feature recognition. @FootnoteText@ @footnote 1@This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Advanced Surface Engineering
Room 323 - Session SE-MoA

Hard Coatings: Preparation, Properties, Wear, and Nanotribology

Moderator: L. Hultman, Linkoping University, Sweden

2:00pm **SE-MoA1 High-resolution TEM Study the Microstructure of W-Si-C Films in the Vicinity of the Crystalline-Amorphous Transition***, **J.E. Krzanowski**, J. Wormwood,* University of New Hampshire

The addition of silicon to transition metal nitride and carbide thin films has generated considerable interest due to reports of greatly enhanced mechanical properties. It has been proposed that the effect of adding Si is to gradually reduce the crystallite size while introducing a thin amorphous interlayer between crystallites, ultimately resulting in an amorphous structure. In our work, we have examined a series of WC/SiC thin films over a composition range where the crystalline to amorphous transition occurs. By using high-resolution transmission electron microscopy, we have obtained a detailed picture of the mechanisms of this transformation in the W-Si-C system. These experiments have led to observations of novel microstructures not previously reported for Si-containing carbide/nitride thin films. A series of WC-SiC thin films has been deposited by RF magnetron co-sputtering, with compositions ranging from 15 to 38% SiC. X-ray diffraction analysis of these films confirmed the crystalline-to-amorphous transition in this compositional range. HRTEM observations revealed the following microstructural changes as the Si content increases: first, we observed fully crystalline nano-crystallites embedded in an amorphous matrix. Next, we observed the formation of larger (~50 nm) domains within which a novel droplet-like morphology of an amorphous phase is found. As Si is further increased, the droplets adopt a morphology where they appear to be strung together as the matrix phase becomes increasingly disordered. Finally, at yet higher Si contents, a spinodal-like two-phase structure is observed where one phase is amorphous and the second is best described as highly disordered. Despite the presence of these extensive microstructural changes, the hardness of the films within this compositional range was essentially constant.

2:20pm **SE-MoA2 Metrology of 1-10 nm Thick CNx Films: Thickness, Density and Surface Roughness Measurements***, D.J. Li,* Northwestern University,Tianjin Normal University*; Y. Chen, **Y.W. Chung**,* Northwestern University

Ultrathin nitrogenated carbon (CNx) films were synthesized using pulsed dc magnetron sputtering. The influence of substrate tilt angle and rotation speed on surface roughness was explored. Atomic force microscopy studies showed that the smoothest films were obtained at substrate tilt of 45ï‚° and rotation speed 20-25 rpm, corresponding to 2-3 rotations per deposited atomic layer. The root-mean-square surface roughness under these optimum conditions is ~0.3 nm when sampled over 20ï‚´20 ï�-m2 areas, increasing to ~0.4 nm when sampled over ~0.05ï‚´3 cm2 using x-ray reflectivity measurements. In addition, x-ray reflectivity measurements showed that the mass density of these CNx films is ~2.0 gm/cc, independent of film thickness from ~1 to 10 nm, consistent with ion beam analysis.

2:40pm **SE-MoA3 Reactive Magnetron Sputtering of Hard Si-C-N and Si-B-C-N Films and Their Properties***, **J. Vlcek**, J. Cizek, S. Potocky, M. Kormunda, J. Houska, P. Zeman, Z. Soukup,* University of West Bohemia, Czech Republic **INVITED**

Based on the results obtained for C-N films a systematic investigation of reactive magnetron sputtering of hard ternary Si-C-N and quaternary Si-B-C-N materials has been carried out. The Si-C-N and Si-B-C-N films were deposited on Si(100) substrates by dc magnetron co-sputtering of silicon and carbon (Si-C-N films) and silicon, boron and carbon (Si-B-C-N films) in nitrogen-argon gas mixtures using a composed C-Si and C-Si-B (at a fixed 20% boron fraction in the erosion track area) target, respectively, with variable Si/C area ratios. Elemental compositions of the films (determined by RBS and ERD), their bonding structure, and mechanical (hardness and friction coefficient) and optical (refractive index and extinction coefficient) properties were controlled by the Si fraction (5-80%) in the magnetron erosion track area, by the Ar concentration (0-75%) in the gas mixture, by the rf induced negative substrate bias voltage (from a floating potential to -500V) and by the substrate temperature (135-800°C). The total pressure and the discharge current on the magnetron target were held constant at 0.5Pa and 1A, respectively. The energy and flux of ions bombarding the target and the growing films were estimated on the basis of the discharge characteristics measured for both the dc magnetron discharge and the rf discharge dominating in a deposition zone. Mass spectroscopy was used to explain differences between sputtering of carbon, boron and silicon from the composed targets in nitrogen-argon discharges. The films, typically 1-2µm thick, were found to be amorphous with a very smooth surface (R@sub a@ less than 1nm) and good adhesion to substrates at a compressive stress less than 1.2GPa. They exhibited hardness up to 35GPa (Si-C-N films) and 50GPa (Si-B-C-N films), enhanced high-temperature oxidation resistance and very high optical transparency (at a high Si content), and promising tribological properties (at a high C content).

3:20pm **SE-MoA5 Using NMR to Probe the Bonding in Amorphous Carbon Nitride Thin Films***, W.J. Gammon,* College of William & Mary*; O. Kraft,* Inst. fur Materialforschung II, Germany*; G.L. Hoatson, A.C. Reilly, **B.C. Holloway**,* College of William & Mary

In this study the chemical bonding in hard and elastic amorphous carbon nitride (a-CNx) films is investigated with 15N, 13C, and 1H nuclear magnetic resonance (NMR) spectroscopy. Nanoindentation yields an elastic recovery of 80%, a hardness of 5 GPa, and an elastic modulus of 47 GPa. Our 13C NMR study demonstrates the lack of sp3 bonded carbon in this material. Furthermore, the 13C and 15N NMR data imply a film-bonding model that has an aromatic carbon structure with sp2 hybridized nitrogen incorporated in heterocyclic rings and in pentagons; a suggestion that is supported by our preliminary total energy calculations of graphite defect structures. Results from 15N and 13C cross polarization (CP) and 1H magic angle spinning (MAS) NMR experiments also suggest that the nitrogen bonding sites are susceptible to protonation. The most likely source of protons is from water absorbed during sample preparation for the NMR experiments. The sensitivity of the surface of a-CNx to water absorption may impact tribological applications for this material.

3:40pm **SE-MoA6 DLC and CNx Coatings Produced by Pulsed Laser and Filtered Vacuum Arc Techniques***, **A.A. Voevodin**, J.G. Jones, T.C. Back, J.S. Zabinski,* Air Force Research Laboratory*; V.E. Strelnitzki, I.I. Aksenov,* Kharkov Physical Technical Institute, Ukraine

Unhydrogenated amorphous diamond-like carbon (DLC) and fullerene-like carbon nitride (CNx, N/C ratio ~ 0.2) are rival surface protection coatings with exceptional mechanical and tribological properties. A comparative study was performed on their benefits for sliding wear protection. The coatings were grown in the same deposition system, using similar substrates, surface preparation procedures, functionally graded interlayers (Ti-TiC-C), and top layer thicknesses. They were produced using pulsed laser deposition (PLD) and filtered cathodic arc deposition (FAD). Samples of laser-DLC, laser-CNx, arc-DLC, and arc-CNx coatings were prepared. Comparisons of coating chemistry, structure, hardness, elastic modulus, internal stress, coefficient of friction (c.o.f.) against steel and SiC balls, wear rate, and wear mechanism in humid and dry environments were performed. PLD and FAD provided very similar coating chemistry, structure and properties. Independent of the growth technique, DLC coatings had hardnesses within 52-57 GPa and elastic moduli within 490-560 GPa. The CNx coatings offered a reasonably high hardness of 28-30 GPa, while their elastic modulus was as low as 160 GPa. There was a clear difference in tribological behavior of DLC and CNx, which depends on the environment humidity. In humid air, DLC coatings had a c.o.f. of 0.1, a very low wear rate, and formed a graphitic transfer film in friction contact. In the same tests, CNx coatings had a c.o.f. of 0.3-0.4, a higher than DLC wear rate, and did not form a transfer film. In this environment, wear tracks on CNx coatings were polished by abrasion wear. In dry nitrogen, DLC coatings had a c.o.f. of about 0.15 and a higher wear rate, while CNx coatings had a c.o.f. 0.03-0.04 and a lower wear rate with formation of a graphitic-like transfer film. The observed difference in mechanical response and tribological performance can be used to optimize selection between DLC and CNx, depending on application requirements.

4:00pm **SE-MoA7 Fabrication and Properties of Ultra-nano, Nano, and Polycrystalline Diamond Membranes and Sheets***, **D.K. Reinhard**,* Michigan State University and Fraunhofer Center for Coating and Laser Applications*; M. Becker,* Fraunhofer Center for Coating and Laser Applications*; R.A. Booth,* Michigan State University and Fraunhofer Center for Coating and Laser Applications*; T.P. Hoepfner,* Michigan State University*; T.A. Grotjohn, J. Asmussen,* Michigan State University and Fraunhofer Center for Coating and Laser Applications

Thin diamond membranes and free-standing sheets are of interest for a variety of potential applications. One such application is the motivation of this research, i.e. achieving diamond electron-stripping foils for use in heavy ion (1 - 11 MeV total energy) accelerators.@footnote 1@ The objective of this research is to produce large area free-standing foils/membranes of diamond. Stripping foils have areas of approximately 1 cm by 1 cm and thickness of approximately 1 µm. They must be positioned and mounted to a metal frame, supported on three sides. This paper describes the film nucleation, synthesis, and subsequent fabrication steps required to make large area free-standing diamond foils. Films are deposited on silicon wafers as ultra-nano (10 nm or less grain size), nanocrystalline (100 nm grain size), and as polycrystalline (micrometer grain size) diamond by varying gas composition, nucleation, power, substrate temperature, growth rate, and pressure. Large area foils are fabricated from each of these film types. Subsequently the diamond is separated from the substrate and mounted as a supported foil. Mechanical properties of the foils before and after mounting are described as a function of film morphology and thickness (0.5 µm to 5 µm). Examples of stripping foils and associated frames are presented. @FootnoteText@ @footnote 1@ C. J. Liaw, Y. Y. Lee, and J. Tuozzolo, "Lifetime of Carbon Stripping Foils for the Spallation Neutron Source, Proceedings of the 2001 Particle Accelerator Conference, Chicago, (2001), 1538.

4:20pm **SE-MoA8 Nanotribological Properties of Nanocomposite and Amorphous CrBN Thin Films***, **D.M. Mihut**, J. Turner, T.P. Butler,* University of Nebraska, Lincoln*; S.M. Aouadi,* Southern Illinois University*; S.L. Rohde,* University of Nebraska, Lincoln

Thin films with nanocomposite and/or amorphous CrBN structures can be successfully used for applications where high hardness, good wear resistance, low roughness and good corrosion resistance are required. CrBN films were deposited on to silicon substrates using reactive unbalanced magnetron sputtering. The deposition was monitored in-situ using spectroscopic ellipsometry. Films were characterized using X-Ray diffraction (XRD), atomic force microscopy (AFM), Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS). Nanotribological behavior of CrBN thin films with differing composition were studied using a Hysitron Triboscope in conjunction with an AFM. Microscratch measurements were carried out in both constant and ramped load modes, after which the wear tracks were imaged and measured using AFM. The failure modes were also investigated using scanning electron microscopy (SEM). The measured friction coefficient, residual wear depth, and percent elastic recovery were compared for CrBN films of differing deposition conditions to begin to develop an understanding of process-property relationships in these new materials.

Surface Science
Room 326 - Session SS1-MoA
Stimulated Processes at Surfaces

Moderator: J.A. Yarmoff, University of California, Riverside

2:00pm **SS1-MoA1 Growth of Ordered and Disordered Arrays of Silicon Pillars During Laser-Assisted Etching***, D. Mills,* ***K.W. Kolasinski,*** Queen Mary, University of London, UK

We report on the formation of conical silicon pillars on a Si(111) substrate by etching with a nanosecond pulsed excimer laser in the presence of SF@sub 6@, HCl or NF@sub 3@. The change in the silicon surface morphology was monitored as the number of shots from the XeCl (308 nm) excimer laser was varied from one to several hundred, for all experiments the energy density at the silicon surface was kept at about 1 J cm@super -2@. Significant changes in pillar morphology result from changing the process gas. This is a clear indication that gas-phase/plasma chemistry occurring in the laser ablation plume and plume/surface interactions are instrumental in the pillar formation mechanism. Initial surface morphology also affects pillar dimensions. Exposure of an unpolished surface results in much sharper pillars for a given number of laser shots than does exposure of the polished side. Modulation of the laser intensity profile by the effects of diffraction can be used to enhance the order of the pillars. For instance, the diffraction profile resulting from irradiation of a Gaussian shaped interface produces concentric rings of pillars. Large areas of pillars, on the order of 1 cm@super 2@, have been formed by rastering the beam across the Si sample under continual laser irradiation at 20-50 Hz. Progress has also been made with the production of ordered arrays of the pillars using near field diffraction effects from fine wires and grids. Further investigation will examine the effects of varying the pressure of the process gas, the partial pressure of process gas mixtures, pre-heating of the surface with an argon ion laser, the effects of pulse repetition rate and diffraction on the pillar height, width and packing densities.

2:20pm **SS1-MoA2 Defect-driven Photodesorption at UV and VUV Excimer Laser Wavelengths***,* ***L. Cramer,*** *S.C. Langford, J.T. Dickinson,* Washington State University

The optical properties of single crystal calcium fluoride make it useful lens material for the ultraviolet to vacuum-ultraviolet region, including possible use at 157 nm (7.8 eV) for high resolution microlithography. Of concern is possible degradation of these properties with prolonged exposure to laser light. Both surface and bulk modification of the material are of interest. Our interest is to obtain fundamental understanding of laser induced emissions (e.g., ions, electrons, and neutrals) from insulators with wide bandgaps (CaF2 has a band gap of ~11.2 eV) and radiation induced surface/bulk modifications We report and compare the measured rates of laser desorption from cleaved surfaces of CaF2 of the observable ionic and neutral species at three excimer laser wavelengths: 157, 193, and 248 nm with pulse lengths ~20-30 ns. Mass selected time-of-flight techniques allows both species and kinetic energies to be determined. At laser fluences well below threshold for plume formation, only positive ions are observed. Ca+ is seen at all of the wavelengths; CaF+ is seen only at 157 nm. The Ca+ intensity vs. fluence shows essentially no dependence on wavelength. Ion energies show slight wavelength dependencies but all emissions are consistent with a multiple-photon electrostatic repulsion model. Neutral emission is dominated by Ca0 and the neutral energy distributions correspond to thermal distributions at relatively high temperatures (> 2500 K). Finally, we report on the role of simultaneous keV electron irradiation co-focused on the laser spot. We observe substantial increases in the laser desorbed products which we contribute to the resulting halide vacancy formation (F-centers).

2:40pm **SS1-MoA3 Hot Electron Generation and Detection from Chemical Reactions on Metal Surfaces***,* ***E.W. McFarland,*** *B. Roldan Cuenya,* University of California, Santa Barbara **INVITED**

Chemical reactions at metal surfaces have associated charge and energy transfer processes that are both ubiquitous and incompletely understood. There is increasing theoretical evidence that the traditional adiabatic description of reaction kinetics is limited, and that many if not most reactions on metal surfaces involve nonadiabatic elementary steps. Non-adiabatic processes in highly exothermic reactions are well known; however, for low energy reactions, experimental observation of charge carriers generated by electronic excitations during the reaction is difficult. A Schottky junction device structure consisting of an ultra-thin metal film deposited on a semiconductor allows direct observation of electrons or holes generated during bond forming reactions at surfaces as a "chemicurrent" analogous to a diode photocurrent. Investigations of the chemical reaction induced electron current during adsorption of atomic and molecular species including, H, O, O2, N2O, NO2, C2H4 and other hydrocarbons on Ag, Au, and Pd surfaces have revealed complex chemically induced electronic phenomena. The adsorption energies span a large range and we find a general tendency of the chemicurrent to increase with increasing energy and a distinct current amplitude and transient behavior for each species and surface. Detailed interpretation of the electronic signature for each species requires understanding of both the electron/hole excitation spectrum as well as the diode electronic characteristics. These data suggest the direct transfer of reaction energy to electronic excitations is a common feature of a wide range of surface reactions and that the unique electronic signal from such reactions might be used for improving our understanding of surface reactions and in creating new devices and sensors directly coupling chemical processes with electronics.

3:20pm **SS1-MoA5 Factors Influencing Ion Yields and Angular Distributions in Electron Stimulated Desorption***, N.S. Faradzhev,* ***D.O. Kusmierek,*** *T.E. Madey,* Rutgers University

The focus of this work is on scattering processes affecting the survival probability and 'depth of origin' of low-energy ions (F@super+@, F@super-@) that pass through condensed ultrathin layers of polar molecules (H@sub2@O, NH@sub3@). The ions are generated by electron stimulated desorption (ESD) of SF@sub6@ adsorbed on Ru(0001) at 25K. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF@sub6@ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Several characteristic angular distributions of F@super+@ and F@super-@ (halo, hexagon) are observed as a function of temperature, coverage, and electron irradiation. Adsorption of overlayers of polar molecules, e.g. H@sub2@O and NH@sub3@ leads to changes in both the F@super+@ and F@super-@ ion intensities (attenuation and enhancement), as well as dramatic changes in the ion angular distributions. Analysis of these changes gives insight into the role of charge-transfer and elastic scattering processes during the passage of ions through ultrathin polar films. The polar coadsorbate can also influence the ESD process itself by modifying polarization energies, low-energy electron lifetimes, and potential barriers for electron tunneling.

3:40pm **SS1-MoA6 Effects of Water Ice Films on Thermal Stability and Electron-activated Decomposition of CF@sub 2@Cl@sub 2@ on Metal Surfaces***,* ***N.S. Faradzhev,*** Rutgers University*; C.C. Perry,* Johns Hopkins University*; D.O. Kusmierek,* Rutgers University*; D.H. Fairbrother,* Johns Hopkins University*; T.E. Madey,* Rutgers University

We report the kinetics of processes, activated by low energy electrons, for an environmentally important molecule CF@sub 2@Cl@sub 2@ co-adsorbed with water ice on metal surfaces (Ru; Au) at low temperature <100K. The results are compared with similar data obtained for CCl@sub 4@. TPD, RAIRS and XPS has been utilized. TPD reveals an increase of thermal stability of molecular CF@sub 2@Cl@sub 2@ on Ru(0001) when deposited under an amorphous solid water (ASW) overlayer at 25K or adsorbed inside ASW ice matrix; dissociation is completely inhibited. Weakly-bound CF@sub 2@Cl@sub 2@ desorbs from ASW surface at ~110K, but desorption of CF@sub 2@Cl@sub 2@ trapped in the ASW matrix is impeded until the onset of ice crystallization at ~155K. All techniques indicate that ionizing radiation (electrons or X-rays) incident on CF@sub 2@Cl@sub 2@/H@sub 2@O layer leads to rapid decomposition of halocarbon, which proceeds via dissociative attachment (DA) of low energy secondary electrons. The rates of decomposition for 1ML of CF@sub 2@Cl@sub 2@ and CCl@sub 4@ are similar on the metal surface and increase in the ASW ice environment indicating a possibly important role of a polar medium in halocarbon dissociation. The highest decomposition cross-sections are observed for submonolayer halocarbon coverage on a water ice surface: 1.0x10@super -15@ cm@super 2@ for CF@sub 2@Cl@sub 2@ and 2.5x10@super -15@ cm@super 2@ for CCl@sub 4@. The cross-sections are identical for halocarbon adsorbed on an ice surface and caged in a water matrix. The initial dominant radiation-induced process in adsorbed CF@sub 2@Cl@sub 2@ is C-Cl bond cleavage. For CF@sub 2@Cl@sub 2@ in ASW, fragments and reaction products include Cl@super -@ and F@super -@, H@sub 3@O@super +@, COF@sub 2@, and CO@sub 2@; for CCl@sub 4@ in ASW, COCl@sub 2@ and C@sub 2@Cl@sub 4@ are also seen. Product distributions, the kinetics of halocarbon damage, and subsequent reaction pathways are qualitatively independent of the radiation source.

4:00pm **SS1-MoA7 Water Enhanced Decomposition and Nanometer Scale Structure Formation Generated by Radiative Exposure of Solid Surfaces***, **K. Nwe**, S.C. Langford, J.T. Dickinson,* Washington State University

Novel nanometer scale structures on insulating inorganic materials with wide bandgaps can be generated by simultaneous exposure of surfaces to electron and laser beams plus low pressure water vapor. Dramatic synergisms are observed on ionic single crystal surfaces due to bond weakening which arises from localized chemisorption. We are able to modify single crystal surfaces of alkali halides and calcium phosphates/carbonates either at the single atomic layer level or, with higher intensities, at the level of several microns. These modifications are due to electronic excitations leading to decomposition of the crystal. Arrays of cones and fractal structures with unique optical properties can readily be generated. Alkali halide and nitrate surfaces exhibit strongly angular dependent â€œblackâ€� surfaces which are generated in a self-organized fashion. The high absorption is due to the high tortuosity of the surface (a â€œstealthâ€� surface). We also quantify that in the presence of water vapor, the rates of both laser and electron beam induced decomposition/desorption increase by as much as an order of magnitude. We present AFM evidence that this is a highly localized, defect mediated mechanism. We suggest that point defect clusters lead to atomic dimension step structures (e.g., kinks) that peel off due to bond weakening from sorbed water derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented.

4:20pm **SS1-MoA8 Electron-stimulated Reactions in Thin Amorphous Solid Water Films on Pt(111).***, **G.A. Kimmel**, N.G. Petrik,* Pacific Northwest National Laboratory

The electron-stimulated production of D@sub 2@ from amorphous solid D@sub 2@O deposited on Pt(111) is investigated as a function of film thickness. The D@sub 2@ yield has two components with distinct reaction kinetics. Using isotopically layered films of H@sub 2@O and D@sub 2@O demonstrates that the D@sub 2@ is produced in reactions that occur at both the Pt/amorphous solid water (ASW) interface and the ASW/vacuum interface, but not in the bulk. The energy for the reactions, however, is absorbed in the bulk of the films and electronic excitations migrate to the interfaces where they drive the reactions. At the Pt(111) surface, the electronic excitations cause dissociation of water molecules at the interface, leading to the build-up of adsorbed hydrogen atoms. A model based on the diffusion of electronic excitations to either interface accounts for the principle experimental observations.

4:40pm **SS1-MoA9 Temperature-Dependent Thresholds for Ion-Stimulated Surface Diffusion: Experiments with Second Harmonic Microscopy***, Z. Wang, **E.G. Seebauer**,* University of Illinois at Urbana Champaign

Ion-surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. The governing kinetic phenomena are often tacitly considered to lie at one of two poles: physical effects where momentum matching dominates, and chemical effects involving thermal activation of atomic bonds according to Arrhenius expressions. Here we report surface diffusion measurements demonstrating behavior that lies at neither pole. Optical second harmonic microscopy is used to image diffusion of Ge and In adsorbed on Si(111) under low-energy noble-gas ion bombardment. Both adsorbates exhibit a surprising new form of tradeoff between substrate temperature and the energy threshold at which ion influences become manifest. Molecular dynamics simulations suggest that the effect originates from changes in surface point defect concentrations. Instantaneous nonuniformities in net surface potential induced by thermal vibrations provide a mechanism by which ions can affect these concentrations nonlinearly. The effects generally increase the rate of mass transport across the surface except for Ge above the Si(111)-(7x7) to (1x1) phase transition, where ion-induced changes in charge-mediated complexation of mobile species with surface defects slows the diffusion.

5:00pm **SS1-MoA10 Femtosecond Photo-generated Carrier and Reaction Dynamics on a Chlorinated Silicon Surface: Reaction Yield Calculation by Rate Equation of Adsorbed Chlorine***, **S. Haraichi**, F. Sasaki,* National Institute of Advanced Industrial Science and Technology, Japan

We have studied the mechanism of a photo-induced reaction of Si/Cl system especially in the low fluence region, which is a promising candidate for an extremely low-damage etching. The following procedures were employed in the femtosecond pump probe experiment to obtain the photo-generated carrier dynamics during the reaction. First, the variation of surface second-harmonic (SH) intensities generated by probe light, which directly reflects surface chlorine coverage, has been measured during a photo-induced reaction. Here both incident lights respectively produces two reaction factors of carrier generation and instantaneous surface vibration. However the pump beam of 3.1 eV photon energy mainly produces carrier generation, and the probe light of 0.95 eV photon energy mainly produces instantaneous surface vibration. In addition, the pump power is set just under the reaction threshold, so the reaction must be induced only when the carrier generation by pump beam and the surface vibration by probe light simultaneously occur on the surface. After obtaining the variation of surface chlorine coverage during a photo-induced reaction, the reaction yield is calculated by using a first and second-order rate equation of the surface chlorine atoms. Second, the reaction yield is calculated for several delays between two beams, and the obtained reaction yield dependence on the delay time reflects the femtosecond photo-generated carrier dynamics. The dynamics can be described by first and second-order kinetics, and both results show no significant difference but the almost equal excitation peak at around 0.4 ps. Here the excitation time constant in the obtained carrier dynamics is 0.1-0.2 ps and tends to decrease with increasing the power of each excitation lights. On the other hand, we have found two relaxation time constants of 0.2-1.0 ps and 1.5-10.0 ps, and both short and long relaxation time constants tend to increase with increasing the excitation power.

Surface Science
Room 327 - Session SS2-MoA

Tribology, Adhesion, and Friction

Moderator: S.P. Jarvis, Trinity College Dublin, Ireland

2:00pm **SS2-MoA1 Super Hydrophobic Interactions: From the Inside and Out***, **J.E. Houston**,* Sandia National Laboratories*; S. Singh,* University of New Mexico*; C.J. Brinker,* Sandia National Laboratories

Considerable interest has recently been directed toward the study of the processing of "super hydrophobic" (SH) surfaces and their unique properties. These materials are generally characterized by hydrophobic molecules in a fractal-like structure and have contact angle in excess of ~150. We present here studies of the behavior of the interaction force vs. relative separation between a scanning force-probe tip and sample surface using the interfacial force microscope (IFM). The measurements include "inside" interactions for both a SH film (contact angle ~165) and hydrophilic tip (~30) coming into contact with the SH surface in water, and the "outside" case for a SH-coated tip in contact with the outer water surface. As expected, the latter case shows the development of a considerable repulsive force before becoming unstable submersing the coated-tip end. However, the inside case shows a marked contrast depending on the nature of the tip. The hydrophilic tip shows only repulsive forces, as it essentially pushes against the inside surface of the water in contact with the SH film. In addition, the SH surface deformation reveals an unusual creep behavior in this case. In contrast, the SH coated tip shows large, long-range attractive forces prior to contacting the SH film, an effect which is often characterized as due to interfacial bubble formation. These results will be discussed in terms of experimental parameters, such as tip speed and the thickness of the SH film, as well as the mechanical properties of the film itself, both wet and dry. The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm **SS2-MoA2 Friction Anisotropy at Pd(100)/Pd(100) Interfaces**, ***A.J. Gellman***, *C.M. Mancinelli,* Carnegie Mellon University

Friction anisotropy has been studied between two Pd(100) single crystal surfaces in an ultrahigh vacuum environment. Friction measurements were made using Pd(100)/Pd(100) interfaces modified by adsorption of octane at coverages ranging from 4 to 40 molecular layers. The relative crystallographic orientation of the two Pd(100) surfaces was systematically varied and friction measurements were made at each orientation as a function of octane coverage. These measurements have revealed that friction is anisotropic with respect to Pd(100) lattice orientation. When the surfaces were aligned, forming a commensurate interface, and sheared along the direction with 4ML of octane at the interface, the static friction coefficient was µ@sub s@ > 8.0 ± 2.0. A minimum in the static friction coefficient was obtained when the two Pd(100) surfaces with 4ML of octane at the interface were misoriented by @theta@ ~ 45°. Under these conditions the static friction coefficient for sliding along the direction of the stationary surface was µ@sub s@ = 4.0 ± 2.0. Higher coverages of octane decreased the friction, but friction anisotropy persisted for coverages of octane as high as 20 ML at the sliding interface between the two Pd(100) surfaces. Wear scares were observed on both surfaces indicating that plastic deformation had occurred during sliding. The observation of friction anisotropy in the presence of disordered overlayers of octane and during shearing of surfaces that deform plastically suggests that friction anisotropy originates with the properties of the bulk crystal lattices rather than surface lattice commensurability. These results corroborate the findings of a previous study of friction anisotropy between Ni(100) surfaces.@footnote 1@ @FootnoteText@ @footnote 1@ Langmuir, 2000, 16(22), 8343.

2:40pm **SS2-MoA3 Direct Observation of Superlubricity**, *J.W.M. Frenken,* Leiden University, The Netherlands*;* ***M. Dienwiebel,*** IAVF AG, Germany*; N. Pradeep, K.B. Jinesh, G.S. Verhoeven,* Leiden University, The Netherlands*; J.A. Heimberg,* Corvis Corporation

We have constructed a frictional force microscope (FFM) that is able to quantitatively track the forces between a tip and sample in three dimensions. At the heart of the FFM is a silicon sensor, the 'Tribolever'. The 3D motion of a metal tip, which is held by this sensor, is detected with four interferometers. The two lateral spring constants of the Tribolevers are typically 1 N/m, which is up to two orders of magnitude lower than the torsional force constants of conventional AFM cantilevers. The spring constant perpendicular to the surface is typically an order of magnitude higher than in the lateral directions. The friction force resolution is as low as 15 pN, even under normal loads up to several tens of nN. We present experimens with W-tips on highly oriented, pyrolytic graphite (HOPG) surfaces. We observe the familiar, atomic-scale stick-slip behavior, in which the tip performs a 'least-resistance', zig-zag path over the corrugated graphite surface. To our surprise, the amplitude of the friction forces depends strongly on the relative orientation of the tip and the graphite surface. When we rotate the graphite around an axis normal to the surface, the average friction force shows characteristic variations between a high value and a near-zero value, close to the detection limit of our FFM. These observations, combined with additional, circumstantial evidence, support a simple interpretation, in which a small graphite flake intervenes between the W tip and the HOPG substrate. Thus, the FFM actually records the lateral forces between two parallel graphite lattices. By rotating the substrate with respect to the tip, we periodically go through fully aligned and completely misoriented configurations. When the misalignment is sufficiently severe, the lateral forces on the C-atoms in the flake cancel, thereby dramatically reducing the total friction force. This phenomenon has been predicted more than ten years ago, and is referred to as superlubricity.

3:00pm **SS2-MoA4 The Role of the Third Body Processes in the Friction and Wear of MoS2 and MoST Coatings**, ***G.Y. Lee***, *I.L. Singer, K.J. Wahl,* U.S. Naval Research Laboratory

The sliding friction behavior of MoST@footnote 1@ (Ti-Mo-S) and MoS@sub 2@ coatings has been investigated by in situ tribometry, which allowed real time observation of third body dynamics. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 to 20 % titanium. Reciprocating tests were performed in both dry (< 4 % RH) and ambient (40-50 % RH) air at a sliding speed of 1 mm/s and 24 N normal load (1.1 GPa mean Hertizan stress) using sapphire hemispheres as counterbodies. All coatings showed similar steady-state friction coefficients: about 0.025 in dry air and 0.06 in ambient air, however titanium containing coatings in ambient air exhibited lower friction coefficients at the beginning of the tests. Titanium containing coatings also showed reduced wear in both dry and ambient conditions. In situ optical microscopy observations identified the formation of a transfer film (third body) on the sapphire hemisphere for all tests. Most of the sliding took place between the transfer film and the wear track indicating that the velocity accommodation was interfacial sliding. The titanium containing coatings exhibited an additional velocity accommodation mode, shearing and extrusion of transfer film, correlated to the higher friction in ambient conditions. The role of the transfer film mobility and mechanical properties in controlling friction behavior will be discussed. @FootnoteText@ @footnote 1@ N.M. Renevier, V.C. Fox, D.G. Teer, and J. Hampshire, Surf. Coat. Tech., 127 (2000) 24-27.

3:20pm **SS2-MoA5 Molecular and Bulk Material Mechanisms of Smooth and Stick-slip Sliding**, ***J. Israelachvili,*** University of California, Santa Barbara **INVITED**

There are at least three quite different contributions to the friction force between two ideal surfaces, i.e., smooth surfaces sliding in the absence of wear: load-dependent friction (which depends on the surface structure or topography), adhesion-dependent friction (which depends on any adhesion between the two surfaces) and viscosity-dependent friction (which occurs when the shearing surfaces are separated by a thin layer of liquid). These contributions depend on the surface molecular structure, the contact area, applied load (or pressure), film thickness, film viscosity, and sliding speed (or shear rate). In addition to these purely surface or interfacial properties, the bulk properties of the materials such as the elastic modulus can also play an important role even in the case of wearless sliding of elastic surfaces. Thus, depending on their shape, the friction can be smooth or proceed via stick-slip. The situation with rough and/or viscoelastic surfaces can be very rich and complex, as can the adhesion between the surfaces, and both may depend critically on a combination of surface and bulk properties. The talk will review some recent experimental results, including theoretical modeling and computer simulations, on such systems, i.e., both rough and smooth, hard and soft, adhesive and non-adhesive, lubricated and unlubricated. Such studies are clarifying the molecular basis of many well-established tribological laws and empirical observations such as Amontons laws and the Stribeck Curve, and are also revealing new insights and relationships between tribological processes at the molecular and macroscopic levels.

4:00pm **SS2-MoA7 Evaluation of the Surface Characteristics and Mechanical Properties of Interconnect Films and their Correlation with CMP Process**, ***P.B. Zantye,*** *A.K. Sikder, A. Kumar,* University of South Florida

Chemical Mechanical Planarization (CMP) has emerged as one of the most widely used Back End of Line (BEOL) semiconductor manufacturing process for fabrication of present generation Cu interconnect structures. CMP is synergistic combination of tribological and chemical phenomena occurring at the surface of the polishing pad and wafer in presence of chemically active slurry. Thus, the frictional forces that act upon the wafer during CMP assume significant importance for effective characterization of the CMP process. In this research the surface characteristics and mechanical properties of various candidate materials Cu (wiring metal) and interlayer dielectrics (ILD) SiLK@super TM@ (soft polymer), and SiO@sub2@ (ceramic) have been evaluated. The surface roughness of the candidate materials was determined using the Atomic Force Microscopy (AFM) technique. The mechanical properties (Young's Modulus and Hardness) of Cu, SiLK@super TM@ and SiO@sub2@ were evaluated usi! ng MTS Nanoindentor@superTM@. The material removal behavior and dry friction characteristics were studied by micro scratch testing and the CMP process of materials under investigation was simulated on the Bench Top CMP tester. The coefficient of friction (COF) was monitored in situ during initial and final part of wafer coupon polishing. The surface characteristics, mechanical properties, dry friction and material removal were then correlated with the CMP process for each material to get an insight in to the polishing behavior of these candidate materials when planarized with different material specific slurries and polishing pads.

4:20pm **SS2-MoA8 A Comparative Study of the Adhesion, Friction, and Mechanical Properties of CF@sub3@ and CH@sub 3@ Terminated Alkanethiol Monolayers**, ***C.M. Doelling***, *H. Ying,* Princeton University*; J.E. Houston,* Sandia National Laboratories*; T.K. Vanderlick, G. Scoles,* Princeton University*; T.R. Lee,* University of Houston

Considerable interest has been given to the potential use of self-assembled monolayer films as lubricants for applications such as MEMS. Of particular interest are fluorinated films because they are inert and show high thermal stability. Research performed directly compares the adhesion, friction, mechanical properties and contact potentials of two alkanethiol SAM films, differing only in the composition of their terminal head group (-CH@sub 3@ vs. -CF@sub 3@). Quantitative data of both friction and normal force was collected using the Sandia-developed interfacial force microscope (IFM). In comparison with the CH@sub 3@-terminated monolayer, we find that the CF@sub 3@-terminated film exhibits a longer-ranged attraction to an approaching metal probe tip, and the work required to separate the surfaces is greater despite the maximum attractive forces being similar. The friction is also larger, as is the force-displacement hysteresis upon loading/unloading cycles. Close inspection of the frictional response shows the presence of "non-contact" friction, namely, significant energy dissipation before the probe and monolayer develop a component of repulsive-contact force. From these findings we conclude that the mechanical behavior of the film is influenced by the strong dipole inherent to the -CF@sub 3@ terminal group. Finally, atomic force microscopy measurements of friction were also undertaken, taking advantage of nanografting to directly compare both types of films using the same probe tip. At small compressive loads, the friction of the fluorinated film is about two times that of the hydrocarbon film, in agreement with the IFM results. @FootnoteText@ The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

4:40pm **SS2-MoA9 Reaction of Trimethylphosphate with TiC and VC(100) Surfaces***, **H.I. Kim**, P. Frantz, S.V. Didziulis,* The Aerospace Corporation*; L.C. Fernandez-Torres, S.S. Perry,* University of Houston

Hard coatings, such as titanium carbide (TiC), are emerging technologies for various tribological applications, including spacecraft bearings due to their higher hardness and greater wear resistance compared to metal components. However, their surface chemical properties, especially with respect to high-performance lubricants, are poorly understood. Therefore, the adsorption and chemical reaction of a model lubricant additive, trimethylphosphate [(CH3O)3PO] (TMP), were investigated on the surfaces of TiC and VC(100) as a function of temperature using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). TMP adsorbs molecularly on both surfaces at cryogenic temperature, and chemical bonding to the surface is evident upon warming to approximately 200 K. At higher temperatures, surface chemical reaction on TiC leads to phosphate-like and carbonaceous products that persist on the surface after heating up to 873 K. The stability of these surface species at such high temperature presents potential implications for modification and lubrication of hard coating surfaces at high temperatures where most organic adsorbates fail to provide tribological benefits. The reaction pathway and the reaction products are determined to be dependent on the initial coverage as well as the substrate chemistry, i.e. TiC vs. VC. These results have interesting implications for potential applications in boundary additives on hard coatings, where desired surface chemical protection may be tuned by the concentration of the organophosphate ester additives in the lubricant and the substrate chemistry.

5:00pm **SS2-MoA10 Degradation of Self-Assembled Monolayer in Humid Environments***, **B.-I. Kim**, T.M. Mayer, M.G. Hankins, M.P. de Boer, B.C. Bunker,* Sandia National Laboratories

Self-assembled monolayers (SAMS) are used extensively to control friction and stiction in micromachines. While as-prepared coatings are effective at minimizing adhesion, coating performance can deteriorate with time in humid environments. We are using the interfacial force microscope (IFM) to monitor the aging behavior of SAMS as a function of temperature, humidity, time, SAM composition, and fabrication procedures. The IFM provides force-distance curves between functionalized scanning probe tips and substrate surfaces while avoiding the "snap-to-contact" problems associated with conventional atomic force microscopy(AFM). We have simultaneously measured both normal and friction forces between a tip and SAM coated surfaces as a function of separation distance. Together with topographic images taken with AFM, we can correlate adhesion and friction with structural information. Our results indicate that adsorbed water can disrupt hydrogen bonds at the SAM-substrate interface, reorganizing the coating to create bare patches that promote adhesion. To date, coatings that have been tested include standard octadecyl trichlorosilane (OTS), tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS), octadecene (reacted with surface Si-H bonds), dichlorodimethylsilane(DDMS), and an octadecyl coupling agent attached to the surface using amine functional groups. At all humidities and temperatures tested, it appears that FOTS coating that have been annealed to promote condensation reactions with surface silanols are most effective at resisting degradation in hot, humid environments. @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.

Surface Science
Room 328 - Session SS3-MoA

Structure and Reactivity of Metal Clusters

Moderator: C.T. Campbell, University of Washington

2:00pm **SS3-MoA1 Catalysis by Supported Metal Nanoclusters***, **D.W. Goodman**,* Texas A&M University **INVITED**

Model catalysts consisting of metal clusters of varying sizes have been prepared on single crystal TiO2 and ultra-thin films of TiO2, Al2O3, and SiO2. The morphology, electronic structure, and catalytic properties of these metal clusters have been investigated with emphasis on the unique properties of those clusters <5.0 nm in size. An array of surface techniques including scanning tunneling microscopy (STM) and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) have been used to study the metal cluster morphology, electronic properties, and chemistry. These studies illustrate the novel physical and chemical properties of nanosized metal clusters, and suggest that their catalytic properties may be tailored for specific chemical transformations.

2:40pm **SS3-MoA3 Gold Nano-Clusters on Rutile TiO@sub 2@(110) - A Combined UHV and High Pressure STM Study***, E. Walström, R. Schaub, E.K. Vestergaard, A. Ronnau, **F. Besenbacher**,* Interdisciplinary Nanoscience Center, Denmark

Through an interplay between scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we show that bridging oxygen vacancies are the active nucleation sites for Au clusters grown on the rutile TiO@sub 2@(110) surface under UHV conditions. We show both experimentally and theoretically that a single oxygen vacancy can bind 3 Au atoms on average. A new growth model for the Au/TiO@sub 2@(110) system involving vacancy-cluster complex diffusion is presented. The fate of the Au nano-particles in various gas environments is studied in detail through a new high-pressure STM capable of atomic resolution at atmospheric pressures. Sintering and morphological changes are followed in-situ when the Au/TiO@sub 2@(110) system is exposed to reducing (H@sub 2@,CO) and oxidizing (O@sub 2@) conditions.

3:00pm **SS3-MoA4 Dimethyl Methylphosphonate Decomposition on Supported Ni Nanoparticles Deposited on a TiO@sub 2@(110) Surface***, **J. Zhou**, Y.C. Kang, K. Varazo, D.A. Chen,* University of South Carolina

Sizes and structures of oxide-supported metal nanoparticles are very important in determining their catalytic reactivity. In our study, the thermal decomposition of dimethyl methylphosphonate (DMMP) on supported nickel nanoparticles has been investigated as a model system to understand the relationship between the particle size and reactivity. All the experiments were performed under UHV conditions by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Our STM studies show that various sizes of Ni particles with uniform particle size distributions can be prepared on TiO@sub 2@(110) surface by varying the diffusion (D) to deposition flux (F). The most uniform size distribution of Ni nanoparticles can be obtained with the lowest D/F ratio. XPS and TPD studies indicate that mainly molecular DMMP adsorbs on the supported Ni nanoparticles at room temperature. Between room temperature and 800 K, the adsorbed DMMP decomposes to produce H@sub 2@ and CO as primary gaseous products and CH@sub 4@ and HCHO as minor products. After heating to 800 K, all carbon desorbs from the surface while atomic phosphorous still remains. DMMP decomposition on various sizes of Ni nanoparticles as well as on the bulk Ni surface will be compared. Furthermore, studies of DMMP reaction will be also carried out on the supported Pt nanoparticles.

3:20pm **SS3-MoA5 Dynamics and Chemical Reactivity of Au on TiO@sub2@ (110) Rutile***, **D. Pillay**, Y. Wang, G.S. Hwang,* University of Texas at Austin

Au has long been known to be chemically inert in its bulk form, as compared to other transition metals, such that it has received little attention as a catalyst. However, Au nanoclusters dispersed on oxide (particularly TiO@sub2@) shows an extraordinarily high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides. But, due to weak metal-oxide interfacial bonding interactions, Au nanoclusters become unstable toward sintering even at moderate temperatures. This may in turn undermine their catalytic activity and selectivity. Hence, along with their chemical reactivity, a detailed understanding of dynamical behaviors of Au atoms is necessary for an accurate description of underlying reaction mechanisms and performance of the oxide supported nanometal catalytic systems under realistic processing conditions. In this talk, we will present our first principles [DFT with plane waves and pseudopotentials] study of Au adsorption and diffusion on regular and defective (with oxygen vacancies) TiO@sub2@ (110) rutile. We will also present the diffusion of oxygen vacancies (Fs center) and their interactions with Au atoms. Based on our calculation results, we will discuss underlying reasons for the enhancement of Au cluster sintering upon exposure to a high-pressure oxygen environment.

3:40pm **SS3-MoA6 Oxygen-Induced Morphological Changes in Cu and Ni Islands on TiO@sub2@(110)**, ***D.A. Chen**, J. Zhou,* University of South Carolina*; Y.C. Kang,* Pukyong National University, South Korea

Metal particles supported on oxide surfaces serve as excellent model systems for developing a better understanding of commercial heterogeneous catalysts. Scanning tunneling microscopy (STM) studies of Cu islands grown on a rutile TiO@sub2@(110)-(1x1) surface demonstrate that these islands disappear from the STM images after exposure to oxygen gas. Based on X-ray photoelectron spectroscopy (XPS) experiments, the disappearance of the Cu islands cannot be explained by the loss of Cu from the surface or by a dramatic change in the electronic properties of the islands. The adsorption of oxygen appears to weaken the Cu-Cu bond, allowing two-dimensional (2D) Cu islands to form on the surface at the expense of the existing three-dimensional (3D) islands. The formation of 2D islands is thermodynamically favorable for Cu based on the lower surface free energy of oxidized compared to that of both Cu and TiO@sub2@. Oxygen-induced disappearance of Ni islands has also been observed, but the rate of disappearance is much slower even though Ni is more easily oxidized than Cu. This effect can also be explained in terms of thermodynamics; oxidation of Ni islands does not reduce the surface free energy of the islands below that of TiO@sub2@, and therefore there is less driving force for the Ni islands to become 2D. As expected, oxidation of Cu islands at 500 K increases the rate of disappearance of the 3D islands. However, oxidation of the Ni islands at 500 K causes significant changes in the surface morphology due to the oxidation of the TiO@sub2@ surface itself. The new titania layers preferentially regrow around the Ni islands, resulting in a much rougher surface.

4:00pm **SS3-MoA7 Chemical Reactions on Free Iridium and Platinum Clusters**, ***M. Andersson**, T. Jarvdalen, P. Nystrom, A. Rosen,* Chalmers University of Technology and Goteborg University, Sweden

In a cluster beam experiment metal clusters are produced with a pulsed laser vaporization source, kept at room temperature or liquid nitrogen temperature. The beam of neutral clusters passes two low-pressure collision cells and clusters and reaction products are detected with laser ionization and time-of-flight mass spectrometry. Thus, the reaction probability in a cluster-molecule collision can be determined.@footnote 1@ We have measured the CO and O@sub 2@ adsorption on iridium clusters, 5-32 atoms. The overall size-dependence in reaction probability is similar for both molecules, with minima at Ir@sub 8@, Ir@sub 12@ and Ir@sub 18@, and a significantly higher reactivity for all clusters with more than 18 atoms. When the cluster source was cooled to liquid-nitrogen temperature, the reaction probability increased. For platinum clusters with more than 6 atoms we measured stable reaction products with both oxygen and hydrogen, with moderate variations with size. Using the two reaction cells we can let the clusters react first with O@sub 2@ and then with H@sub 2@ and observe that reaction of Pt@sub n@(O@sub 2@)@sub m@ with H@sub 2@ results in removal of oxygen atoms from the cluster. This is interpreted as formation of a water molecule, which subsequently desorbs. The efficiency of the catalytic water formation is high on all cluster sizes measured (7-30 atoms), with only a weak dependence on cluster size.@footnote 2@ @FootnoteText@@footnote 1@ M. Andersson, J.L. Persson, A. Rosen, J. Phys. Chem. 100, 12222 (1996).@footnote 2@ M. Andersson, A. Rosen, J. Chem. Phys. 117, 7051 (2002).

4:20pm **SS3-MoA8 STM Study of Copper Growth on ZnO(0001)-Zn and ZnO(0001bar)-O Surfaces**, ***O. Dulub**,* Tulane University*; L. Vogel Koplitz,* Loyola University*; M. Batzill, U. Diebold,* Tulane University

The study of Cu particles on ZnO surfaces is of great interest due to the wide application of this system in the low-temperature synthesis of methanol, the water-gas shift reaction, and the production of hydrogen by steam reforming. The mechanism that enhances the catalytic activity of Cu is still poorly understood. Therefore, a detailed study of this system on the atomic level is desirable. Scanning Tunneling Microscopy (STM) has been used to study the room temperature growth of Cu on the polar (0001)-Zn and (0001bar)-O surfaces of zinc oxide. The (0001)-Zn surface prepared by sputtering and annealing at 500-750°C, shows flat terraces with a high density of triangular pits and islands. STM shows that Cu grows on the (0001)-Zn surface as three-dimensional clusters at coverages between 0.05 and 0.25 monolayers (ML)); two-dimensional (2D) islands are only observed at very low coverages (0.001-0.05 ML). The average size of the 3D clusters increases with coverage and their density increases slowly. The size and morphology of Cu clusters depends on the terrace size of the substrate. The triangular pits and islands on the terraces do not act as preferred nucleation sites for Cu, but, surface roughness and sputter damage change the growth mode to more 2D-like. The Cu clusters are well-separated and exhibit a well-defined hexagonal shape. Equilibrium crystal shape analysis of the largest clusters yields an apparent work of adhesion of 3.4 ± 0.1 J/m@super 2@, which is size dependent and decreases with the size of the cluster. The morphology of the clean (0001bar)-O surface is distinctly different from that of the (0001)-Zn surface. The terraces are smooth and have no small islands. Formation of two-dimensional Cu clusters at coverages of less than 0.1 ML was observed on the (0001bar)-O surface.

4:40pm **SS3-MoA9 Charge Exchange between Alkali Ions and Nanocrystal Metal Surfaces**, ***G. Liu**, J. Yarmoff,* University of California, Riverside

Au nanocrystals grown on TiO@sub 2@(110) possess unique catalytic properties, which depend on the cluster size.@footnote 1@ Presumably, the catalytic properties are the result of the electronic configuration of the nanocrystals. Earlier, we showed that the probability for neutralization of low energy alkali ions scattered from metal surfaces is determined by the local electrostatic potential (LEP) a few Å's above the scattering site.@footnote 2@ In the present work, we are using the charge exchange between alkali ions and metallic nanocrystals as a probe of their electronic structure. 2 keV @super 23@Na@super +@ ions were scattered from Au nanocrystals grown on TiO@sub 2@(110), and the neutral fractions of the Na particles singly scattered from Au were measured with time-of-flight. As the average size of the Au nanoclusters increases, the neutral fraction decreases until a uniform Au film is formed. The neutral fraction of Na scattered from bulk Au is very small (~2%) due to the large work function of Au. For small Au clusters, however, the neutral fractions can be as high as 30% or more. The high neutral fraction of the small Au clusters suggests that the alkali ions are coupling to electronic states that are specific to the nanocrystals. The work function change, measured as a function of cluster size, shows a smooth change from the clean TiO@sub 2@(110) surface to that of bulk gold. In order to understand the influence of the work function on the neutral fraction, Cs was deposited onto Au/TiO@sub 2@(110) surface to controllably decrease the work function. In addition, the dependence of the neutral fraction on the ion exit angle and energy was studied. @FootnoteText@ @footnote 1@X. Lai, T. P. St. Clair, M. Valden, and D. W. Goodman, Prog. Surf. Sci. 59 (1998) 25.@footnote 2@C. B. Weare and J. A. Yarmoff, Surf. Sci. 348 (1996) 359.

5:00pm **SS3-MoA10 Electronic Detection of Oscillatory Reactions on Supported Platinum Particles**, ***M.C. Wheeler**,* University of Maine*; R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology

A MEMS device, capable of surface temperature control and electrical resistance measurements, has been used to detect and explore the oscillatory reaction of CO oxidation on oxide-supported platinum particles. The behavior has been monitored for a range of conditions, but as an example, when the supported platinum is heated to 165°C in a 340 ppm CO/air mixture at atmospheric pressure, periodic switching between a low-resistance (excess CO) state and a high-resistance (excess oxygen) state is observed. During these cycles, the resistance ranges from 7.1 k@ohm@ to 17. k@ohm@ and back to 7.1 k@ohm@ over a period of 200 s. The resistance switching that we have studied on small (on the order of 30 nm) platinum particles is likened to the temporal oscillations of the reaction on platinum films@footnote 1@ and single crystal samples,@footnote 2@ which were monitored by infrared and photoemission electron microscopy respectively. We have shown that the frequency of the resistance oscillations can be manipulated by varying the CO partial pressure in order to influence the rate of CO uptake. Also, synchronization observed between oscillations for physically separate devices in multi-element arrays is evidence that the oscillations are due to a globally-coupled, mass-transfer and reaction rate effect. Indeed, effects such as doubling of the oscillation frequency on neighboring devices are similar to the rate behavior observed by Yamamoto et al. In addition to the global synchronization, transient oscillations are observed prior to switching that suggests microscale-coupling occurs between the individual platinum particles on the support. @FootnoteText@@footnote 1@ Yamamoto, Surko, and Maple, J. Chem. Phys. 103, 8209 (1995).@footnote 2@ G. Ertl, Science 254, 1750 (1991).

Thin Films
Room 329 - Session TF-MoA
Atomic Layer Deposition and Low-k

Moderator: S.M. George, University of Colorado

2:00pm **TF-MoA1 The Application of Plasma for Metal Atomic Layer Deposition for Cu Interconnect Technology***, S.M. Rossnagel,* ***H. Kim,*** IBM T.J. Watson Research Center **INVITED**

As the semiconductor dimensions scale down to sub-65 nm regime with implementation of Cu interconnect technology, the need for introducing metal thin film deposition techniques with excellent conformality and thickness control at the nanometer scale has been increased. Atomic layer deposition (ALD) is expected to play an important role in depositing thin layers in nanoscale Si device manufacturing. Among the key materials used for modern semiconductor processing, thin films of inert, refractory or noble materials will continue to be used in interconnect applications as diffusion barriers, seed and adhesion layers as well as potential front end applications such as contacts or gate metallization. The plasma technologies that have been widely used for various aspects of the semiconductor device processing can be extended into ALD areas. Plasma enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than both conventional thermal ALD and chemical vapor deposition. This low temperature process makes PE-ALD more attractive for emerging low-k interconnect materials. In addition, since ALD is surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. In this presentation, we will present the PE-ALD of Ta-based thin films for Cu interconnect technology and the surface modification by plasma for metal and nitride ALD processes.

2:40pm **TF-MoA3 Copper Atomic Layer Deposition Using In Situ-Generated Cu@sub 3@Cl@sub 3@ and Hydrogen Radicals***, M.D. Groner, S.M. George,* University of Colorado

Copper (Cu) atomic layer deposition (ALD) has been achieved using in situ-generated Cu@sub3@Cl@sub3@ and hydrogen radicals. The Cu ALD chemistry involves copper chloride adsorption on the substrate followed by copper chloride reduction to copper metal using hydrogen radicals. The copper chloride precursor, Cu@sub3@Cl@sub3@, is generated in situ when a small Cl@sub2@ or SnCl@sub4@ gas pulse transported by a carrier gas contacts a high surface area Cu braid at T> 200 °C. The in-situ generation of Cu@sub3@Cl@sub3@ overcomes the stability problems associated with using a heated CuCl source to generate the copper chloride. The Cu ALD is performed using a "moving sample" reactor in which a pneumatic transfer arm shuttles the sample between the Cu@sub3@Cl@sub3@ dosing region and the inductively coupled plasma (ICP) hydrogen radical source. This reactor design is important because close proximity to the hydrogen radical source is necessary to overcome efficient hydrogen radical recombination on the reactor walls. Cu ALD films have been grown on glass, sapphire, and silicon substrates. The Cu ALD films nucleate well on the various substrates after hydrogen radical exposures. Cu ALD growth rates of >1 Å/cycle have been achieved as determined by real-time in situ optical thickness measurements of the Cu film growth. The Cu films are very shiny and copper-colored and display a high reflectivity. X-ray diffraction (XRD) analysis of the Cu films show distinct (111), (200), (220) and (311) diffraction peaks with no additional XRD peaks. Preliminary studies have shown successful Cu ALD at substrate temperatures ranging from ~200-260 °C. Further results will be presented on the dependence of growth temperature, copper chloride precursor exposure and hydrogen radical exposure.

3:00pm **TF-MoA4 Dynamic Equipment and Process Simulation for Atomic Layer Deposition Technology***,* ***W. Lei****, Y. Cai, L. Henn-Lecordier, G.W. Rubloff,* University of Maryland

While the self-limiting growth of atomic layer deposition (ALD) makes it a promising process for thin film deposition, the rapid precursor gas cycling required poses manufacturability challenges. We have developed dynamic simulation models for equipment and process behavior to explore the influence of detailed design on : (1) surface chemistry and resulting material quality; (2) manufacturing throughput; (3) materials utilization for environmental (ESH) and cost metrics; and (4) real-time sensor system design for integrated metrology and advanced process control. The dynamic simulators are flexible in accommodating a variety of process and surface chemistries as well as equipment designs. For a mini-chamber design motivated by manufacturing throughput requirements, we have compared operational modes based on static vs. dynamic gas flow, which shows ESH benefits for the former without sacrifice of throughput. The simulator reveals time-dependence analysis of ALD dynamics as a function of surface chemistry and equipment design, providing guidance for integrated metrology. Based on these results, we are developing a novel ALD reactor for process and metrology development which emulates the conditions found in emerging commercial reactors. @FootnoteText@ Supported by the National Institute of Science and Technology and by the NSF/SRC Center for Environmentally Benign Semiconductor Manufacturing.

3:20pm **TF-MoA5 Al@sub 2@O@sub 3@ Atomic Layer Deposition for the Enhancement of MEMS Performance and Reliability***,* ***C.F. Herrmann****, N.D. Hoivik, F.W. DelRio, V.M. Bright, Y.C. Lee, S.M. George,* University of Colorado

Ultrathin and conformal films deposited using Atomic Layer Deposition (ALD) can enhance the reliability and performance of MEMS devices. Al@sub 2@O@sub 3@ ALD films are particularly useful because the Al@sub 2@O@sub 3@ ALD surface chemistry is very favorable and amenable to growth on a wide variety of substrates. Al@sub 2@O@sub 3@ ALD films on electrostatically-actuated polysilicon cantilever switches were found to prevent electrical shorting and increase the number of actuation cycles before device failure. In addition, the resonant frequencies of the cantilever beams were also increased by Al@sub 2@O@sub 3@ ALD films resulting from added stiffness. ALD can also be utilized to deposit robust and reliable hydrophobic coatings. The initial MEMS device is optimized for hydrophobic precursor attachment by: 1) covering the MEMS surface uniformly with a continuous adhesion layer; 2) providing a high surface coverage of hydroxyl groups for maximum precursor attachment; and 3) smoothing and removing nanometer-sized capillaries that may otherwise lead to microcapillaries and stiction problems. Quartz crystal microbalance (QCM) studies have been used to monitor the attachment of various chlorosilane and dialkylaminosilane hydrophobic precursors on the Al@sub 2@O@sub 3@ ALD adhesion layer. The QCM results are consistent with the deposition of a dense hydrophobic film on the Al@sub 2@O@sub 3@ adhesion layer. The hydrophobic films on Al@sub 2@O@sub 3@ ALD adhesion layers on silicon wafers were observed to increase dramatically the contact angle. The film properties and adhesion energies were also measured for hydrophobic films on MEMS cantilever beams. After submersion in water, the hydrophobic-coated beams showed much less stiction than the uncoated beams.

3:40pm **TF-MoA6 Processes and Properties of Porous CVD Low-k Materials***,* ***Y. Travaly****, M. Van Hove, G. Beyer,* IMEC / SPDT / ITSMI, Belgium*; K. Maex,* IMEC / SPDT, Belgium **INVITED**

The aggressive down scaling of device dimensions in integrated circuits requires the introduction of non-traditional materials such as porous CVD low-k dielectrics together with thinner copper diffusion barrier with improved step coverage and conformality along via and trench side walls. This results in a number of concerns with respect to both the low-k film and Cu diffusion barrier to be implemented. Regarding the low-k dielectric, it appeared over the last few years, that not only its electrical properties are of importance but also its compatibility with the process steps encountered in the course of its integration. We therefore identified a number of key properties such as porosity, bulk diffusion of wet chemicals, slurries and barrier precursors, etc. and studied them in relation with surface sealing by plasma treatments, liner deposition or metallic barrier. For the Cu barrier, a number of factors come into play and influence dramatically the interconnect delay (RC delay) especially for the most aggressive pitches. Among these factors, one can easily control the quality of the barrier interface with the low-k or the Cu as well as the minimum barrier thickness. The cross-sectional barrier profile in interconnect appears also to be of prime importance for both RC delay and barrier reliability. To improve the step coverage and minimize the barrier area, we have considered various approaches including a highly conformal atomic layer deposition (ALD) process. However, when used in combination with porous low-k dielectrics, an ALD process gives rise to other issues such as the diffusion and interaction of ALD precursors with the various layers (low-k, hard masks) present in the dielectric stack. We studied these interactions and identified suitable methods to prevent detrimental effects. Ultimately, we studied the reliability of the Cu/low-k system in relation to barrier integrity.

4:20pm **TF-MoA8 Deposition of Low k OSG Films Exhibiting Enhanced Mechanical Properties by PECVD***, J.L. Vincent, R.N. Vrtis,* ***A.S. Lukas****, M.L. O'Neill, B.K. Peterson, M.D. Bitner, G.J. Karwacki,* Air Products and Chemicals, Inc.

Silica is the traditional insulating material used in interlayer dielectrics and has a k of 3.9-4.2. To achieve the lower k's required for the next generation of IC's, methyl (Me) groups may be added to the silicate structure by using organosilane precursors. The lower k in the resulting organosilicate glass (OSG) is attributed to the decreased density, increased hydrophobicity, and reduction of the polarizability of the material. We previously demonstrated the use of diethoxymethylsilane (DEMS) to deposit OSG films by PECVD with k's of 2.7-3.3 (dense) and 2.0-2.5 (porous). However, this decrease in k comes at the expense of the mechanical properties due to the disruption of the silicate network by terminal Si-Me. Our modeling studies show that the benefit of adding Me to lower the k diminishes after a Si/Me ratio of about 2/1 in the OSG material, yet the mechanical properties continue to decline as the Si/Me ratio approaches 1/1. Our dense DEMS OSG films (k = 3.0) are deposited at temperatures > 350 C. These films have excellent mechanical strength and a Si/Me ratio of 2/1. However, our process for porous DEMS OSG (k < 2.5) requires a deposition temperature below 280 C, resulting in a Si/Me ratio close to 1/1 and significantly decreased mechanical strength. We found that the Me incorporation can be reduced in by using a precursor mixture of DEMS and a second silica source without Me groups. This allows the control of the terminal Me content in the final film chemically, as opposed to using process conditions such as high temperature or plasma power. We were successful in depositing OSG films with Si/Me ratios of 2/1 from precursor mixtures at deposition temperatures as low as 200 C. For example, a porous OSG with a post-anneal k of 2.2 and a nanoindention hardness of about 0.6 GPa was deposited at 270 C. This is a nearly 2-fold increase in the mechanical strength as compared to films with identical k deposited without the second silica source.

4:40pm **TF-MoA9 Expanding Thermal Plasma for Low-k Dielectrics: Guiding the Film Chemistry by Means of Selected Dissociation Paths in the Plasma***,* ***M. Creatore****, Y. Barrell, W.M.M. Kessels, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

As the need for low-k dielectrics in the ULSI technology becomes urgent, the research primarily focuses on the deposition of novel materials with appropriate electrical properties and on the challenges concerning their integration with subsequent processing steps. Within this framework, plasma-enhanced chemical vapour deposition of organosilicate glass films is considered promising due their chemical structure similar to SiO@sub 2@, which leads to a simpler process integration. In this contribution we address the remote expanding thermal plasma (ETP) as a novel technique for the deposition of low-k carbon-doped SiO@sub 2@ films from Ar/hexamethyldisiloxane (HMDSO)/oxygen mixtures. We have obtained low-k films which exhibit k values (yet not optimised) in the range 2.9-3.4 (at 1 MHz) and still fairly good mechanical properties (hardness of 1 GPa, modulus of 10 GPa). These results were not expected because literature, in general, reports on low-k films deposited from precursors with 2 Si-O and 1 Si-C bonds per Si atom (e.g., dimethoxymethylsilane and diethoxymethylsilane), in order to reach a compromise between dielectric and mechanical film properties. Our approach, on the contrary, utilizes HMDSO (apparently not suitable due to the high Si-CH@sub 3@: Si-O bond ratio) because the ETP technique allows selecting different fragmentation paths for the precursor and this can eventually be turned to the progressive cleavage of Si-C bonds. The relatively easy control on the process kinetics can be monitored by means of gas phase diagnostics, such as Mass Spectrometry and Cavity Ring Down Spectroscopy. The information on the HMDSO dissociation paths allows tailoring the organic functionalities in the low-k films by means of IR absorption spectroscopy, XPS, and spectroscopic ellipsometry.

5:00pm **TF-MoA10 Photoresist Removal on Porous Low-k Materials Using an Energetic (100s of eV) Oxygen Neutral Beam***, D.J. Economou,* ***Q. Wang,*** University of Houston*; B. White,* AMD and International SEMATECH*; P.J. Wolf,* Intel and International SEMATECH*; T. Jacobs,* Philips Semiconductors*; J. Fourcher,* International SEMATECH

Integration of porous low-k materials for interconnect technology present many challenges to the etch, ash and cleans processes. One challenge is the post etch removal of photoresist on open porous low-k films. Porous low-k films are very susceptible to damage by plasma processing, which can raise the overall keff of the film. Traditionally, a pure oxygen plasma ash is one method used for photoresist removal on CVD dielectrics. This method cannot be applied to exposed low-k films, because chemical and physical damage occurs. Successful photoresist removal on low-k films can be achieved by reducing chemistries or dilute O2 processes in RIE etch tools. This work shows how an energetic (100s of eV) oxygen neutral beam can be used to strip photoresist, without physical or electrical damage to the exposed low-k material. @FootnoteText@ Work at UH supported by International SEMATECH.

AVS 50th Anniversary Plenary Session
Room 310 - Session AP-TuM

Information

Moderator: M. Grunze, Universität Heidelberg, Germany

8:20am **AP-TuM1 Light Optical Nanoscopy in Cellular Biophysics*, C. Cremer*,** *U. Spoeri, A.V. Failla, B. Albrecht, Ch. Wagner, A. Schweitzer, L. Hildenbrand, I. Upmann, J. Rauch, G. Kreth, N. Kepper, Ch. Engelbrecht,* Univ. of Heidelberg, Germany*; A. Rapp,* Inst. for Molecular Biotech., Germany*; M. Hausmann,* Univ. of Freiburg, Germany*; D. Toomre,* Yale Univ.*; S. Martin, A. Pombo,* Medical Res. Council, UK*; T. Cremer,* Univ. of Munich, Germany **INVITED**

For many studies in cellular biophysics, it is highly desirable to develop optical methods for the analysis of specific biological nanostructures in the interior of three-dimensionally conserved cells. Here, important structural parameters to be considered are topology, i.e. mutual positions and distances of constituting subunits, as well as information about the size of such objects. In the low energy range, this has become possible by development of novel methods of far-field light fluorescence microscopy. Spectral Precision Distance Microscopy [SPDM] is based on labelling of neighbouring objects with different spectral signatures, spectrally selective registration, high precision position monitoring, and careful calibration of chromatic aberrations, cross talk etc. In combination with confocal laser scanning microscopy, SPDM allowed the measurement of spatial positions and mutual distances ("topology") of DNA sequences in specific human nuclear gene domains down to the 30 - 50-nanometer range. Theoretical considerations supported by "Virtual Microscopy" computer simulations indicated that using "Point Spread Function (PSF) Engineering" approaches with a suitably modified PSF, even at the fluorescence photon count number typical for single molecule fluorescence emission, a topological resolution limit down to the few-nanometer range with a precision in the subnanometer range might become feasible. For example, Spatially Modulated Illumination [SMI] far field light microscopy provides a PSF with the required properties; presently, experimental distance measurements in the direction of the optical axis down to the few nanometer scale, with a precision in the one-nanometer range (about 1/500 of the exciting wavelength) have been realized. Furthermore, SMI-approaches have been used to measure the diameter of individual fluorescent targets down to a few tens of nanometer, corresponding to about 1/16 of the exciting wavelength used.

9:00am **AP-TuM3 Biological Applications of Micro and Nanoscale Devices*, H.G. Craighead,*** Cornell University **INVITED**

Micro and nanoscale technologies are providing new possibilities for investigating life processes at the sub-cellular and molecular level. Electrical and optical probes can be constructed to enable increasingly fine scale resolution of the dynamic processes taking place in living systems. Similar approaches are allowing for analysis of increasingly small amount of biochemicals with the ultimate limit of single molecule analysis being seriously considered. Methods of fabricating micro and nanoscale interfaces with controlled structure and chemical composition are also providing vehicles for exploring the response of living cells to their environment. These same technologies may be exploited for a new biotechnology, making greater utility of active biomolecules combined with electronic and optical devices. This talk will explore some of the activity in the development of these new biological tools and approaches.

9:40am **AP-TuM5 Atomic-scale Device Fabrication in Silicon*, M.Y. Simmons,*** University of New South Wales, Australia **INVITED**

Over the past three decades the driving force behind the expansion of the microelectronics industry has been the ability to pack ever more features onto a silicon chip, achieved by continually miniaturising the size of the individual components. However, after 2015 there is no known technological route to reduce device sizes below 10nm. We demonstrate a radical new technology for atomic-scale (0.1nm) device fabrication in silicon using a combination of scanning tunnelling microscopy and atomic precision crystal growth. In particular we focus on the ability to place individual phosphorus atoms in silicon at precise locations and encapsulate them in epitaxial silicon with minimal diffusion and segregation of the dopants. We present results demonstrating the power of this approach both towards the controlled fabrication of atomic-scale devices in silicon, and towards the construction of a solid-state silicon based quantum computer.

10:20am **AP-TuM7 Nanometer Computing*, S.C. Goldstein,*** Carnegie Mellon University **INVITED**

The continuation of the remarkable exponential increases in processing power over the recent past faces imminent challenges due in part rising cost of design and manufacturing and the physics of deep-submicron semiconductor devices. A promising solution to these problems is offered by an alternative to CMOS-based computing, chemically assembled electronic nanotechnology (CAEN). In this talk we discuss the challenges and opportunities posed by CAEN-based computing. We briefly describe recent work in CAEN from the prospective of a computer architecture. The challenges arise from the set of assembly primitives inherent in bottom-up manufacturing. These primitives all but eliminate the ability to create arbitrary connections between devices. The manufacturing methods also imply defect densities which are significantly higher than today's. We show how molecular devices and post-manufacturing reconfiguration can overcome both these obstacles.

11:00am **AP-TuM9 Electronic Materials in the 21st Century: Is the Future Different from the Past?*, H.L. Stormer,*** Columbia University and Bell Labs, Lucent Technologies **INVITED**

The 20 century may well go into history books of technology as the century of the silicon chip. Silicon and its siblings, the III-V semiconductors, are unquestionably dominating electronics and photonics as we know them. These are just a handful of elements from the periodic table. Why these? What makes them so successful? Are there things they cannot do? Could we overcome such limitations by reaching out to other elements? Which ones and why? Nobody has good answers to these technologically and economically extraordinary important questions. But we can speculate.

Applied Surface Science
Room 324/325 - Session AS-TuM

Image Analysis and Polymer Characterization

Moderator: F.A. Stevie, North Carolina State University

8:40am **AS-TuM2 Advances in Chemical Imaging: NanoSAM and NanoESCA*, J. Westermann,*** *G. Schaefer, D. Funnemann, M. Maier,* Omicron NanoTechnology, GmbH, Germany

Electron spectroscopy has been a proven tool for scientific applications for decades. Challenging new applications are emerging from the fields of semiconductor and nanotechnology research and a key issue for these areas is the non-destructive imaging of sensitive structures with nanoscale dimensions. Characterization of their chemical composition and electrical properties goes hand in hand with this. We report on the development of two novel electron microscopes for chemical imaging that meet these requirements, especially for lateral image resolution in the nanoscale range. I. NanoSAM We present electron optical concepts and first results of a truly UHV compatible SEM column designed to meet the requirements for high-resolution with high beam currents. Performance checks on nanostructured samples demonstrate spot sizes below 3 nm at 15 keV beam energy and better than 5 nm at 3 keV, with sample currents being suitable for Auger electron analysis. Latest static Auger and SAM results, demonstrating the outstanding spatial resolution, will be shown. II. NanoESCA We present a parallel imaging electron microscope with an integrated high-resolution energy filter for Imaging XPS. It consists of a Photo Emission Electron Microscope (PEEM) with a large angular acceptance and an aberration corrected energy filter. The microscope allows for imaging with chemical contrast (Imaging ESCA) by energy filtering of photoelectron images. The analyzed energy of the photoelectron images ranges from threshold photoemission to 1600 eV. The instrument has been characterized with laboratory and synchrotron excitation sources. The spatial resolution limit measured so far in imaging ESCA mode is about 150 nm. The measured energy resolution follows the theoretical calculations. We show XPS spectra and energy filtered image series (video sequences) of: AlGaAs heterostructures, microstructured Au/Si and Ag/Ta samples.

9:00am **AS-TuM3 Correlation of XPS and AFM Images for Polymer Blends*, J. Farrar,*** *K. Artyushkova, J.E. Fulghum,* University of New Mexico*; F. Xu, N. Bantan, J. Khan,* Kent State University

Multi-technique analysis of heterogeneous polymer samples, based on AFM and XPS imaging, will provide a more complete picture of the sample under study than either technique alone. AFM provides both topographical and phase contrast information on the nanometer scale, but no chemical information is provided. Imaging XPS provides elemental and chemical information on the micron scale. A method to chemically identify the observed phases in AFM through correlation with quantitative XPS imaging will be discussed. Correlating the data from both techniques involves resizing, image alignment, resolution matching, and classification methods. The approach will be applied to a patterned polymer surface of known properties for validation and then to heterogeneous polymer blends of polystyrene/polybutadiene for phase identification. This project represents one aspect of the Active Knowledge Mesh Model (AKM) that is currently under development in our laboratories. AKM is a comprehensive image analysis system that integrates data from different techniques into a realistic three-dimensional model, visualizing structure and morphology, in multicomponent heterogeneous samples. This work has been partially supported by NSF ALCOM (DMR89-20147), NSF CHE-0113724, NSF IGERT CORE and UNM.

9:20am **AS-TuM4 XPS and Confocal Microscopy Data Fusion for Polymer Characterization***, **K. Artyushkova**, J.E. Fulghum, J. Fenton, J. Farrar,* The University of New Mexico*; J. Khan, F. Xu, N. Bantan,* Kent State University

Advances in materials development require a three-dimensional characterization of complex polymeric samples in terms of both chemical structure and morphology over feature sizes ranging from nanometers to millimeters. Correlating information from multiple techniques is one method for the development of a comprehensive 'picture' of the material under study. New opportunities for multi-technique correlations arise from the improved spatial resolution and decreased acquisition times now available in a variety of imaging methods. Imaging XPS and confocal microscopy (CM) are complementary techniques that, in combination, allow for the visualization of the internal structure of heterogeneous polymer samples. Quantitative chemical information that is readily available from the surface sensitive XPS images and spectra will be used to extract quantitative data from confocal images, which are acquired from different depth levels throughout the sample. The XPS and CM data sets can then be 'fused' to provide a surface-to-bulk visualization of changes in polymer chemistry. This work has been partially supported by NSF CHE-0113724 and NSF IGERT CORE program.

9:40am **AS-TuM5 Solvent Enhanced Surface Modification of Polymers Accompanying AFM Tip Induced Mechanical Stresses***, **F. Stevens**, R. Leach, J.T. Dickinson,* Washington State University

The response of thin polymer films and bulk surfaces to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by an AFM tip in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "protrusion" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have made a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface of several molecular weights in four solvents with dramatic differences in response. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by AFM. Extending this work, we have added temperature as a parameter, performing the tip stimulation at temperatures from 0 - 120 C. Major changes in the structures formed occur at higher temperatures due to increased solvent mobility and polymer mechanical properties with temperature.

10:00am **AS-TuM6 SF5+ Ion Beam Damage of Poly(Acrylates) Studied using Time of Flight Secondary Ion Mass Spectrometry***, **M.S. Wagner**, G. Gillen,* National Institute of Standards and Technology

Recent advancements in instrumentation for Secondary Ion Mass Spectrometry (SIMS) have focused on the development of polyatomic primary ion sources. Polyatomic ions have been shown to increase the secondary ion yields of molecular ions from organic materials when compared with monoatomic ions of similar mass. Furthermore, some polymer films, notably poly(methyl methacrylate) and poly(ethylene glycol), display the unusual characteristic of maintaining their characteristic molecular ion signals after extended polyatomic ion bombardment. This study focuses on the effect of the chemical structure of the polymer on its stability under extended SF5+ ion bombardment. The damage of spin cast polymer films by 5 keV SF5+ was studied using positive and negative ion static Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). A class of poly(acrylate) polymers with systematic changes to the monomer structure were investigated to determine the effects of polymer structure on the stability of their characteristic ion signals under 5 kV SF5+ bombardment in the ion dose range from 2.5 x 10@super 13@ - 5 x 10@super 14@ SF5+ ions/cm@super 2@. Preliminary results have shown that poly(methacrylic acid) and poly(methyl methacrylate) were stable under extended SF5+ bombardment while poly(methyl acrylate) was not, suggesting a role for the methyl group on the central carbon in the stabilization of the polymers under SF5+ bombardment. Monte Carlo calculations using the SRIM software@footnote 1@ show that the penetration depths of fluorine and sulfur ions in these polymers were the same despite the different damage characteristics, highlighting the importance of the chemical structure of the polymer on its stability under polyatomic ion bombardment. This study describes the breadth of applicability of SF5+ sputtering to the depth profiling of polymer films. @FootnoteText@ @footnote 1@ More information on this program can be found at http://www.srim.org.

10:20am **AS-TuM7 Time-of-Flight Secondary Ion Mass Spectrometry of Ordered Polymeric Monolayers: Effect on Tertiary Structures***, J.A. Gardella, Jr., **R. Rey-Santos**,* State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Poly(dimethylsiloxane) (PDMS) plays very important roles in biological and pharmaceutical applications. A similar study of poly(methylmethacrylate) published by Nowak et al in Analytical Chemistry in 2000 was used as a model. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is one of the most powerful techniques for polymer study. TOF-SIMS was used to study the fragmentation mechanism of this polymer. Using a statistical chain breaking model of PDMS helped us to understand the fragmentation pattern obtained in the spectra. The Langmuir-Blodgett (LB) technique helps us to prepare a molecular monolayer at the air/water interface. The LB technique was used to prepare well-ordered monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FTIR) is an ideal technique for surface study to obtain information about molecular structures. It has been used to compare results from amorphous, solution cast films to that from ordered, LB films of PDMS. An ion formation mechanism for PDMS was investigated to get information of the long-range forces between polymer chains.

10:40am **AS-TuM8 Grazing Incident X-ray Diffraction Study of Poly(alkylthiophene) Thin Films on Various Substrates***, M. Morita, T. Koga, H. Yakabe, S. Sasaki,* Kyushu University, Japan*; O. Sakata,* JASRI, Japan*; **A. Takahara**,* Kyushu University, Japan

The crystalline aggregation states of organic semiconductor molecules in thin films might play an important role in the performance of organic semiconductors. The purpose of this study is to reveal the crystalline orientation and crystallinity of spin-coated poly(3-hexylthiophene)[P3HT] on Si-wafer substrate at the nearã€€surface region and internal phase. The surface crystalline states of P3HT thin film were studied with synchrotron radiation in-plane grazing incidence x-ray diffraction GIXD. Surface modification of Si-wafer with perfluorohexylethyltrimethoxysilane prior to P3HT coating resulted in the preferential orientation with the alkyl side chains normal to the substrate surface. In contrast, the surface modification of Si-wafer with vacuum ultraviolet(VUV)-ray with wave length of 172nm or n-octadecyltrimethoxysilane resulted in the orientation with the alkyl side chains parallel to the substrate.

11:00am **AS-TuM9 Study of Water-Induced Reorganization of Amphiphilic Graft Copolymers Containing Poly(2-hydroxyethyl methacrylate) and Polydimethylsiloxane by Angle-dependent X-ray Photoelectron Spectroscopy***, **L. Chen**,* State University of New York at Buffalo*; A.P. van Bavel,* Eindhoven University of Technology, The Netherlands*; J.A. Gardella,* State University of New York at Buffalo

The free air surface composition and water-induced reorganization of a series of amphiphilic graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] backbones and hydrophobic poly(dimethylsiloxane) (PDMS) side chains prepared by both photoinduced-radical and anionic polymerization techniques were studied by angle-dependent X-ray Photoelectron Spectroscopy (XPS). Copolymers with broad molecular weight distributions (MWD; e. g. Mw/Mn = 3.0) were prepared by the radical copolymerization technique. Copolymers with narrow MWD (e. g. Mw/Mn = 1.1) were prepared by the anionic copolymerization technique. The free air surface composition of copolymers was studied as a function of MWD, PDMS bulk content and PDMS graft length. It was found that anionically prepared copolymers with narrow MWD have higher PDMS surface concentration than radically prepared copolymers with broad MWD. PDMS surface concentration increased with increasing PDMS bulk content. For a given PDMS bulk content, a longer PDMS graft chain gave a surface richer in siloxane. The water-induced reorganization of copolymers was studied as a function of MWD, PDMS graft length and water exposure time. The dry films were exposed to water (hydration) and then frozen in a nitrogen gas purge to preserve the surface composition during XPS analysis. The XPS results showed both MWD and PDMS graft length influenced the extent of the graft chain reorganization at the surface.

11:20am **AS-TuM10 The Role of Polymer Architecture and Environmental Humidity on the Interfacial Conformation and Properties of Surface-adsorbed Poly(l-lysine)-graft-poly(ethylene Glycol) Co-polymer***, **F. Assi**, S. Pasche, L. Feuz, N.D. Spencer, M. Textor,* ETH Zurich, Switzerland

The development of protein-resistant surfaces is of central interest in the context of biosensor chip development and for the design of medical implants in contact with blood. Self-organized films of PEG based co-polymers on different oxide surfaces are one system that has been investigated by a variety of surface characterization techniques in order to establish systematic correlations between the polymer composition/structure, interface architecture and interaction with protein-based biological media. A class of co-polymeric molecules of special interest is based on a poly(L-lysine) backbone, charged positively due to the presence of protonated amine groups at a neutral pH, and grafted with poly(ethylene glycol) side chains (short: PLL-g-PEG). Although the protein-resistant properties of these films have already been demonstrated, little is known about the effect of the co-polymer interfacial architecture on the resulting protein resistance. One of the most important factors turns out to be the polymer conformation in the adsorbed state, which depends not only on the polymer architecture but also on the environment the polymer, is exposed to. We report results that elucidate the surface conformation of PLL-g-PEG of different molecular architecture at various humidity levels in air as well as in contact with aqueous solutions, studied by means of atomic force microscopy (AFM, for the polymer conformation and adhesion properties) and ellipsometry (ELM, for the layer thickness). AFM force-distance measurements in compression between a 5-µm SiO@sub 2@ sphere and a PLL-g-PEG-coated substrate showed a good correlation with the architecture of the polymer. Furthermore, tensile-mode (pull-off) AFM studies were used to quantify the adhesion strength level of the polymeric molecules at oxide surfaces. The experimental results for different polymers were finally compared to the results of self-consistent field calculations.

11:40am **AS-TuM11 Ultra-fast Laser Ablation as a Facilitator for Depth-dependant Characterization of High Pigment Volume Concentration Organic Coatings***, **L.T. Keene**, C.R. Clayton, G.P. Halada, T. Fiero,* State University of New York at Stony Brook

The strong dielectric nature of most organic coatings, particularly those used on an industrial scale, presents the scientific investigator considering a depth-profiling approach to chemical characterization of such organic coatings with a serious challenge. The ultra-fast optical phenomenon of femtosecond laser ablation presents one possible solution to such a problem. An apparent athermal, non-selective ablation process becomes possible when the pulse temporal scale reaches the femtosecond (10@super -15@ s) level. This remarkable property of femtosecond-class lasers enables the multi-layer. removal of organic/inorganic composite coatings for the purpose of chemical characterization as a function of coating depth@footnote 3,4@ If proven experimentally, this capability becomes attractive when considering the depth-analysis of materials that demonstrate either strong dielectric properties (and, hence, resist depth profiling via traditional charged particle beam methods) or are chemically inhomogeneous in nature (which generally cause problems such as selective sputtering). This talk will focus on the experimental use of ultra-fast laser ablation for the facilitation of depth-profiling high solids organic coatings with particular emphasis placed on military application two-component solvent-based polyurethane coatings containing a variety of inorganic pigments and fillers.@footnote 1,2@ The high dielectric and chemically inhomogeneous natures of these coatings pose a demanding application for uniform laser removal without chemically modifying the host material. Cross-sectional analysis of the materials via Scanning Electron Microscopy (SEM) / Energy Dispersive Analysis of X-rays (EDS) will be shown. Ablation of the aforementioned materials was conducted both in atmosphere as well as high vacuum. Chemical modification of host material due to the ablation process will be discussed via the results of Fourier Transform Infrared Spectroscopic analysis of ablated material before, and after, ablation. Morphological features of ablated regions collected via high-resolution scanning confocal profilometry as a function of the processing parameters, and how these features limit the removal depth resolution, will be shown. @FootnoteText@ @footnote 1@ S. McKnight, J. Beatty, Mechanisms of Military Coatings Degradation, ARL Weapons & Materials Directorate, (1999)@footnote 2@ 1. C.R. Hegedus, et. al., "A Review of Organic Coating Technology for U.S. Naval Aircraft," Journal of Coatings Technology, Vol. 61, No. 778, pp 31-42, (1989)@footnote 3@ L. Keene, G. Halada, C. Clayton, S. McKnight, W. Kosik, "Novel Techniques for the Investigation of Long-term Photo-degradation of Mult-layer Polymer Coatings," in State-Of-The-Art Application of Surface and Interface Analysis Methods, The Electrochemical Society Proceeding Series, Pennington, NJ, (199th Electrochemical Society Meeting; Washington D.C.) (2001)@footnote 4@ A.A. Serafetinides, M.I. Makropoulou, C.D. Skordoulis, A.K. Kar Appl. Surf. Sci. 42-56 (2001) 180

Biomaterial Interfaces
Room 307 - Session BI-TuM
Cell/Surface Interactions

Moderator: K.E. Healy, University of California, Berkeley

8:20am **BI-TuM1 Modulation of Vascular Smooth Muscle Cell Behavior by Tuning Substrate Compliance***, X.Q. Brown, **J.Y. Wong**,* Boston University

During the development of vascular occlusive disease, abnormal vascular smooth muscle cell (VSMC) proliferation and deposition of extracellular matrix leads to hardening of the vessel. Recent studies have shown that changes in substrate compliance affect cell adhesion, migration and differentiation in several different cell types. However, effects of substrate stiffness on the behavior of VSMCs have not yet been investigated. Using polydimethyl siloxane (PDMS), we are able to create substrates with Young's modulus ranging from 3x10@super 4@ Pascal (Pa) to 2x10@super 6@ Pa, which is the range of elasticity that has been reported for a human aorta. We found that changes in substrate compliance affect the behavior of VSMCs. There is a 0.7 fold increase in cell number attached to stiff substrata (2x10@super 6@ Pa) compared to soft substrata (3x10@super 4@ Pa) and a 0.8 fold increase in cell area on stiff substrata. However, the rate of VSMC proliferation on stiff substrata is only 66% that of VSMC on soft substrata. Our results show that VSMCs are capable of sensing and responding to changes in substrate compliance in a range that is physiologically relevant, and PDMS is a useful tool to study the effect of substrate compliance on cell behavior. Our results support our hypothesis that during the development of vascular occlusive disease, changes in VSMC behavior leads to changes in the biochemical and biophysical properties of the vessel, which in turn influence the behavior of VSMCs.

8:40am **BI-TuM2 Mechanical and Biochemical Analyses of Cell Adhesion Strengthening Using Micropatterned Substrates***, **N.D. Gallant**, A.J. García,* Georgia Institute of Technology

Cell adhesion to fibronectin (FN) involves integrin binding and subsequent adhesion strengthening, which includes integrin clustering, interactions with cytoskeletal and signaling components to form focal adhesions (FA), and cell spreading. We applied micropatterning methods to control FA size and position to analyze the contributions of FA assembly to adhesion strength. Microcontact printing was used to pattern alkanethiol self-assembled monolayers into arrays of circular adhesive islands (2, 5, 10, 20 µm dia) with a non-adhesive background.@footnote1@ NIH3T3 fibroblasts adhered to FN-coated islands and remained constrained to the patterns presenting a nearly spherical morphology. Cells assembled robust adhesive structures that localized to the micropatterned islands and contained typical components of FA. Cell adhesion strength to FN-coated micropatterned islands was quantified using a spinning disk device that applies a well-defined range of hydrodynamic forces to adherent cells.@footnote2@ Adhesion strength exhibited significant time- and adhesive area-dependent increases. Comparison of experiments for equivalent contact areas showed a 9-fold increase in adhesion strength over time, independent of cell spreading. Bound integrins were quantified using a cross-linking/extraction/reversal biochemical technique.@footnote3@ Significant area dependence was also seen in integrin binding on micropatterned substrates and a correlation between increasing integrin binding and adhesion strength was observed. These results demonstrate that FA assembly, independently of changes in cell morphology, contributes significantly to adhesion strengthening. This work provides an experimental framework for the functional analysis of FA components in adhesive interactions. @FootnoteText@ @footnote

1@N.D. Gallant et al., Langmuir 18, 5579-5584, 2002.@footnote 2@A.J. García et al., J. Biol. Chem. 273, 10988-10993, 1998.@footnote 3@A.J. García et al., Mol. Biol. Cell 10, 785-798, 1999.

9:00am **BI-TuM3 The Use of XPS, SIMS, and Immunostaining to Examine the Behavior of Extracellular Matrix upon Cell Detachment from a Smart Polymer***, **H.E. Canavan**, X. Cheng, B.D. Ratner, D.G. Castner,* University of Washington

The temperature-dependent behavior of poly(n-isopropylacrylamide) (NIPAM) is directly transmitted to cells cultured on these surfaces. At culture temperatures, cells behave similarly to those on tissue culture polystyrene (TCPS); after being cooled to room temperature, cells cultured on NIPAM spontaneously detach as contiguous sheets. In comparison, cells grown atop the TCPS surface remain attached for hours or days, requiring the use of enzymatic digestion or physical scraping to detach them. In addition, cell sheets detached from NIPAM surfaces appear to retain their function upon transfer to another growth surface, possibly due to the concurrent detachment of at least one protein of the Extracellular Matrix (ECM), fibronectin (FN). However, the extent to which ECM detaches from the NIPAM surface has remained unknown. We present a thorough examination of the cellular response to NIPAM using X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), and immunostaining. XPS is used to make a quantitative comparison of the amount of protein atop NIPAM after cell removal. The primary proteins of the ECM (FN, laminin, and collagen) are examined using immunostaining to determine which of the ECM proteins studied lift off with the cellular layer. In addition, SIMS is used to identify the presence and identity of proteins left at the NIPAM surface after liftoff. Finally, the low-temperature liftoff technique is compared to other traditional cell removal protocols. Our SIMS, XPS, and immunoassay results suggest that low-temperature liftoff of the cell monolayer from the NIPAM surface is accompanied by the majority of the components of the ECM.

9:20am **BI-TuM4 Neurite Outgrowth on Well Characterized Surfaces: Chemically and Spatially Controlled Fibronectin and RGD Substrates***, **Z Zhang**, R. Yoo, M. Wells, T.P. Beebe, Jr.,* University of Delaware*; R. Biran, P. Tresco,* University of Utah*; J. Hyun, W. Jun, A. Chilkoti,* Duke University

Study of axonal growth and ligand-receptor interactions requires specificity and careful characterization of the biomaterial substrates to which the neurons bind. Without highly specific surface characterization, it would be impossible to predict the effects of ligand surface density, spatial distribution, and conformation on the outgrowth of a neuron. Here we report two different methods of surface modification (a heterobifunctional crosslinker and Pluronics @super TM@) for immobilization of fibronectin (FN) and fibronectin-derived RGD-containing peptides to the substrates. Proteins and peptides were immobilized to glass surfaces at different concentrations. Various surface analytical techniques, such as contact angle, x-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were used for analysis of the substrates at each step of the two different chemistries involved. After immobilization of fibronectin and RGD-containing oligopeptides, the modified surfaces were plated with dorsal root ganglia neurons of the rat. Neuron outgrowth rates on the various surfaces were measured and different bioactivity was observed on different modified surfaces. In order to spatially control neurite outgrowth on the substrates, patterned and gradiently FN-covered surfaces were synthesized and tested for bioactivity. An amphiphilic comb polymer presenting oligoethylene glycol side-chains was used to create microcontact-printed patterned surfaces because of its excellent protein repellant and cell resistance properties.

9:40am **BI-TuM5 Surfaces Engineered to Target Integrins to Direct Cell Adhesion and Function***, **A.J. Garcia**,* Georgia Institute of Technology **INVITED**

Cell adhesion to adsorbed extracellular matrix proteins and adhesive sequences engineered on synthetic surfaces plays a critical role in numerous biomaterial, tissue engineering, and biotechnological applications. Cell adhesion to adhesive motifs is primarily mediated by integrin adhesion receptors. In addition to anchoring cells, supporting cell spreading and migration, integrins provide signals that direct cell survival, proliferation, and differentiation. We have developed two biomolecular strategies for the engineering of surfaces to control integrin binding and cell adhesion in order to direct cell function. The first approach focuses on surfaces presenting well-defined chemistries that control protein adsorption to modulate integrin binding in order to potentiate cell adhesion and signaling thereby directing cell differentiation. In a second approach, we have engineered fibronectin- and collagen-mimetic surfaces presenting controlled ligand densities in a non-fouling background that promote the binding of specific integrin receptors and direct adhesive interactions. These surface engineering strategies provide a basis for the rational design of robust biospecific surfaces that tailor adhesive interactions and elicit specific cellular responses for the development of bioactive implant surfaces, 3D hybrid scaffolds for enhanced tissue reconstruction, and growth supports for enhanced cellular activities.

10:20am **BI-TuM7 Atomic Force Microscopy Imaging and Force Spectroscopy of Microbial Cell Surfaces***, **Y.F. Dufrene**,* Université Catholique de Louvain, Belgium **INVITED**

The advent of atomic force microscopy (AFM) has recently opened a wide range of novel possibilities for probing microbial cell surfaces on the nanoscale.@footnote 1@ Using AFM imaging in aqueous solution, microscopists can visualize cell surface nanostructures (surface layers, appendages), follow physiological changes (germination, growth) and monitor the effect of external agents (antibiotics, metals) in real-time.@footnote 2@ Further, using force spectroscopy, researchers can learn about local biomolecular interactions and physical properties. Spatially resolved force mapping offers a means to determine physical/chemical heterogeneities at the subcellular level, thereby providing complementary information to classical characterization methods. Force measurements allow the cell surface elasticity to be determined.@footnote 3@ Functionalizing the AFM tip with chemical groups or biomolecules enables quantitative measurements of surface charge,@footnote 4@ surface hydrophobicity@footnote 5@ and receptor-ligand interactions. Finally, single-molecule force spectroscopy can be applied to cell surface molecules to gain insight into their mechanical properties.@footnote 6@ Clearly, these new AFM-based experiments contribute to improve our understanding of the structure-function relationships of microbial cell surfaces and will have considerable impact on biotechnology and medicine. @FootnoteText@@footnote 1@Y.F. Dufrene, J. Bacteriol., 184, 2002, 5205-5213. @footnote 2@Y.F. Dufrene, C.J.P. Boonaert, P.A. Gerin, M. Asther, P.G. Rouxhet, J. Bacteriol., 181, 1999, 5350-5354. @footnote 3@H.C. van der Mei, H.J. Busscher, R. Bos, J. de Vries, C.J.P. Boonaert, Y.F. Dufrene, Biophys. J., 78, 2000, 2668-2674. @footnote 4@F. Ahimou, F.A. Denis, A. Touhami, Y.F. Dufrene, Langmuir, 18, 2002, 9937-9941. @footnote 5@Y.F. Dufrene, Biophys. J., 78, 2000, 3286-3291. @footnote 6@B.C. van der Aa, R.M. Michel, M. Asther, M.T. Zamora, P.G. Rouxhet, Y.F. Dufrene, Langmuir, 17, 2001, 3116-3119.

11:00am **BI-TuM9 Molecule Specific Imaging Analysis of Carcinogens in Breast Cancer Cells using Time-of-Flight Secondary Ion Mass Spectrometry***, **K.J. Wu**, J.N. Quong, M.G. Knize, K.S. Kulp,* Lawrence Livermore National Laboratory

The concentration and localization of intracellular chemical compounds such as pharmaceuticals and carcinogens are important, specifically for application in physiology and medicine. Cooked muscle meats contain small amounts of rodent carcinogens belonging to the heterocyclic amine class of compounds and are implicated in human cancers at various organ sites. 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) is the most mass abundant in cooked foods. PhIP is a genotoxic carcinogen, which has been demonstrated to cause dose-dependent mammary and prostate tumor formation in rats. In this report we will present the results on time-of-flight secondary ion mass spectrometry (TOF-SIMS) studies of several MCF7 line of human breast cancer cells. Protocols for high vacuum compatible tissue and cell culture preparation have been developed. Such direct imaging approach permits an acquisition of element and molecule-specific images directly from the cell surface. The results show the intracellular concentration and distribution of low level carcinogenic compounds such as PhIP in flash-frozen MCF7 cells; the time dependent effects of heterocyclic amine carcinogens interaction with MCF7 cells. We will discuss two major efforts to further the imaging mass spectrometry applications for biological samples: ME-SIMS approach to enhance the ionization yields and multivariate analysis data reduction technique for compound distribution on cell surfaces. @FootnoteText@ This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

11:20am **BI-TuM10 Preparation and Characterization of Chemically Patterned Surfaces for Cell-Surface Interaction Studies***, **D. Marton**, E.A. Sprague,* The University of Texas Health Science Center at San Antonio*; K. Cho,* University of Michigan Medical Center*; J.C. Palmaz,* The University of Texas Health Science Center at San Antonio

There is significant evidence that surface chemistry plays a major role in the way proteins and living cells interact with biomaterial surfaces. These phenomena could be best studied on surfaces with designed and identifiable chemically different areas. For this purpose we developed surface patterning techniques that combine vacuum deposition (dc sputtering or evaporation) and sputter removal of material. Four types of patterned surfaces were developed. Substrates were made of either pre-treated hydrophilic silicon or hydrophobic Teflon. Two types of specimens were created using each substrate type. The first set of patterned surfaces, called "dot pattern" comprised of carbon, stainless steel and gold dots of nominal 25 micron diameter directly deposited on the clean substrates through a stainless steel mask with a polka-dot type hole arrangement. The second set of patterned surfaces, called "hole pattern" were produced by first depositing a continuous layer of carbon, stainless steel or gold. The specimens were then sputtered through the holes of the mask using 1-2 keV Ar ions until the underlying Teflon or silicon became exposed. Typical film thicknesses were 5-10 nm. All specimens were analyzed to verify the patterning on five areas using ToF-SIMS imaging and some using XPS imaging. Pattern definition depends on mask apposition, and, in the case of insulating specimens, on charging effects. In general, the hole patterns have sharper boundaries than the dots. Using an in vitro cell migration model, human aortic endothelial cells were observed to respond to the different patterns with respect to cell shape and cell migration rate. Pattern dependent protein adherence was also observed.

11:40am **BI-TuM11 Drug Testing and Environmental Toxin Detection using Cell-based Biosensors***, **A. Natarajan**, P. Molnar, K. Sieverdes, A. Jamshidi, J.J. Hickman,* Clemson University

In the last decade the threat of environmental pollution, biological warfare and new diseases has increased research into cell-based biosensors. The need for more advanced methods to evaluate candidates has pushed this area of research even further. Cells are natural sensors in the body and react to different bioactive compounds in specific ways. Our research exploits this feature, using the ion channels of electrically active cells like cardiac myocytes, to create a database of specific responses. These responses can then be used to detect the acute presence of a substance. A traditional method of studying drug and toxin effects has been low throughput patchclamp electrophysiology. Our cell-based biosensor consists of a uniform monolayer of cardiac myocytes on a microelectrode array (MEA) with 60 substrate-integrated electrodes. The microelectrode arrays are surface modified and the media used for the cells is defined. Surface analysis was used to verify surface modifications. Long-term recordings of beating cells produced extracellular field potentials in the range 100 µV to 1200 µV, with a beating frequency of 0.5 to 4 Hz. The toxins tested were classified as drugs (epinephrine), heavy metals (Cadmium) and pyrethroids, a group of synthetic pesticides. Pyrethroids modify sodium channels thus disrupting nerve cells in insects. Epinephrine is a well-known stimulant for the heart. Cadmium chloride causes serious illnesses with the same symptoms as lead poisoning. Concentrations used were mainly 1, 10 and 100 µM. Each of the above substances produced specific responses in the action potential signals, changing amplitude, frequency and shape. 10 µM Epinephrine increased spike frequency from 4 Hz to 6 Hz. Our goal is to replace patchclamp electrophysiology with microelectrode arrays as a means to testing many drugs and toxins. Future work involves making this system more stable, creating a larger database and extending the use for chronic detection of compounds.

High-k Gate Dielectrics and Devices Topical Conference
Room 317 - Session DI-TuM

High-k Dielectric Growth and Processing

Moderator: R.L. Opila, University of Delaware

8:20am **DI-TuM1 Effects of Transistor Fabrication Process Conditions on Electrical Characteristics of High-k Gate Dielectrics***, **G. Bersuker**, P. Zeitzoff, G.A. Brown, J. Gutt, N. Moumen, J. Peterson, J. Barnett,* International Sematech*; B.H. Lee,* International Sematech, Korea*; C.H. Lee, S. Gopalan, N. Chaudhary, Y. Kim, C. Young, P.S. Lysaght, H.-J. Li, M. Gardner, R.W. Murto, H.R. Huff,* International Sematech **INVITED**

Comprehensive evaluation of high-k materials for gate dielectric applications requires fabrication of transistor test structures. The complex fabrication process includes several operations employing highly reactive ions, which may potentially affect electrical performance of the high-k materials. It is, therefore, critical from a materials evaluation standpoint to separate intrinsic properties of high-k dielectrics from process-related effects. The latter is the focus of this investigation. In particular, we concentrate on the charging problem associated with high-k materials, which appears to be one of the major factors affecting threshold voltage and mobility in high-k gate dielectric transistors. Our results demonstrate high sensitivity of the high-k films to the transistor fabrication process conditions. It is shown that electrical properties of gate stacks fabricated with a variety of combinations of ALD and MOCVD Hf-based dielectric compositions can be greatly affected by process-induced charges (PIC). PIC caused by negatively charged ions and/or electron trap inducing species may accumulate in the area of the high-k film exposed to various plasma operations during post gate definition processing (such as poly etch, ash/clean and spacer deposition). These contaminants may diffuse under the gate during subsequent high temperature processing and adversely affect device performance. Significant dependence of the electrical characteristics on the process scheme employed for the transistor fabrication complicates the evaluation of the intrinsic properties of the high-k gate dielectrics.

9:00am **DI-TuM3 Characteristics of High-k Gate Dielectric Formed by Oxidation of Sputtered Hf/Zr/Hf Thin Fims on the Si Substrate***, H.-D. Kim, **Y. Roh**, N.-E. Lee, C.-W. Yang,* Sungkyunkwan University, Korea

Recently, high-k gate oxide have been extensively investigated to overcome the problems such as large leakage current caused by the direct tunneling through extremely thin SiO@sub 2@. We previously demonstrated that simple oxidation of sputtered Hf thin films on Si results in HfO@sub 2@HfSi@sub x@O@sub y@ stacked high-k gate oxides simultaneously with excellent physical and electrical properties; negligible hysteresis, excellent EOT value (1.2 nm) and low leakage current (2 X 10@super -3@ A/cm@super 2@ at 1.5 V after compensating the flatband voltage). In this work, we further investigated the characteristics of high-k gate dielectric formed by the oxidation of Hf/Zr/Hf film (1.5 nm) deposited on the Si substrate by a sputtering method. The oxidation and annealing were performed at 500~800 °C for 60~120 min under O@sub 2@ ambient and at 500~900 °C for 30~60 min under N@sub 2@ ambient, respectively, in furnace. To form MOS capacitors, Pd gate was thermally evaporated on the HfO@sub 2@ film using a shadow mask with circular dots. We found that the electrical properties of MOS devices with oxidized Hf/Zr/Hf film are further improved as compared to those obtained after oxidizing single Hf film with same thickness (i.e., 1.5 nm) In addition to the negligible hysteresis, we obtained the EOT value of 1.15 nm and the leakage current density of 4.2 X 10@super -3@ A/cm@super 2@ at -3 V. More importantly, the deterioration of high-k gate oxide caused by high-temperature oxidation and/or annealing processes drastically minimized. For example, even after the 900 °C oxidation of Hf/Zr/Hf film, EOT and leakage current density were 1.37 nm and 2.78 X 10@super -6@ A/cm@super 2@ at -3 V, respectively. We speculate that this improvement is due to the minimization of undesirable SiO@sub 2@ formation between High-k oxide and Si. These results, as well as further investigation of physical properties of the samples using XPS, will be presented at the conference.

9:40am **DI-TuM5 Study of ZrO@sub 2@ Initial Stage Deposition on Si(100) During High Vacuum Chemical Vapor Deposition***, **Z. Song**, R.D. Geil, D.J. Crunkleton, V.L. Wahlig, B.R. Rogers,* Vanderbilt University

ZrO@sub 2@ is a potential high-k material to replace SiO@sub 2@ gate dielectrics in MOSFET devices. Electrical and structural requirements of the gate dielectric dictate that these layers will be significantly less than 10 nm thick. Studies of the initial stages of ZrO@sub 2@ deposition is needed in order to create an abrupt, low defect interface with silicon. In this work, we used atomic force microscopy (AFM), spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) to study the initial deposition behavior of ZrO@sub 2@ films. Films were deposited at pressures of 10@super -5@ to 10@super -4@ Torr and substrate temperatures of 250 to 450 °C. We observed a transition from 3D growth to 2D growth. These results suggest that a deposition temperature greater than 350 °C is needed to form a uniform film.

10:00am **DI-TuM6 Thin Film Growth and Composition Characterization of Hafnium Oxide Grown on Surface Treated Silicon by Atomic Layer Deposition***, **R. Inman**, A. Deshpande, G. Jursich,* American Air Liquide

New materials are needed for future generation of semiconductor devices and hafnium oxide along with silicate and aluminate combinations continue to show promise for meeting stringent demands of the gate dielectric insulator layer in CMOS transistors. In this critical application, film growth needs to be well controlled by process conditions and deposition requires high level of conformality as layer thickness extends below 100 nm dimension and more complex gate geometries are proposed. To best serve these requirements, atomic layer deposition is an ideal method of growing such films. In this work, thin films of hafnium oxide were deposited on Si(100) substrates by means of atomic layer deposition (ALD) technique using tetrakis(diethylamino)hafnium precursor. The resulting composition and purity of these films were determined at different substrate temperatures using x-ray and Fourier Transform Infrared (FTIR) spectroscopies. FTIR studies confirmed that the resulting films are relatively free of carbon contamination and provided a measure of hydroxyl groups in the film. The kinetics of film growth was also investigated by measuring film thickness as a function of substrate temperature and reagent pulsing characteristics. The thickness measurements indicated a relatively mild inverse temperature dependence of film growth in the range of 250 - 350 C. The cycle number dependence of film growth was examined at both high and low cycle number in order to infer the nucleation growth of the film. These results will be presented using Si substrates with different surface treatments.

10:20am **DI-TuM7 The Effect of Hf Content in Liquid Precursor on the Properties of Mist Deposited Ultra-Thin Films of HfSiO@sub 4@***, **K. Chang**, K. Shanmugasundaram,* The Pennsylvania State University*; D.-O. Lee, P. Roman, P. Mumbauer,* Primaxx Inc.*; J.R. Ruzyllo,* The Pennsylvania State University

Ultra-thin (<10nm) films of hafnium silicate formed by mist deposition method for gate dielectric application in advanced MOS devices were investigated. Precursors with Hf:Si ratio of 0.103:1, 0.276:1, and 1:1 were prepared to investigate the effect of Hf content on mist deposition process and film characteristics. MOS capacitors were fabricated for electrical characterization using Pt gate electrode. The Hf composition in the HfSiO@sub 4@ film was analyzed with angle-resolved X-ray photoelectron spectroscopy. The 1:1 precursor resulted in 12.6 at.% of Hf in the film and 7.5 at.% of Hf was obtained in the HfSiO@sub 4@ film deposited with 0.103:1 precursor. Deposition rate of HfSiO@sub 4@ linearly increases with the Hf content in the precursor even though the Hf composition in the film didn't scale in the same order. Despite the difference in Hf content of the precursor, an interfacial oxide 2.2nm ~ 3.0nm thick was always detected by transmission electron microscopy. Through electrical characterization, it was determined that the obtained gate stacks feature an equivalent oxide thickness of 0.8nm ~ 1.5nm depending on the process. It is postulated that the lower EOT is caused by Hf diffusion from HfSiO@sub 4@ film during thermal treatment step and lower EOT of the interfacial layer. For lower EOT of the interfacial oxide, higher Hf content in the precursor is needed. Using 1:1 precursor, EOT 1.5nm HfSiO@sub 4@ thin film is deposited with leakage current density of less than 1×10@super -2@ A/cm@super 2@.

10:40am **DI-TuM8 The Effect of Surface Preparation and Post Growth Annealing on the Thickness and Composition of High-k Layers Grown on Silicon***, T. Conard,* IMEC, Belgium*; R.K. Champaneria, P. Mack,* Thermo Electron, UK*; R.G. Vitchev,* Facultes Universitaires Notre-Dame De La Paix (FUNDP), Belgium*; R.G. White, **J. Wolstenholme**,* Thermo Electron, UK

The move to high-k materials for gate dielectrics brings with it a new set of parameters that require characterisation. As with silicon dioxide, the thickness of the layer must be measured but, in addition, the thickness of any intermediate layer must be measured also. The chemistry of the intermediate layer is likely to affect the electrical properties of the layer and therefore needs to be understood along with the factors that affect this chemistry. XPS has an information depth that is similar to the thickness of the layers and, therefore, can be used to characterise them. If the information depth is controlled by varying the photoelectron emission angle (angle resolved XPS or ARXPS) more information becomes available. Thickness of surface and subsurface layers can be measured with accuracy and precision. The chemical state of each component of the material can also be determined and the distribution of chemical states within the layer can be measured. Since no material is removed during the measurements, ARXPS can be regarded as a non-destructive technique. This technique has been used to analyse HfO2 and Al2O3 layers on silicon prepared by ALD or MOCVD. A comparison will be made of the layers grown on relatively thick (up to ~1 nm) silicon oxide with those grown on thin oxide layers and on layers containing nitrided SiO2. It will be shown how XPS and ARXPS can determine the effect of the preparative method on the thickness of the layers and the chemical states of the component materials. The results will be presented in the context of those on the same materials from other techniques.

11:00am **DI-TuM9 Si and Ge Surface Functionalization Characterized by In Situ and Ex Situ Infrared Spectroscopy***, M.M. Frank,* IBM T.J. Watson Research Center and Rutgers University*; M.-T. Ho, S. Dörmann, C.-L. Hsueh,* Rutgers University*; L.J. Webb, N.S. Lewis,* California Institute of Technology*; S. Rivillon,* Rutgers University*; O. Pluchery,* Université Paris 6, France*; **Y.J. Chabal**,* Rutgers University

Chemical functionalization and passivation of semiconductor surfaces is often necessary to foster uniform nucleation and high-quality interface formation in the deposition of ultrathin high-@kappa@ gate dielectrics and organic films. To understand the formation of such monolayers in wet, gaseous, or ultra-high vacuum environments, it is desirable to monitor surface reactions in situ. Utilizing infrared absorption spectroscopy, we have achieved such in situ monitoring with submonolayer sensitivity. We have performed both in situ and ex situ studies to gain mechanistic insight into surface chemical reactions on HF-etched, mostly H-terminated Si and Ge surfaces. Chemical species studied include: Cl, supplied via gas phase and wet chemistry, enabling subsequent activation of the Si substrate through hydroxylation; trimethylaluminum (Al(CH@sub 3@)@sub 3@) and other metal organic precursors, to initiate homogeneous atomic layer deposition or chemical vapor deposition of high-@kappa@ gate dielectrics (Al@sub 2@O@sub 3@ and HfO@sub 2@) onto hydrogen-terminated Si; and alkyl groups from wet chemistry, to passivate the Si. In particular, we shed light on the reactivity of Si-CH@sub 3@ and metal-CH@sub 3@ species formed in reactions with organic high-@kappa@ precursors and in wet chemical passivation. On Ge, we are investigating hydrogen passivation in HF using in situ methods, as well as the oxidation of such passivated surfaces. We compare and contrast the passivation and oxidation mechanisms on Si and Ge substrates.

11:20am **DI-TuM10 Plasma Deposition of RuO@sub2@ on HfO@sub2@ for Gate Electrode Applications***, **D.B. Terry**, J.M. Doub, G.N. Parsons,* North Carolina State University

Ruthenium-based metals are potential candidates for gate electrodes in advanced gate stack applications. The detailed structure of the interface between high-k dielectrics and the gate metal will be important to maintain low equivalent oxide thickness, but the effect of metal deposition on the high-k/metal interface structure is not known. We have deposited RuO@sub2@ metal from Tris-tetramethyl-heptadianato Ru (Ru TMHD) introduced downstream from a remote N@sub2@O plasma at 365 and 500°C, and examined the deposited film and interface structure using Auger and X-ray photoelectron spectroscopies. The growth rate at 500°C is approximately twice that at 365°, and films show some evidence for N and C incorporation, consistent with the 250°C decomposition temperature of the Ru TMHD. Based on AES results, the O/Ru ratio is larger for the films deposited at higher temperature. Because of the difference between the oxidizing and reducing environments in CVD processing, we expect that metallic oxides such as RuO@sub2@ will result in different metal/dielectric interface structure than for elemental metal/dielectric interfaces. To examine the role of deposition chemistry on interface structure, several thicknesses of RuO@sub2@ have been deposited by plasma CVD on HfO@sub2@ formed in our lab by atomic layer deposition. The effect of HfO@sub2@ surface structure, and the trends in RuO@sub2@ composition with film thickness determined using AES and XPS will be presented and discussed.

11:40am **DI-TuM11 Novel Ultra-thin TiAlO@sub x@ Alloy Oxide for New Generation of Gate Dielectric*, W. Fan,*** Northwestern University*; S. Saha, B. Kabius, J.M. Miller, J.A. Carlisle, O. Auciello,* Argonne National Laboratory*; S.Y. Li, V.P. Dravid, R.P.H. Chang,* Northwestern University*; C. Lopes, E.A. Irene,* University of North Carolina, Chapel Hill

A novel TiAlO@sub x@ alloy oxide has been developed and studied as an alternative gate oxide material for CMOS devices (patent pending). Ultra-thin TiAl (3:1) films with physical thickness 3-20 nm were grown on n-Si (100) by sputter deposition. In-situ oxidation was then performed by using both molecular oxygen (P=1.0x10@super -3@ Torr) and atomic oxygen sources (P=1.0x10@super -4@ Torr). The formed TiAlO@sub x@ exhibits amorphous structure on Si, as revealed by XRD and TEM analyses. In-situ XPS study shows that a full oxidation of TiAl can be achieved at 500@super o@C using both oxygen sources. However, the TiAlO@sub x@ layer formed through atomic oxygen annealing presented a leakage current 150 times lower than the one with molecular oxygen annealing. Since both Ti and Al have more negative oxide formation energies than Si, the presence of Ti and Al at the interface with Si significantly reduces the formation of interfacial SiO@sub x@. It has been confirmed by XPS depth profile, ellipsometry and cross-sectional TEM, which revealed ~1 nm SiO@sub x@ layer formed at the oxide/semiconductor interface with 500@super o@C oxidation. The amorphous TiAlO@sub x@ layer with equivalent oxide thickness (EOT) of 1.7 nm and negligible hysteresis was obtained via atomic oxygen exposure at 500@super o@C, exhibiting high permittivity (~30) and low leakage current density (1.2x10@super -2@ A/cm@super 2@). After post deposition annealing with top gate electrode in place, the leakage was further improved and reached 5.4x10@super -5@ A/cm@super 2@. Furthermore, extended study shows that a full transition of TiAl to TiAlO@sub x@ can be accomplished at room temperature by exposure to atomic oxygen beam. Interfacial SiO@sub x@ formation, therefore, was completely eliminated and TiAlO@sub x@ layer with EOT less than 1 nm was achieved on Si. @FootnoteText@*This work was supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.@.

Electrochemistry and Fluid Solid Interfaces
Room 326 - Session EC+SS-TuM

Water at Interfaces I: Structure and Electrochemistry

Moderator: E.M. Stuve, University of Washington

8:20am **EC+SS-TuM1 A Microreactor System for Electrocatalytic Kinetics: Methanol Oxidation on Platinum Electrodes at Elevated Temperature*, N. Arvindan,*** *L. Arnadottir, E.M. Stuve,* University of Washington

We describe a silicon-based microreactor for measurement of electrocatalytic rate constants for methanol oxidation on platinum and modified platinum electrodes. The device consists of silicon and pyrex wafers bonded together by a Teflon treatment to create an enclosed flow channel 0.25 mm deep, 1.5 mm wide, and 25 mm long. The flow channel includes deposited platinum lines for fluid heating, temperature measurement, and a counter electrode. A separate palladium line serves as a reference electrode. The working electrode is inserted into an opening in the flow channel. The working electrode can be a single crystal, polycrystalline sample, or actual supported catalyst. The microreactor can accommodate mixed metallic catalysts such as PtRu. Methanol oxidation is measured at constant potential following a step from a non-reacting potential. Accumulation of surface species like CO is subsequently measured by linear sweep voltammetry. These two measurements enable the overall oxidation rate of methanol to be compared with the CO oxidation rate. Reaction studies over the range of 80 to 100 Â°C show that methanol oxidation occurs at the same rate as CO oxidation, consistent with the series reaction path (methanol to CO to carbon dioxide) being the dominant mechanism. The results conclusively show that thermal desorption of CO is insignificant, even at temperatures as high as 95 Â°C. At 95 Â°C turnover rates vary from 0.1 to 1 per second for the respective potential range of 400 to 600 mV vs. RHE. These results show that unmodified polycrystalline platinum is an effect catalyst for methanol oxidation at 95 Â°C and support the feasibility of high temperature direct methanol fuel cells.

8:40am **EC+SS-TuM2 In Situ Characterization of Nucleation and Growth During Electrochemical Deposition of Copper*, A. Radisic,*** Johns Hopkins University*; M.J. Williamson,* University of Virginia, Charlottesville, current address Lawrence Berkeley National Laboratory*; M.C. Reuter, S.J. Chey, R.M. Tromp, F.M. Ross,* IBM T.J. Watson Research Center*; P.C. Searson,* Johns Hopkins University

In current copper metallization technology, copper is electrodeposited onto a barrier layer pre-covered by a thin copper seed layer. As the feature sizes of the trenches and vias continue to shrink, strategies for direct deposition of copper onto the barrier layer need to be explored. Copper electrodeposition on diffusion barrier layers occurs through 3D island growth, and hence nucleation and growth play an important role in determining the properties of metallization. We have studied nucleation and growth processes during electrochemical deposition of copper using the in situ transmission electron microscopy.@footnote 1@ This is a real time, high resolution imaging technique that allows us to study the evolution of island density with time, as well as the spatial and temporal correlations between islands. In this study we report on the nucleation and growth parameters for copper electrodeposition, obtained using both ex situ and in situ experimental techniques. We examine the relationship between potential, solution chemistry, and island density. Furthermore, we show that under appropriate experimental conditions, a high density of copper islands and a continuous thin copper film can be obtained at the surface. @FootnoteText@ @footnote 1@ F. M. Ross, Growth processes and phase transformations studied by in situ transmission electron microscopy. IBM Journal of Research, 44, 489-501, 2000

9:00am **EC+SS-TuM3 Electrochemical Synthesis of Multifunctional Building Blocks for Nanosystems*, P.C. Searson,*** Johns Hopkins University **INVITED**

Electrochemical synthesis is an important tool in the fabrication of multicomponent or layered structures with high aspect ratio. Nanometer size particles, such as nanorods or nanowires exhibit many unique properties associated with their inherent shape anisotropy. For example, ferromagnetic (FM) nanowires exhibit unique and tunable magnetic properties due to the shape anisotropy and the small wire dimensions. The introduction of multiple segments along the length of a nanowire can lead to further degrees of freedom associated with the shape of each segment and the coupling between the layers. For example, modifying the diameter, composition, and layer thicknesses in multilayer FM/NM (NM = nonmagnetic material) nanowires it is possible to tailor the orientation of the magnetic easy axis and properties such as the Curie temperature, coercivity, saturation field, saturation magnetization, and the remanent magnetization. The unique properties of multisegment nanowires can also be exploited in suspensions where the manipulation and assembly of nanometer scale particles has become an important tool in nanotechnology. The ability to bind molecules with different functionalities to different components in multisegment nanowires introduces an additional degree of freedom that is potentially important in enhancing surface reactions, immobilizing molecules, and assembling scaffolds for tissue engineering.

9:40am **EC+SS-TuM5 Photoexcited Electrodeposition of Cu Structures on p-Si(001)*, C. Scheck,*** *Y.-K. Liu, P. Evans,* The University of Alabama*; G. Zangari,* University of Virginia*; R. Schad,* The University of Alabama

Selective growth of metals on semiconductors has recently raised considerable interests, due to its possible application in the direct formation of interconnects on Si. We produced small structures by photo-excited electroless plating of Cu on p-type Si(001). The p-type substrate forms a Schottky barrier with the solution which inhibits the plating process. Local illumination creates minority carriers which become available to discharge metal ions. The illumination was done by converging a 1-5 mW laser beam to a 1-2mm focus diameter on the substrate in the plating solution using an optical microscope. We analyzed the diameter of the growing dots as a function of laser light wavelength and intensity, illumination duration, composition of the solution and charge carrier lifetime in the substrate. The dimensions of the dots are determined by the diffusion length of the excited minority carriers. The lateral dimensions of the produced structures are found to decrease with reduced laser wavelength or intensity but is independent of the duration of the illumination. Shorter minority carrier lifetimes in the semiconductor substrate lead to a further reduction of structure dimensions. The effect of spontaneous background precipitation on the Si surface is studied as a function of solution composition. The optical reflectivity can be related to the fractal surface roughness.

10:00am **EC+SS-TuM6 Ultrahigh Vacuum Studies of Static and Dynamic Solid Oxide Electrocatalysts by Field Ionization and Spectroscopic Techniques***, **R.A. Manghani**, V.K. Medvedev, E.M. Stuve,* University of Washington

Understanding solid oxide fuel cell reactions and electrochemical promotion of catalysts requires a complete description of the three-phase boundary (catalyst/electrolyte/fluid) under both static and dynamic (that is, reacting) conditions. We have undertaken two approaches to examine solid oxide electrocatalytic surfaces under well-defined, ultrahigh vacuum (UHV) conditions. The first method uses field ionization and field emission methods to probe the static properties of the three-phase boundary. A platinum field emitter tip of radius 35 nm was studied in a highly oxidized state and in the form of a Pt/ceria supported catalyst. Subsurface oxygen, which has been implicated in the NEMCA effect, was prepared on the platinum tip by oxygen ion sputtering at high temperature. Local work function measurements were performed by field emission microscopy to examine the oxide surface with and without chemisorbed oxygen. Pt/ceria surfaces were prepared by coating the Pt tip with a ceria adlayer and then evaporating platinum onto the ceria coating. The reactions of hydrocarbons (methane and butane) and water were examined on the Pt/ceria substrates by field ionization microscopy and mass spectrometry (time-of-flight and Wien filter modes). The second method uses a full solid oxide fuel cell (SOFC) operating in an ultrahigh vacuum system. The UHV-SOFC permits study of solid oxide anodes for direct oxidation of hydrocarbons such as methane and butane. The anode consists of a ceria coated YSZ pellet (5 mm diameter), which has a sealed tube on the cathode side to deliver oxygen at approximately 1 mbar. The anode side was studied by x-ray photoelectron spectroscopy, Auger electron spectroscopy, and quadrupole mass spectrometry while being exposed to the hydrocarbon reactant. The UHV-SOFC thus allows surface analysis of a dynamic electrocatalyst surface. This work is supported by the Office of Naval Research.

10:20am **EC+SS-TuM7 Molecular Ordering at Liquid-Liquid Interfaces***, **M.L. Schlossman**,* University of Illinois **INVITED**

Our view of molecular ordering in Langmuir monolayers at the water-vapor interface influences our understanding of molecular ordering at other interfaces, including liquid-liquid interfaces for which structural information is scarce. We present a comparative study of monolayers of long-chain alkanols at the water-vapor and water-hexane interfaces using x-ray reflectivity to highlight significant differences between these two interfaces. The molecules in the Langmuir monolayer form an ordered phase of nearly rigid rods. In contrast, at the water-hexane interface the alkanol molecules form a condensed phase with progressive disordering of the chain from the hydroxy to the methyl group. Surprisingly, at the water-hexane interface the density in the head group region is 10 to 15% greater than either bulk water or the ordered head group region found at the water-vapor interface. It is conjectured that this higher density is a result of water penetration into the head group region of the disordered monolayer. The alkanol monolayers at the water-hexane interface also undergo a solid to gas phase transition as a function of temperature. X-ray off-specular diffuse scattering is used to directly probe the statistical distribution of domains in monolayers of a fluorinated alkanol near the transition temperature. Evidence that the domains are of equilibrium size suggests that the domain line tension can be determined from these measurements.

11:20am **EC+SS-TuM10 Water-Graphite Interaction and the Behavior of Water near Graphite Surface***, M. Grunze, **A.J. Pertsin**,* Universität Heidelberg, Germany

A new, orientation-dependent water-graphite potential, which reproduces MP2-level quantum chemistry calculation results for the water-graphite complex, is suggested. The potential is used in grand canonical Monte Carlo simulations of the behavior of water confined between graphite surfaces. Comparative simulations using an isotropic potential are made to see the manifestations of the orienting effect of the water-graphite interaction in the structural and thermodynamic properties of the interfacial region. The shear behavior of water confined between the graphite surfaces is also explored to gain a better understanding of the effect of water on the friction and wear of graphitic carbons.

11:40am **EC+SS-TuM11 Molecular Structure at Interfaces between Water and Metal, Metal Oxide, or Polymer Studied by Sum Frequency Generation Spectroscopy***, **K. Uosaki**, R. Yamamoto, S. Nihonyanagi,* Hokkaido University, Japan

Sum frequency generation (SFG) measurement was carried out to investigate the molecular structure at the interfaces between aqueous solution and metal, metal oxide, or ploymer. Potential dependent water structure at metal elctrode, photo-induced hydrophilicity at titunium dioxide and the conformation of molecular chain of polyelectrolyte brush under various environment were studied.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI+NS-TuM

Magnetic Imaging and Magnetic Spectroscopies

Moderator: G.D. Waddill, University of Missouri - Rolla

8:20am **MI+NS-TuM1 Characterization of Magnetic Thin Films and Nanostructures using Electron Microscopy***, **D.J. Smith**,* Arizona State University **INVITED**

The reduced dimensions of magnetic thin films and nanostructures lead to major and often unexpected changes in magnetic properties and behavior. In addition to intrinsic scientific importance, these novel characteristics have obvious relevance to current and projected technological needs. Successful implementation of this technology requires a detailed understanding of materials growth mechanisms. Chemical and crystallographic structure must be correlated with micromagnetic structure and dynamic response before the fundamental limits of device performance can be firmly established. For example, atomic-level imaging and microanalysis of structural and chemical changes induced by changes in growth temperature or by post-deposition annealing are essential for explaining enhanced magnetic properties of antiferromagnetic pinning layers and magnetic tunnel junctions. And electron holography allows direct visualization of magnetization behavior within patterned nanostructures. This talk will provide an overview of electron microscopy and related techniques, with illustrative examples that demonstrate the major contributions being made to ongoing studies of magnetic thin films and nanostructures.

9:00am **MI+NS-TuM3 Imaging of Magnetic Nanoislands at the Thermal Stability Limit***, **M. Bode**, O. Pietzsch, A. Kubetzka, R. Wiesendanger,* University of Hamburg, Germany

Within the past decade spin-polarized scanning tunneling microscopy (SP-STM) became a mature tool for high spatial resolution imaging of the static domain structure of ferro- and antiferromagnetic surfaces.@footnote 1-3@ Recently, we successfully observed the temperature-dependent switching behavior of Fe monolayer islands which were pseudomarphically grown on a Mo(110) substrate and exhibit an perpendicular easy axis. Our SP-STM results show that at temperatures between 15 and 26 K Fe islands consisting of 250-600 atoms (area 20-40 nm@super 2@) are superparamagnetic, i.e., they change their magnetization direction on a time scale of 0.1-1000 s. Small islands were found to switch more often than larger islands as can be expected on the basis of anisotropy barrier considerations. A quantitative analysis reveals, however, that the observed size-dependent variation of the switching rate is much larger than theoretically expected. Possible origins of this behavior are discussed in terms of the island shape and environment. @FootnoteText@@footnote 1@ S. Heinze et al., Science 288, 1805 (2000).@footnote 2@ A. Wachowiak et al., Science 298, 577 (2002).@footnote 3@ M. Bode, Rep. Prog. Phys. 66, 523 (2003).

9:20am **MI+NS-TuM4 Scanning Tunneling Spectroscopy of Magnetic Impurities at Metal Surfaces***, **M.A. Schneider**,* Max Planck Institute for Solid State Research, Germany **INVITED**

A single magnetic impurity in a metal host is a paradigm of many-body physics in electronic systems. The spin-flip scattering of host electrons at the impurity site leads to the formation of a correlated electron state, the Kondo state. Only recently has it become possible to study this state using Scanning Tunneling Spectroscopy (STS) for magnetic surface impurities.@footnote 1-5@ Through this method, magnetism and properties of the adsorbate-host interaction can be determined in a local, atomic-scale measurement. The Kondo state is characterized by the formation of a resonance at the Fermi energy, which allows to access the characteristic energy scale, the Kondo temperature T@sub K@ of the system. We discuss the properties of the Kondo state created by the interaction of the magnetic atom with surface and bulk electrons, and the role of the tunneling process in the appearance of the resonance in STS spectra. The interaction of the magnetic impurity with two-dimensional surface-state electrons is demonstrated by the measurement of a resonant scattering phase-shift for Co adsorbed on Ag(111).@footnote 4@ However, this interaction with surface-state electrons is only weak, the main properties of the Kondo state are determined by the interaction with bulk electrons. This is corroborated by experiments comparing Co impurities on various Cu surfaces where the decisive role of the number of interaction channels to bulk electrons in the atomic-scale system is shown.@footnote 5@. @FootnoteText@ @footnote 1@ J.-T. Li, W.-D. Schneider, R. Berndt, B. Delley, Phys. Rev. Lett. 80, 2893(1998)@footnote 2@ V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, N. S. Wingreen, Science 280, 567 (1998) @footnote 3@ H.C. Manoharan, C. Lutz, D. M. Eigler, Nature 403, 512 (2000)@footnote 4@ M. A. Schneider, L. Vitali, N. Knorr, K. Kern, Phys. Rev. B 65, 121406(R) (2002)@footnote 5@ N. Knorr, M. A. Schneider, L. Diekhöner, P. Wahl, K. Kern, Phys. Rev. Lett. 88, 096804 (2002).

10:00am **MI+NS-TuM6 A Practical Guide to the Interpretation of Point-contact Andreev Reflection Data***, **R.J. Soulen**, G.W. Woods, I. Mazin, M. Osofsky,* Naval Research Laboratory

Point-contact Andreev reflection (PCAR), has become a useful tool in determining the spin polarization, P, of magnetic materials. It consists of establishing a point contact between a sharpened superconductive point and a magnetic base (or, vice versa), and measuring the conductance G of the junction as a function of the applied voltage, V. The value of P can be extracted from the conductance data through use of a modified Blonder, Tinkham, Klapwijk (BTK) model of the supercurrent conversion at the superconductor-metal interface (Andreev reflection). This algorithm, however, does not take into account several factors which depend on properties of the point contact: whether it is in the ballistic or diffuse regime, ratio of the spreading resistance to the junction resistance, the value of the superconducting energy gap. These properties are often difficult to measure or estimate so that the practitioner is left without a means to assess the error in the value of P. We have systematically examined these effects (by theory and experiment) and can offer some new and practical guidance on how to correct for them and to estimate the error. We use data on several materials (CrO2, SrRuO, and LaSrMnO) taken in our laboratory and in others to illustrate the process.

10:20am **MI+NS-TuM7 Preparation and Magneto-Optical Spectroscopic Studies of Diluted Magnetic Semiconductor Quantum Dots and Related Nanostructures: Potential Building Blocks for Spintronics Applications***, **D.R. Gamelin**, D.A. Schwartz, P.V. Radovanovic, N.S. Norberg, J.D. Bryan,* University of Washington **INVITED**

Diluted magnetic semiconductors (DMSs) are currently the focus of intense applications-oriented research in the emerging area of spin-based electronics, or "spintronics." DMS nanostructures such as quantum dots (DMS-QDs), quantum wells, quantum wires, and epitaxial thin films are pivotal architectural elements in many proposed spintronics devices including spin-dependent LEDs, field-effect transistors, and quantum computers. A central challenge facing the development of this technology is the identificati on of semiconductors that combine the necessary properties of conductivity and ferromagnetic ordering at temperatures above room temperature. This seminar will present our group's recent advances in the development of direct routes for preparation of freestanding high-quality DMS quantum dots. Emphasis will be placed on the application of magneto-optical spectroscopic methods (including magnetic circular dichroism and Zeeman spectroscopies) to study the electronic structural properties of these materials. Spectroscopic identification of ligand field, charge transfer, and excitonic transitions in DMSs will be presented in the context of their functional properties. The use of variable-temperature variable-field magneto-optical methods to define ground state spin-orbit splittings, and the influence of such splittings on the magnitudes of semiconductor band level Zeeman splittings, will also be discussed.

11:00am **MI+NS-TuM9 Magnetic Linear and Circular X-ray Dichroism Studies of the Magnetic Instability of Fe(x)Ni(1-x) Pseudomorphic Thin Films Exhibiting the Invar Effect***, **S.A. Morton**,* Lawrence Berkeley National Laboratory*; M. Hochstrasser,* Lawrence Livermore National Laboratory*; N.A.R. Gilman, R.F. Willis,* Pennsylvania State University*; G.D. Waddill,* University of Missouri - Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory

At a composition of 65% Fe, bulk Fe(x)Ni(1-x) alloys exhibit the invar effect: a sudden change in the atomic volume which is associated with a dramatic change in the magnetic ordering from a high-spin high-volume state to a low-spin low-volume state at higher Fe concentrations; this results in a collapse in the magnetic moment and Curie temperature. Magnetic X-ray Linear Dichroism measurements of the Fe and Ni 3p exchange splitting have been used as a probe of the element specific Fe and Ni magnetic moments for ultra thin fcc FeNi/Cu(100) films across the full compositional range. These results have been further complemented by composition dependent Magnetic X-ray Circular Dichroism measurements of the element specific orbital and spin moment contributions. The data shows excellent agreement with published neutron and SQUID magnetometry measurement and with theoretical predictions of the Fe and Ni atomic moments based upon the 2gamma state model and the Slater Pauling Curve. Furthermore, the data demonstrate the potential for the use of magnetic linear dichroism as a quantitative element specific magnetometer in a wide variety of magnetic thin film systems.

11:20am **MI+NS-TuM10 Magnetic Circular X-ray Dichroism of Gd2O3 Nanoparticles***, **K. Uvdal**, R.M. Petoral, Jr., F. Söderlind, P.-O. Käll,* Linköping University, Sweden

In this study we are investigating the possibilities to use magnetic circular X-ray dichroism (MCXD) to probe the magnetic properties of Gd2O3 nanoparticles. The Gd2O3 nano particles were further characterized by means of X-ray Photoelectron Spectroscopy (XPS) to investigate the elemental composition the nanoparticles as well as verifying the oxidation level. The particle size of Gd2O3 nanoparticles is estimated from Atomic Force Microscopy (AFM) and transmission electron microscopy (TEM). The elemental composition shows high carbon content, which is expected due to the synthesis pathway. The relative carbon content could be reduced by Ar sputtering of the Gd2O3 nano particles, in good agreement with earlier studies on CoO. MCXD is used to determine the orbital-to-spin relative magnetic moment. It is shown that the orbital-to-spin relative ratios are greatly enhanced for sputtered sample. Gd2O3 nanoparticles show a superparamagnetic behaviour at room temperature and a large orbital contribution to the magnetic moment at low temperature. MCXD is show to be a powerful tool for investigating magnetic properties of small volume samples.

11:40am **MI+NS-TuM11 Magnetism in Transition-metal Alloy Films: Lineshape Analysis of Magnetic Linear Dichroism Angle-selective Photoemission Spectra***, **R.F. Willis**, N.A.R. Janke-Gilman,* The Pennsylvania State University

MLD photoemission measurements using synchrotron radiation to excite atomic core levels are reported for thin epitaxial films of transition-metal binary alloys.@footnote 1@ Careful background subtraction gives spectral lineshapes which are analyzed to give information on the magnitudes of the elemental magnetic moments and the degree of local magnetic order. The width of the dichroism spectrum is shown to relate to the magnitude of the moment, while the amplitude reflects the local magnetic anisotropy and ordering. Dichroism spectral widths and amplitudes are plotted as a function of alloy composition, reflecting changing magnetic behavior. The elemental spectral widths track the Slater-Pauling curve showing changing moments as a function of changing composition. Changing spectral amplitudes are compared with neutron scattering results which show changing magnetic anisotropy and magnetic order. @FootnoteText@ @footnote 1@ Measurements taken on Beamline 7.0.1 at the Advanced Light Source, Berkeley, CA.

Microelectromechanical Systems (MEMS)
Room 320 - Session MM-TuM

Development and Characterization of MEMS and NEMS Materials

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

8:20am **MM-TuM1 MEMS and NEMS from Chemical Vapor Deposited Nanodiamond Materials***, **J.E. Butler**,* Naval Research Laboratory **INVITED**

Nanodiamond films grown by chemical vapor deposition exhibit a number of remarkable properties desirable for MEMS and NEMS. These include high Young's Modulus, thermal diffusivity, dielectric breakdown strength, mass density, secondary electron yields, fracture toughness, optical transparency, corrosion resistance, biological stability, and more. The nucleation, growth, and doping of these films on diverse substrate materials, including Si, poly Si, SiO2, and various metals, will be described along with various methods of processing into structures and devices.

9:00am **MM-TuM3 Engineering the Surface Properties of Ultrananocrystalline Diamond for High-Performance MEMS Devices***, **A.V. Sumant**, D.S. Grierson,* University of Wisconsin, Madison*; J.E. Gerbi, J.A. Carlisle, O. Auciello,* Argonne National Laboratory*; R.W. Carpick,* University of Wisconsin, Madison

Characterization of MEMS and NEMS devices at small length scales is extremely important in order to understand the factors that dictate the performance of these devices. Ultrananocrystalline diamond (UNCD), in particular, has exceptional physical, electrical, chemical and tribological properties (nearly equivalent to those of single crystal diamond). UNCD is being considered as one of the most promising materials for the fabrication of high performance MEMS devices. However, little is known about the surface chemistry of this material, and how such surface chemistry will affect the UNCD performance, particularly in case of rolling or sliding contacts at both the micro and nano level. We have carried out detailed, systematic studies of UNCD thin films by various analytical techniques including Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and atomic force microscopy (AFM) to understand the chemical nature, phase, and microstructure of the UNCD surface. We have found that there is a significant difference in the structural and chemical properties between the as-grown UNCD top surface and the underside of the film as revealed after etching away the substrate. Characterizing the underside of the film is particularly important because in most cases (e.g. micro-engines and cantilever based switches), the underside of the film makes contact with the underlying surface below. We will discuss how these properties are influenced by various aspects of the microwave PECVD growth process, including the initial nucleation pre-treatment and the gas chemistry used during growth, and how one can engineer the surface by tuning these growth parameters. Finally, we will discuss how such changes may affect UNCD performance at MEMS length scales.

9:20am **MM-TuM4 AlN-based MEMS and NEMS Resonator Devices***, **A.E. Wickenden**, L.J. Currano, M. Dubey,* U.S. Army Research Laboratory*; S. Hullavarad, R.D. Vispute,* University of Maryland, College Park

Electromechanical resonator devices using piezoelectric aluminum nitride (AlN) actuation are being developed for RF filters operating in the MHz-GHz frequency range. Composite structures are required for these micro- and nanoelectromechanical systems (MEMS, NEMS) devices, which include the piezoelectric film, metal electrode layers, and a flexural layer. AlN film quality is very dependant on the growth technique, and differences in crystallinity impact the subsequent piezoelectric response of the film. We have demonstrated the pulsed laser deposition (PLD) of highly oriented AlN thin films on Pt-terminated composite MEMS/NEMS structures. Characterization by X-ray diffraction demonstrates a FWHM of 0.2°, a ten-fold improvement over sputtered AlN films typically used in this application. Pattern transfer techniques have been developed for these composite device structures at both micro- and nano-scale. Fully released AlN MEMS beam resonator structures have been fabricated and tested. These devices demonstrate strong electromechanical response, with a 500 nm deflection observed in a fixed-fixed beam with a resonant frequency of 250 kHz. Device dimensions for resonant frequencies near 1 GHz are predicted to scale to near one micron in length and hundreds of nanometers in cross-sectional area. Free-standing 200nm wide x 150nm thick x 10µm long AlN beams with aligned metal electrodes have been demonstrated, using direct-write electron beam lithographic patterning techniques. We will present detailed harmonic and modeshape analysis of AlN MEMS resonators in the 0.15-15 MHz frequency spectrum, and highlight current results in the development of AlN NEMS resonators.

9:40am **MM-TuM5 Anchor Optimization for Quality Factor Improvement in Microresonators***, **L.J. Currano**, A.E. Wickenden, M. Dubey,* U.S. Army Research Laboratory

Arrays of microresonators are of considerable interest for low-cost, high precision RF filters. The quality factor (Q) of a resonator is the figure of merit which determines the amount of signal lost from input to output as well as the slope of the cutoff of a bandpass filter. Some of the factors that degrade the quality factor in mechanical resonators are geometry and material properties, thermoelastic noise, and the transduction mechanism.@footnote 1@ Several discussions of the noise and dissipation mechanisms in microresonators have been published.@footnote 2@ One of the most important loss mechanisms is the transmission of mechanical strain energy to the substrate. The magnitude of strain energy transmitted to the substrate can be manipulated by changing the geometry of the interface between device and substrate. The quality factor for similar PZT-based clamped-clamped beam resonator devices has been found to double by changing the geometry of the anchor slightly. New models are necessary for reducing mechanical losses in the simplest resonator structure, a doubly clamped beam. Finite element analysis provides a vehicle for examining the losses due to transmission of strain energy from the resonator into the substrate and a window into some of the design methods that can be used to minimize mechanical losses. A finite element model which calculates the strain energy transmitted to the substrate in a clamped-clamped resonator beam has been devised, and the results show that the losses steadily decrease with anchor width. Results from the model along with results from electrical testing of PZT resonator devices will be presented. @FootnoteText@@footnote 1@A. N. Cleland and M. L. Roukes, "Noise processes in nanomechanical resonators," Journal of Applied Physics, vol. 92 pp 2758, 2002.@footnote 2@J. R. Vig, "Noise in microelectromechanical systems resonators," IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control, vol. 46 pp. 1558, 1999.

10:00am **MM-TuM6 Chemical Control of Mechanical Energy Dissipation in Micromechanical Silicon Resonators***, **Y. Wang**, J.A. Henry, M.A. Hines,* Cornell University

Why are we unable to predict the dynamical performance of nanoscale devices from the well-known properties of macroscopic materials? For example, the quality (or Q) of micromechanical resonators plummets as the size of the device is reduced. We will show that the role of surface effects on energy loss cannot be ignored at this length scale. To investigate the role of surface dissipation, we have fabricated silicon torsional resonators with predominantly Si(111) faces. The resonators' surfaces are then chemically modified and characterized by infrared spectroscopy. Resonators terminated by an atomic layer of hydrogen have the lowest energy loss but the quality of the resonator decreases with time even in high vacuum (10@super -8@ Torr). Quantitative analysis of the time-dependent frequency shift suggests that the increased losses observed in vacuum are correlated with chemical adsorption. The quantitative effects of a variety of adsorbates will also be discussed. When the H-monolayer is replaced by one type of self-assembled monolayer (SAM), a small decrease in initial quality is observed; however, SAMs-terminated devices are much more stable with time. This stability is attributed, in part, to increased chemical resistance; however, aggressively oxidizing environments still lead to performance degradation. A second type of SAM leads to much higher energy losses. The chemical origins of this difference will be discussed.

10:20am **MM-TuM7 Vapor-Phase Lubricants: Nanometer-scale Lubrication Mechanisms and Uptake on Silicon***, **W. Neeyakorn**, M.R. Varma, J. Krim,* North Carolina State University

The concept of lubricating high temperature bearing surfaces with organic vapors which react with a surface to form a solid lubricating film has existed for at least forty years, with substantial efforts beginning in the 1980's and continuing to the present day. While vapor-phase lubricants have primarily been studied within the context of macroscopic system performance, they may well prove to be of critical importance to tribological performance in sub-micron mechanical systems as well. This is because the vapor phase may ultimately prove to be the most effective, if not only, means to deliver and/or replenish a lubricant that can withstand a variety of extreme environmental conditions that a MEMS device is likely to encounter. In order to investigate the viability of vapor-phase lubrication for MEMS applications, we have studied molecular scale tribological properties and gas uptake rates for four known organophosphate lubricants in controlled environments on silicon and gold substrates. The first study involves Quartz Crystal Microweighing investigations of the uptake rates of lubricant vapors from the vapor phase in vacuum conditions. With the intent of modelling actual MEMS contacts, we have also constructed a simple nanomechanical system consisting of a Scanning Tunneling Microscope tip dragging on the surface of a Quartz Crystal Microbalance electrode. This system allows us to monitor lubricant performance in realistic sliding conditions of up to 2 m/s. Finally, work is in progress to study the effect of these vapor-phase lubricants on actual MEMS devices with contacting silicon surfaces.@footnote 1@ @FootnoteText@@footnote 1@ Work supported by NSF and AFOSR.

10:40am **MM-TuM8 Can We Predict Friction and Wear in MEMS?***, **E.E. Flater**,* University of Wisconsin - Madison*; A.D. Corwin, M.P. DeBoer,* Sandia National Laboratories*; C.K. Bora, M.E. Plesha, R.W. Carpick,* University of Wisconsin - Madison

The design of reliable MEMS devices that involve sliding or rolling surfaces requires a predictive capability for friction and wear. We will describe our efforts to predict friction in MEMS by connecting single asperity friction measurements via atomic force microscopy (AFM) with multi-asperity friction measurements in a newly-developed MEMS friction test device through the use of analytical models of contact between rough surfaces. We will show that AFM resolves critical roughness features of MEMS surfaces from the nm-to-Âµm scale. From this information, we derive surface roughness parameters that are used as inputs to predict the interfacial mechanics using generalized models based on the Greenwood-Williamson approach and fractal surface models, respectively. We will discuss the validation of these approaches with reference to single-asperity AFM experiments and multi-asperity MEMS friction test device experiments.

11:00am **MM-TuM9 Nanomechanical Characterization of Digital Micromirror Devices*, G. Wei*,** *B. Bhushan,* The Ohio State University*; J. Jacobs,* Texas Instruments, Inc.

The Digital Micromirror Device (DMD) lies at the heart of Texas Instruments' Digital Light Processing@super TM@ (DLP@super TM@) technology, enabling the next generation of bright, lightweight projection displays. The DMD comprises a surface-micromachined array of up to 2.07 million mirrors fabricated on top of an SRAM array. The nanomechanical properties of the thin-film structures formed in the manufacturing process are important to the performance of the DMD. In this paper, the nanomechanical characterization of various materials used in the manufacture of the DMD has been performed using a nanoindentation technique. Properties including Young's modulus, hardness, scratch resistance, fatigue, and fracture toughness of the corresponding materials have been measured and analyzed. The impact of these properties on mirror performance is discussed.

11:20am **MM-TuM10 Measurement of Mechanical Properties of Silicon Nitride Thin Film at Cryogenic Temperatures*, W. Chuang*,** *T. Luger,* University of Maryland, College Park*; R. Fettig,* NASA Goddard Space Flight Center*; R. Ghodssi,* University of Maryland, College Park

Mechanical properties of MEMS materials at cryogenic temperatures are investigated to extend MEMS sensors and actuators into space and low temperature applications. Two-dimensional micro-shutter arrays, made in silicon nitride thin film, are being developed at NASA Goddard Space Flight Center (GSFC) for use in the James Webb Space Telescope (JWST). Reliability and exact mechanical properties of silicon nitride thin film at cryogenic temperatures are crucial in the development of the JWST. We have developed and installed a measurement setup inside a focused ion beam (FIB) system, which can provide scanning electron microscopy (SEM) and mask-less ion milling, to measure the mechanical properties of MEMS materials from room to cryogenic temperatures. A variety of low-stress silicon nitride T-shape cantilevers suspended on silicon micromachined v-grooves are fabricated as test devices. The resonant frequency method is used in experiments to minimize the required calibration in the measurement setup at different temperature ranges. A lead-zirconate-titanate (PZT) translator and a silicon diode are utilized as the actuator and temperature sensor in the measurement setup, respectively. Experiments are performed to measure resonant frequency, damping, coefficient of thermal expansion, Young's modulus, fracture strength and fatigue properties of the test devices from room to cryogenic temperatures. The measured resonant frequencies are varied from 15.81 kHz at 25.5 K to 14.61 kHz at 298 K (room temperature). The higher resonant frequency is consistent with the expected increased Young's modulus of silicon nitride thin film at cryogenic temperatures. The preliminary measurement results, detailed fabrication process and configuration of the measurement setup will be presented.

11:40am **MM-TuM11 Pointwise Strain Mapping a Multilayer MEMS Mirror Using Synchrotron Radiation*, Y.N. Picard*,** *S.M. Yalisove, E. Dufresne, C. Cionca, J. Guzman, R. Clarke,* University of Michigan, Ann Arbor*; D. Walko,* Argonne National Laboratory*; O.B. Spahn, D.P. Adams,* Sandia National Laboratories

Precise control over surface curvature of micromirror devices is critical for developing communications and power delivery applications. Furthermore, the control of this curvature must be maintained over time and in a range of operating conditions. Curvature control ultimately requires understanding of how stress in reflective coatings and thermal-stress compensation layers affect the ultimate performance of a variety of micromirror designs (different geometries, thickness, clamping arrangements, etc). Highly localized, non-destructive strain measurement techniques are required to assess variations in stress across and through micromirror coating layers on the actual device. We present results of strain mapping across a metal-coated polysilicon micromirror using a micron-sized x-ray beam at the Advanced Photon Source. Prior to x-ray analysis, a high reflectivity, low stress film of 10 nm Ti/150 nm Au was deposited by DC planar magnetron sputtering on a 2.25 micron thick, 500 micron diameter polysilicon mirror that had been etch-released prior to film deposition. A 10keV x-ray beam was focused down to a 5.3x12.8 micron spot size using two bendable Kirkpatrick-Baez mirrors and then used for point-by-point detection of Au and Si diffraction peaks. The peak positions were then measured and used to determine strain in the respective thin film after comparison to a standard powder sample. Because the freestanding micromirror was still clamped to the substrate, variations in strain were anticipated and indeed detected. Results of measured in-plane and out-of-plane strain for both the Au film and the polysilicon mirror will be presented, where an up to 23% variation in strain is detected from the center to the constrained edges of the micromirror. We also discuss strain resolution by this method and estimate that 3-5 MPa of stress can be resolved point-to-point within each material layer.

Manufacturing Science and Technology
Room 309 - Session MS-TuM

Packaging and Role of Interface Engineering in IC Processing

Moderator: L. Larson, SEMATECH

8:20am **MS-TuM1 Challenges and Advances in Packaging Technology Development for IC Processing*, H. Hosack,*** Semiconductor Research Corporation **INVITED**

Traditionally packaging provides isolation of the chip from the environment and a space transformation from the chip bond pads to leads compatible with connections to the outside world. With the recent increases in frequency and power dissipation in high performance microprocessors, and the advent of portable electronics, the requirements for electronic packaging are rapidly expanding not only to continuing increases in performance, but also to radically different functionality in areas such as photonics, RF, and MEMS. These new needs require complete re-thinking of packaging with the view that the die-package is a sub-system in itself, and the need is to produce this complete sub-system with optimized total performance at a minimum cost. The areas of critical importance in this sub-system view will be those areas that address the interface between the die back-end and the package. By eliminating unduly specialized work on either the chip or package in isolation, redundant effort can be minimized and device performance can be optimized. The challenges inherent in optimizing the chip-package interface include the spectrum of electrical issues, thermo-mechanical issues, and metrology. These issues are being addressed by package-chip interface solutions that not only optimize the sub-system in its present configuration but also by novel schemes that employ new materials, new signaling mediums, and reallocation of interface functions between the package and the chip. These new approaches include novel schemes such as incorporating portions of the traditionally on-chip metallization as a part of the package, non-contact chip-to-package signaling, and 3D packaging. This discussion describes the critical issues that must be addressed in this new view of package functions, as well as the status of some of the unique solutions that are being researched to provide the optimized chip-package sub-system.

9:00am **MS-TuM3 Interfacial Engineering for Reliability Improvement of Cu/Low k Interconnects*, P.S. Ho,*** University of Texas **INVITED**

With continuing device scaling, interfaces of dielectrics, metals and semiconductors become increasingly important in controlling the yield and reliability of devices and interconnects. Beyond the current 130 nm technology node, the implementation of low k dielectrics causes serious reliability concerns for Cu interconnects due to their weak thermomechanical properties. This paper will first discuss the role of interfaces in controlling the reliability of the Cu damascene structure, particularly regarding electromigration and stress voiding. Several approaches of interfacial engineering to improve Cu interconnect reliability will be discussed, including surface processing and overcoat layers to reduce mass transport and to increase adhesion strength. Central to these approaches is the optimization of the chemical bonding to improve the properties of interfaces and low k dielectrics. The effects on electromigration and stress voiding of Cu/low k interconnects will be discussed.

9:40am **MS-TuM5 Forming Laminar Cu/Substrate Interfaces: Vacuum vs. Electrochemical Processing**, *N.P. Magtoto, J. Liu, J. Lei, X. Zhao,* ***J.A. Kelber,*** University of North Texas **INVITED**

The nucleation and conformal growth of a Cu film on a metal or dielectric barrier substrate is of critical importance for the production of reliable interconnects. This phenomenon has been studied extensively at the vapor/solid interface, where surface science experiments carried out in vacuum or ultrahigh vacuum (UHV) can generally be applied directly to industrial thin film fabrication methods (e.g., sputter deposition). Such studies have demonstrated that the initial growth mode of Cu on various substrates is extremely sensitive to surface chemistry, and this can lead to highly variable results during real world processing. In many cases, including Si:C:H films,@footnote1@ silane-treated Ta,@footnote2@ and sapphire(0001),@footnote3@ initial 2-D growth on a dielectric or air-exposed metal substrate is enhanced by substrate hydroxylation prior to Cu deposition. This has important consequences for designing processes that are insensitive to incidental oxidation. In contrast, the situation at the electrolyte/solid interface is complex, and fundamental issues like the role of ad-atom mobilities or surfactants in film nucleation are not well understood. Kinetic measurements and in-situ STM provide only limited information.. This talk will review the enhancement of Cu 2-D growth at the vapor/solid interface, and discuss recent efforts to identify conformal vs. 3-D growth during electrodeposition, including the prospects for using monolayer concentrations of ad-atoms, such as iodine, to enhance conformal growth in additive-free environments. @FootnoteText@ @footnote1@. M. Pritchett, N. Magtoto, and J. Kelber, Thin Solid Films (in press) @footnote2@. X. Zhao, M. Leavy, N. P. Magtoto and J. A. Kelber , Thin Solid Films 415, 308 (2002) @footnote3@. C. Niu, K. Shepherd, D. Martini, J. Tong and J. A. Kelber, and D. R. Jennison and A. Bogicevic, Surface Science 465, 163 (2000).

10:20am **MS-TuM7 Challenges and Advances in Thin Film Mechanics*, Z. Suo,*** Princeton University **INVITED**

Devices in modern technologies have complex architectures, small feature sizes, and diverse materials. The close proximity of dissimilar materials leads to unusual fracture behaviors. A scientific understanding of these behaviors is significant for the development of the future technology. In particular, rate processes, such as creep, subscritical cracking, and ratcheting, limit the long term reliability of the interconnects. Drawing on recent experiments and models, this talk describes a channel crack in a brittle film on an underlayer. When the underlayer is compliant (e.g., a low k dielectric), the driving force on the channel crack is very large. When the underlayer creeps (e.g., a polymer), the crack velocity is set by the viscosity in the underlayer, as well as by subcritical cracking in the brittle film. When the underlayer is plastically deformable (e.g., a metal), on thermal cycling, the crack can grow in the brittle film by ratcheting deformation in the underlayer. I also discuss the use of these phenomena to measure mechanical properties at the small scale. PDF files of papers are available at http://www.princeton.edu/~suo/ Keywords: Interconnects, fracture, creep, plasticity.

Nanometer Structures
Room 308 - Session NS-TuM

Nanowires

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

8:20am **NS-TuM1 Growth and Characterization of Single-Crystal ZnO Nanowires***, Z. Zhu, T. Chen, Y. Gu, G. Neumark,* ***R.M. Osgood Jr.,*** Columbia University

One-dimensional ZnO nanowires have attracted increasing interest for both fundamental and applied studies of short-wavelength optoelectronic nanodevices. This talk reports a systematic study of effect of the variation of growth parameters, including growth temperature, growth time and catalyst (Au) film thickness, in determining the collective and individual structure of ZnO nanowires. Our single-crystal ZnO nanowires were grown on different-orientation silicon and sapphire substrates via vapor-phase transport. The synthesized ZnO nanowires were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS) and photoluminescence (PL) spectroscopy. Room-temperature photoluminescence spectra of the ZnO nanowires revealed a strong, narrow excitonic emission at ~ 380 nm and a very weak green emission band at ~ 508 nm. The full width at half maximum (FWHM) of the excitonic emission at ~ 380 nm was ~ 95 meV, indicating that the ZnO nanowires are of good optical quality. SEM measurements were made of ZnO nanowires grown on silicon substrates with Au films of different-coverage. The growth studies have shown that, as the Au-thin-film coverage decreases, the width and area density of the nanowires decreases while the length of the nanowires increases. In addition, the SEM measurements of the ZnO nanowires, grown at different substrate temperatures, show that the spatial uniformity of ZnO nanowires is strongly dependent on substrate temperature. Strategies of manipulating the spatial orientation of ZnO nanowires for practical applications are being explored by using nanofabrication techniques such as electron-beam lithography to pattern the substrates and build blocks to confine the growth of the ZnO nanowires; these studies will be reported in this talk.

8:40am **NS-TuM2 Growth and Characterization of ZnO Nanowires***,* ***J.B. Baxter****, E.S. Aydil,* University of California, Santa Barbara

ZnO is a wide band gap semiconductor with applications in UV optoelectronics, transparent conducting oxide coatings, piezoelectronics, and photovoltaics. Nanostructured ZnO can exhibit quantum confinement effects and enable applications requiring high surface area such as sensors and dye sensitized solar cells. We have grown monodisperse ZnO nanowires by chemical vapor deposition (CVD) using the organometallic precursor zinc acetylacetonate (Zn(acac)@sub 2@) in the presence of oxygen. Nanowire diameters depend on the growth conditions and range from 16 nm to 100 nm. The growth morphology depends sensitively on the substrate and the partial pressure of Zn(acac)@sub 2@. On a-plane sapphire, nanowires grow epitaxially and perpendicular to the substrate in dense arrays and with in-plane rotational order. X-ray diffraction pole figures confirm the epitaxial relationship ZnO(0001)||Al@sub 2@O@sub 3@(11-20) and ZnO(11-20)||Al@sub 2@O@sub 3@(0001). Conversely, nanowires grow on c-plane sapphire in one of three directions relative to the substrate owing to ZnO(0001)||Al@sub 2@O@sub 3@(10-14) epitaxy and the trigonal symmetry of the substrate. Controlled sublimation and delivery of the solid precursor is challenging. However, we are improving our ability to control nanowire growth by studying the evaporation and decomposition of Zn(acac)@sub 2@ using thermogravimetric analysis and mass spectrometry and by monitoring the presence of the Zn(acac)@sub 2@ with in situ Fourier transform infrared (FTIR) spectroscopy. Dense ZnO nanowires with high surface area can be grown on various oxide substrates, making them suitable for replacing the mesoporous semiconductor in dye sensitized solar cells. Single crystal ZnO nanowires offer improved conduction pathways compared to sintered nanoparticles used currently, where electron transport occurs by a hopping mechanism.

9:00am **NS-TuM3 Structure, Defect and Cathodoluminescence Studies of GaN Nanorods and Nanowires***,* ***L.C. Chen,*** National Taiwan University, Taiwan*; C.S. Shen, S.C. Shi,* National Taiwan University*; S. Dhara, C.T. Wu, K.H. Chen,* Academia Sinica, Taiwan*; C.W. Hsu, C.C. Chen,* National Taiwan Normal University

Single-crystalline GaN and related 1D nanostructures, specifically, binary InN, AlN along with their ternary In@sub 1-x@Ga@sub x@N and In@sub 1-x@Al@sub x@N counterparts have been successfully grown by catalytic chemical vapor deposition. Their structure and optical properties are investigated by scanning and transmission electron microscopy, Raman, photoluminescence (PL) as well as cathodoluminescence (CL) techniques. Diameter and position selective growth of these 1D nitride nanostructures has been demonstrated by pre-treatment of the substrate surface with size-controlled catalyst. Oriented growth of the nanorods was also obtained under hetera- or homo-epitaxial conditions. While PL measurements usually give spectral data from numerous nanowires and nanorods with a broad distribution of diameter, the CL measurements (from room temperature down to 4 K) can easily be performed on single nanowire or nanorod. A higher CL peak position of individual GaN nanorod than that of bulk GaN film was observed, indicating the presence of strain in the pristine nanorod, which is also confirmed by X-ray diffraction analyses. In addition, a blue shift of CL peak position with decreasing the diameter of GaN nanorod was noticed. However, the magnitude of the peak shift is much more pronounced than that estimated from quantum confinement. Finally, Ga@super +@ ions implantation of these GaN 1D nanostructures has been studied using 50-keV Ga@super +@ focused ion beam. Phase transformation and defect structure evolution as a function of irradiated ion-beam fluence is also investigated by electron-microscopy-based techniques.

9:20am **NS-TuM4 Onset of Nanowire Growth by Vapor-Liquid-Solid (VLS) Epitaxy***,* ***J.W. Dailey****, J.L. Taraci, T. Michael, J.C. Thorp, S.T. Picraux,* Arizona State University

We report on CVD growth of Ge and Si nanowires on Si substrates by the Vapor Liquid Solid (VLS) technique. While many groups have formed random clusters of Si nanowires at high pressures by VLS, relatively little effort has been directed at the controlled CVD growth of epitaxial arrays of nanopillars or nanowires directly onto Si substrates. In our studies Au nanodots are formed by UHV evaporation on hydrogen terminated Si (100) and (111) substrates. Subsequent selective area growth is carried out using digermane or disilane at pressures from 1 x 10-2 to 1 x 10-5 T and temperatures from 400 to 600 C. At the lower pressures (representative of gas phase MBE) we observe the growth of Ge nanopillars that nucleate at the AuSi eutectic and grow vertically and laterally, undergoing coalescence as growth continues. RBS and ion channeling are used to establish the VLS substrate orientation and temperature dependent kinetics of the Ge nanopillar growth, and SEM elucidates the morphological evolution of the nanopillars. At pressures above 10-4 T we observe an abrupt change in the nature of the growth from a relatively slow nanopillar growth to a much more rapid nanowire growth. The nanowires are distinguished by long narrow axial growth structures with much slower lateral growth. The transition from nanopillar to nanowire growth is interpreted in terms of a nucleation-limited process. Due to the small lateral dimensions (10 to 50 nm) of these 3-D structures lateral strain relief is expected to occur and large lattice mismatches should be accommodated without defects, in contrast to large area heteroepitaxy. These CVD nanoscale structures could form the basis for new in situ synthesis of 3-D Si device structures on Si substrates.

9:40am **NS-TuM5 Functional Semiconductor Nanowires and Their Optical Properties*, P. Yang*,** University of California, Berkeley **INVITED**

Nanowires are of both fundamental and technological interest. They represent the critical components in the potential nanoscale electronic and photonic device applications. In this talk, I will introduce the vapor-liquid-solid crystal growth mechanism for the general synthesis of nanowires of different compositions, sizes, orientation and doping profile. Particularly, synthesis and organization of different types of heterostructured nanowires will be discussed. Wide band gap semiconductor nanostructures with near-cylindrical geometry and large dielectric constants exhibit two-dimensional ultraviolet and visible photonic confinement (i.e. waveguiding). Combined with optical gain, the waveguiding behavior facilitates highly directional lasing at room temperature in controlled-growth nanowires with suitable resonant feedback. The nanowire optical emission has been studied in detail using high-resolution optical microscopy. The waveguiding behavior of individual zinc oxide (ZnO, GaN) nanowires depends on the wavelength of the emitted light and the directional coupling of the photoluminescence (PL) to the emission dipoles of the nanowire. Pumping at high pulse intensity leads to the transition from spontaneous to stimulated emission, and analysis of the polarization, linewidth, and spacing of the spectral features facilitates identification of the transverse and longitudinal cavity modes and their gain properties. The observation of lasing action in arrayed and isolated ZnO/GaN nanowires without requiring fabrication of mirrors suggests the single-crystalline, well-facetted nanowires can indeed function as effective resonance cavities. This concept of using well-cleaved nanowires as natural optical cavities may be extendable to many other different semiconductor systems. @FootnoteText@ @footnote 1@ Y. Wu, R. Fan, P. Yang, Nanolett, 2, 83, 2002.@footnote 2@ M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science, 292, 1897, 2001.@footnote 3@ J. Johnson, H. J. Choi, K. P. Knutsen, R. D. Schaller, R. J. Saykally, P. Yang, Nature Materials, 1, 101, 2002.@footnote 4@ J. Johnson, H. Yan, R. Schaller, L. Haber, R. Saykally, P. Yang, J. Phys. Chem. B, 105, 11387, 2001.

10:20am **NS-TuM7 Mo@sub 3@Se@sub 3@ Nanowires - Mechanical and Electrical Properties at the Nanoscale*, A. Heidelberg,*** Trinity College Dublin, Ireland*; J.W. Schultze,* Heinrich-Heine-Universität Düsseldorf, Germany*; G. Staikov,* Forschungszentrum Jülich, Germany*; J.J. Boland,* Trinity College Dublin, Ireland

Low dimesional organic and inorganic materials like nanowires and nanotubes have attracted much interest as potential building blocks for nanotechnology. This interest can be traced to the novel structural and electronic properties of these materials. Here we describe a study that measures the electronic and mechanical properties of the inorganic polymer (LiMo@sub 3@Se@sub 3@)@sub n@ together with nanowire-networks that have been synthesized by exchanging the Li-counterion with different alkylammonium- and pyridinium-ligands. (LiMo@sub 3@Se@sub 3@)@sub n@ forms quasi-1D crystals and is structurally related to the Chevrel phases. It can be viewed as a condensation polymer of Mo@sub 3@Se@sub 3@ units. The crystals can be dissolved in polar solvents with @epsilon@ > 45. In these solvents the crystals disassemble into single nanowires with a diameter of 0.6 nm (from crystal data and TEM) and bundles of nanowires, depending on the solutions concentration. From solution, single nanowires, bundles of nanowires or films of nanowires can be cast on various substrates. Both, the wires themselves as well as the nanowire films are highly conductive but susceptible to electrical degradation (oxidation) in air. The ion exchanged wires form self assembled networks with an inter-wire spacing determined by the length of the side chain of the alkylammonium- and pyridinium-ligands. Conductivity measurements on these nanowire networks at different temperatures and oxidation times show that conduction is activated and occurs via a percolation mechanism. The mechanical properties of single nanowires or bundles were studied using a SPM-nanomanipulator. This instrument allows us to controllably apply forces (µN-nN range) to supported Mo@sub 3@Se@sub 3@-nanowires to effect nanoscale manipulations. Using the lateral force data of the manipulations, the mechanical properties like Youngs modulus and tensile strength of the wires can be measured.

10:40am **NS-TuM8 Defect Mediated Electronic Transport in Nano and Molecular Wires*, D.A. Bonnell,*** *S. Kalinin, M. Freitag, A.T. Johnson,* University of Pennsylvania

Any rational approach to nanostructure design necessitates a fundamental understanding of the properties of the constituents, as well as collective behavior of ensembles. We have developed 2 new approaches to measuring local electromagnetic properties based on scanning probes that can be applied to nano and molecular wires, Scanning Impedance Microscopy and Nano Impedance Spectroscopy. These approaches access the frequency dependence of electronic transport over 3-6 orders of magnitude, depending on experimental conditions. The frequency dependence can be used to determine mechanisms of electronic transport, particularly the processes that occur at defects. We demonstrate this approach by determining the local electronic structures of individual defects in single walled carbon nanotubes. We then generalize to nanowires and molecular wires.

11:00am **NS-TuM9 Electronic Structure and Excited States of One-dimensional Polydiacetylene Nanowire*, M. Akai-Kasaya*,** *K. Shimizu, A. Saito, M. Aono, Y. Kuwahara,* Osaka University and SORST JST, Japan

The polydiacetylene (PDA) nanowire can be fabricated at designated positions by using a STM probe tip on a self-assembled monomolecular (SAM) layer.@footnote 1@ The fabricated PDA wire grows out in a straight line and extends to a sub-micrometer length on the surface. The fully extended conjugated backbone of the PDA is not only expected to function as an electrically conducting nanowire but is also interesting in terms of exploring physics in one-dimensional (1D) systems. In this work, the density of states of individual polymers and constituent monomers were studied by STS. The STS spectrum delineating the density of states of PDA wire clearly reveals the theoretically predicted @pi@-band and band edge singularities of the 1D conjugated polymer. We have also observed a fascinating spectrum with a narrow gap, which is suggested to be due to the existence of the charge-carrying polaron states on a polymer backbone. Furthermore, we demonstrated that an exited state took place in an isolated polymer nanowire following the polymerization. The voltage pulse initiates additive polymerization, which proceeds instantaneously to both sides of the monomer array on the SAM layer. Before and after polymerization within the disabled feedback loop, the tunneling current shows the accountable difference due to the steady-state current on the monomer and derived polymer, respectively. However, the anomalous current, which often continues for few hundred micro-seconds, has been observed simultaneously with inception of the polymerization. We have estimated statistically the time of onset and duration of the current and correlation with the length of the derived polymer wire. And then, it can be concluded that the detected anomalous current results from the vibrational excitation states of a derived molecular nanowire. These results are remarkable and interesting in terms of one molecular science. @FootnoteText@@footnote 1@Y. Okawa and M. Aono, Nature 409, 683 (2001).

11:20am **NS-TuM10 STM and DFT Study of Gadolinium Silicide on Si(100)*, B.C. Harrison,*** University of North Carolina at Chapel Hill, Ireland*; J.J. Boland,* Trinity College Dublin, Ireland

The fabrication and characterization of low-dimensional nanoscale structures is motivated by the desire to produce materials and devices with novel optical, structural, and electronic properties. Due to the difficulties in nanoscale fabrication by a top-down approach, self-assembly of nanoscale materials represent an attractive alternative. Rare earth silicide on the Si(100) surface is one such system that has attracted significant interest over the past several years. Nanostructures of various silicides@footnote 1,2,3@ have been formed with high aspect ratios, micrometer length scales, large mechanical strengths, and metallic character; all of which make them potential candidates for nanoscale interconnects or device components. However, these nanowires cannot be successfully used in electronic circuits until the morphology and placement of wires are controlled. This study focuses on Gadolinium Silicide (GdSi@sub 2@) on Si(100) since this silicide forms nanowires and has the smallest lattice constant mismatch in the wire growth direction of any of the available rare earth silicides at growth temperatures. Scanning Tunneling Microscopy data and DFT calculations results are coupled to determine the morphology of the various phases of GdSi@sub 2@ on the Si(100) surface. Furthermore, STM images are acquired from room temperature to wire-growth temperatures in order to study the atomic structure and growth processes of the initial wetting layer and nanowires themselves. At least three forms of the wetting layer and two forms of wires will be discussed in connection with an overall surface phase diagram for GdSi@sub 2@ on Si(100). @FootnoteText@@footnote 1@ Chen, Y.; Ohlberg, D. A. A.; Williams, S. J. Appl. Phys. 2002, 91, 3213.@footnote 2@ Chen, Y.; Ohlberg, D. A. A.; Medeiros-Riberio, G.; Chang, Y. A.; Williams, S. Appl. Phys. Lett. 2000, 76, 4004.@footnote 3@ Nogami, J.; Liu, B. Z.; Katkov, M. V.; Ohbuchi, C.; Birge, N. O. Phys. Rev. B 2001, 63, 233305-1.

11:40am **NS-TuM11 Theoretical Calculation of the Thermal Conductivity of Semiconducting Nanowires***, **N. Mingo**, L. Yang,* NASA-Ames Research Center

An atomistic Green function theoretical formalism to compute phonon transport in nanostructures will be presented, and its application to several different problems will be discussed. In particular, we present calculations of the thermal conductivity of Si and Ge nanowires, and compare these with some experimental results [D. Li et al., submitted]. One important problem that has not yet been extensively studied in an atomistic framework, is that of ballistic vs. diffussive phonon transport. Using our atomistic Green function approach, we study the transition from ballistic to diffusive phonon transport, occuring as the system's length increases. The way in which this transition takes place is largely determined by properties of its boundary. We will discuss the ballistic-diffusive transition in terms of atomic properties of the wire and its coating. Differences between (111) and (110) orientated nanowires are shown to be of more importance in the ballistic regime than in the diffusive one. Finally, a two parameter model, with the parameters depending only on bulk material properties, is also derived. Using this method we obtained good predictive calculations of the thermal conductivity of Si nanowires. The method employs the full phonon dispersion relations of bulk Si. The relative importance of specific nanowire modes not present in bulk, as the system's size becomes smaller, will be discussed. The results and methods presented offer an exciting new range of possibilities in the study and development of thermal transport through nanosized devices.

Organic Films and Devices
Room 318/319 - Session OF+EM-TuM

Molecular and Organic Films and Devices-Electronics

Moderator: A.R. Duggal, GE Global Research

8:20am **OF+EM-TuM1 Charge Transport and Charge Injection in Polymer Field Effect Transistors***, **H. Sirringhaus**,* University of Cambridge, UK **INVITED**

Conjugated polymer semiconductors have been intensely researched over the last 15 years as active layers in solution-processed semiconducting devices, such as field-effect transistors. Here we will disucss recent progress in understanding the charge transport physics of conjugated polymer semiconductors. Particular emphasis will be on polaronic relaxation effects, distinction between interchain and intrachain charge transport, and the physics of charge injection from a metal electrode into a polymer a semiconductor. Polymer field effect transistors offer new opportunities for the controlled manufacturing of active electronic circuits by a combination of solution processing and direct printing. Control over the morphology of the polymer semiconductor is obtained by making use of self-organisation mechanisms, such as liquid-crystalline phase behaviour. Techniques such as surface energy-assisted inkjet printing or embossing can be used to manufacture integrated polymer transistor circuits.

9:00am **OF+EM-TuM3 High Mobility Organic Field Effect Transistors***, **S.E. Sysoev**, V.V. Podzorov, E.M. Loginova, M.E. Gershenson,* Rutgers University

Both organic thin film transistors (OTFTs) and organic single crystal field effect transistors (OFETs) are of primary interest for the characterization of the transport properties of novel organic materials.@footnote 1@ At the present, a comparison between these two approaches shows that the mobility is low on the deposited thin films, which is attributed to interface and grain boundary phenomena.@footnote 2@ In the case of single crystal OFETs there are several key factors, which affect their performance (the mobility and on/off ration). We will report on optimization of the OFET fabrication process, which allowed to reproducibly obtain the values of µ ~ 10 cm@super 2@/Vs. To the best of our knowledge, this is the highest mobility reported for organic field-effect devices at room temperature. In addition, in contrast to the TFTs, our devices demonstrate the threshold-less operation, gate voltage in-dependent mobility and very small subthreshold slope. @FootnoteText@@footnote 1@D. Tsamouras et al. Appl. Phys. Lett. 80, 4528 (2002). @footnote 2@T. Komoda et al. Jpn. J. Appl. Phys., 41, 2767 (2002).

9:20am **OF+EM-TuM4 Growth Dynamics and Electrical Properties of Pentacene Ultra-thin Films***, **R. Ruiz**, A. Mayer, G. Malliaras,* Cornell University*; R.L. Headrick,* University of Vermont*; A.Y. Kazimirov, J.R. Engstrom,* Cornell University

Organic/inorganic interfaces play a crucial role in the rapidly growing field of molecular electronics. Even though huge progress has been achieved in the understanding of electronic transport in conjugated molecular materials, a complete study that relates the nucleation and growth mechanisms with charge transport properties in pentacene thin films is still missing, especially within the first few monolayers adjacent to the gate substrate where charge transport is believed to occur. Pentacene thin films were evaporated onto silicon oxide substrates and analyzed by in-situ synchrotron X-ray scattering and ex-situ atomic force microscopy (AFM). The evolution of the first monolayers was studied by monitoring the intensity of scattered X-rays at the anti-Bragg position. Layer coverages were then extracted from the X-ray intensities using a simple growth model and compared to AFM micrographs. Film evolution as a function of substrate temperature will also be discussed. Thin film transistors were also fabricated with these films for electrical characterization showing a field effect hole mobility of 0.1 cm@super 2@/V·sec.

9:40am **OF+EM-TuM5 Optical and Electronics Properties of Poly(o-Methoxyaniline) (POMA) for Organic FET Applications***, **R.P. Shrestha**, D.X. Yang, E.A. Irene,* University of North Carolina at Chapel Hill

The optical properties of spin coated thin films of poly(o-methoxyaniline) (POMA) was investigated using spectroscopic ellipsometry (SE) and optical absorption spectroscopy in the visibleâ€“near UV optical range. A Gaussian oscillator optical model was used to fit the data obtained from SE. Atomic force microscopy (AFM) was used to characterize film roughness and these results were also evaluated in the optical model. We have investigated the effect of different spin deposit conditions including spin rate, and concentration of solution and deposition ambient on the POMA film thickness, surface roughness, optical and electronic properties. Organic thin film field effect transistor fabrication was carried out using POMA on a gold line structure that formed the source and drain contacts and with SiO2 covered Si wafer as the gate dielectric and substrate, respectively. Device characteristics are presented.

10:00am **OF+EM-TuM6 An Optical and Electronic Properties Study of a Stable n-Type Organic Semiconductor: N,N'-bis(3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxydiimide***, **D.X. Yang**, R.P. Shrestha,* University of North Carolina at Chapel Hill*; T.J. Dingemans,* Delft University of Technology, The Netherlands*; E.T. Samulski, E.A. Irene,* University of North Carolina at Chapel Hill

The use of organic semiconductors in the electronic devices typically requires stable and reliable n and p-type semiconductors. Stable p-type organic semiconductors are well known, but useful n-type organic semiconductors are rare mainly due to their relative reactivity. In this study, a novel n-type organic semiconductor: N,N'-bis(3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxydiimide (NDA-n2) is investigated. NDA-n2 is stable up to 200 °C in air and shows excellent solubility in THF and CH@sub 2@Cl@sub 2@. Also, its co-planar packing structure could yield high electronic mobility. NDA-n2 film was spin-cast onto SiO@sub 2@ coated Si wafer substrate. The optical properties were determined using spectroscopic ellipsometry (SE) and optical absorption spectroscopy in the visible near UV optical range. The optical properties were obtained from the experimental data using a Gaussian oscillator model and regression analyses. The results show four absorption peaks around 4.60 eV, 3.87 eV, 3.68 eV and 3.48 eV. Atomic force microscopy (AFM) was used to obtain surface roughness which was included in the optical model using the Bruggeman effective medium approximation. Electrical properties were determined from simple structures and correlated with film deposition parameters. PN junctions were formed and evaluated.

10:20am **OF+EM-TuM7 Organic Semiconducting Materials for Plastic Electronics*, Z. Bao,*** Bell Labs, Lucent Technologies **INVITED**

Organic electroactive materials are now being considered as the active materials in displays, electronic circuits, solar cells, chemical and biological sensors, actuators, lasers, memory elements, and fuel cells. The flexibility of their molecular design and synthesis makes it possible to fine-tune the physical properties and material structure of organic solids to meet the requirements of technologically significant applications. In this talk, the performance of several new organic semiconducing materials will be presented. These materials are designed for high performance, long-term stability, and ease of fabrication.

11:00am **OF+EM-TuM9 Localized Deposition of Thin Films of Conducting Polyaniline on Microhotplates for Chemical Sensing*, G. Li,*** *S. Semancik,* National Institute of Standards and Technology

A procedure for directly processing thin films of conducting polyaniline on MEMs microhotplates is described. The method allows the fabrication of conductometric gas microsensors within microarray platforms. It combines alternating electrochemical and electroless surface polymerization steps along with the localized heating capability of microhotplates to selectively deposit strongly adhering, smooth and compact films on the hybrid (metal/SiO@sub 2@) surfaces of microhotplate sensing elements. The polyaniline films within the arrays can be deposited using different processing parameters and then further fuctionalized electrochemically. In this way, both the film thickness and film conductance can be efficiently fine-tuned to desirable values. Film thickness varies in the sub-micron range and the film conductivities range from insulating up to the order of magnitude 10@super 2@ S.cm@super -1@. In addition, we describe the effect of these film characteristics on the temperature programmed sensing performance of the microsensors to various gases (methanol, H@sub 2@O, CO and NH@sub 3@ etc at 1-1000 ppm concentrations in air).

11:20am **OF+EM-TuM10 Polymeric Aperture Masks for High Performance Organic Integrated Circuits*, D.V. Muyres*,** *T.W. Kelley, P.F. Baude, S. Theiss, M. Haase, P. Fleming,* 3M

We present here the use of polymeric aperture masks to fabricate high performance pentacene-based integrated circuits. The aperture masks are fabricated using a laser ablation process with capabilities of generating 10 micron features. A mask set consisting of 4 to 6 aligned layers has been fabricated and has been used to demonstrate functional rf-powered integrated circuits with 20 micron gate lengths. Devices consisted of shadow-mask patterned layers of gold, alumina and pentacene. TFT mobilities greater than 2 cm2/Vs were measured and propagation delays from 7-stage ring oscillators of less than 5 microseconds were observed. This all-additive, dry patterning method has been extended to the production of samples as large as 6 â€œ x 6 â€œ. Larger aperture masks are under investigation and continuing efforts are focused on automation of the alignment process.

11:40am **OF+EM-TuM11 Conducting Nanofibers Integrated with Surface Micromachined Structures**, *D. Czaplewski,* ***H. Liu,*** *J. Kameoka, R. Mathers, G. Coates, H.G. Craighead,* Cornell University

We present a non-lithographic approach to the formation of oriented polymer nanowires on patterned surfaces. We utilized MEMS structures to deposit conducting nanofibers integrated with patterned electrodes on the surface of a silicon chip. The MEMS structures, used as scanned electrospray sources, are bulk micromachined silicon tips fabricated using microfabrication techniques. A 5 kV potential was applied between the MEMS tip and a rotating counter electrode, which was used to control the orientation of the fibers on the silicon chip containing the measurement electrodes. The nanofibers would form from the extraction of a liquid jet from the silicon tip under an applied electric field. The fibers would dry in transit to the counter electrode, thus depositing single cylindrical fibers. We deposited nanofibers made from a mixture of poly(ethylene oxide) and polyaniline on surface patterned electrodes. Fibers, with diameters ranging from 600 nm to 20 micrometers, were deposited on a set of 4 electrodes, used in a 4 point probe configuration. We measured the conductivity of the fibers, which is consistent with previous reports. We have deposited poly(ethylene oxide) fibers suspended over trenches with diameters as small as 50nm. Additionally, we have used this method to deposit fiber arrays, forming polymer junctions. This method can be used to deposit polymers of various compositions integrated with topographical and surface features.

Plasma Science and Technology
Room 315 - Session PS+TF-TuM

Plasma Enchanced Chemical Vapor Deposition

Moderator: D.C. Guerin, Naval Research Laboratory

8:20am **PS+TF-TuM1 PECVD, From the Laboratory to Mass Production*, J.P.M. Schmitt*[1]*,*** Unaxis Management Incorporated, Switzerland **INVITED**

After a rapid recall of the "alchemist" age of gas decomposition by an electrical arc, the gradual birth of PECVD is described in the early 70's. The richness of PECVD potential was then realised creating expectations for a long list of potential applications. Soon after the first industrial applications of PECVD were demonstrated. A look back at the pioneering days of PECVD allows to identify and discuss the key attributes of PECVD that made (and keep) this technology attractive for film coating. In the early 80's PECVD was hype and was the objet of active research. Basic research teams activity focused on the complex mechanisms involved in the PECVD process. First were understood the basic steps such as electron induced molecular dissociation and particle-surface processes. It is only later that far more complex mechanisms such as dust formation were found to be also extremely important. The status of knowledge on basic mechanisms will be reviewed. In the last 15-20 years a wide variety of configurations for the plasma reactors were tested. Instead of a complete zoological classification of all variations, we relate various classes of plasmas with their most marking attributes to the PECVD process key mechanisms. If in the 80's PECVD was already at work in mass production plants, it is in the 90's that a full set of production related problems were actively addressed. Self-cleaning was found a highly desirable ability for a PECVD tool. This requirement combined with high throughput demand led to new classes of equipment and processes. The application field of PECVD also stretched from the food industry the most sophisticated high tech industry. PECVD is today facing new challenges. The glass substrate size for the flat display industry is about to exceed 2m@super 2@ still requiring good uniformity and high throughput. PECVD has also the opportunity to prove itself into new fields such as semiconductor epitaxy or deposition of organic based films with functional groups.

9:00am **PS+TF-TuM3 Plasma-enhanced Deposition of Silicon and Metal Oxynitride Films in a High-density Ammonia Discharge**, *Z.G. Xiao,* ***T.D. Mantei,*** University of Cincinnati

Silicon, titanium, zirconium, and chromium oxynitride films have been grown in a high-density electron cyclotron resonance (ECR) ammonia discharge. The organosilicon deposition precursors for silicon oxynitride were hexamethyldisiloxane and tetramethylsilane, while the organometallic deposition precursors for metal oxynitride were titanium (IV) isopropoxide and tetrakis(dimethethlyamino)titanium, zirconium 2-methyl-2-butoxide and zirconium t-butoxide, and bis(ethylbenzene)chromium. The plasma-grown films had nanoindentation hardness values of 12 - 14 GPa for SiN, 20 - 28 GPa for TiN, 17 - 21 GPa for ZrN, and 25 - 31 GPa for CrN. Deposition growth rates were 40 - 50 nm/min for silicon oxynitride and 10 - 20 nm/min for the metal oxynitrides. X-ray photoelectron spectroscopic (XPS) analyses showed the nitrogen content of silicon, titanium, and zirconium oxynitrides to be 31% - 38%, while the CrN nitrogen content was 15%. The SiN films grown from hexamethyldisiloxane were colorless and transparent while films grown from tetramethylsilane had the characteristic dark color of Si@sub 3@N@sub 4@. The TiN and ZrN films had the characteristic brass and white gold colors of TiN and ZrN reference samples while the CrN samples were gray. The SiN films lasted 800 hours in an ASTM B117 accelerated salt-fog corrosion test without visible corrosion, and the TiN and ZrN films lasted 1000 hours without visible color change or corrosion.

9:20am **PS+TF-TuM4 Identification of the Growth Precursors for Hydrogenated Amorphous Carbon Growth*, J. Benedikt*[2]**, *R.V. Woen, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The plasma chemistry and plasma composition of argon/acetylene expanding thermal plasma, used for fast (up to 70 nm/s) hydrogenated amorphous carbon (a-C:H) film deposition, was studied by means of Cavity Ring Down absorption Spectroscopy and Mass Spectrometry. Since the electron temperature in expanding thermal plasma beam is low (less than 0.3 eV) electron impact processes can be neglected and acetylene dissociation is argon ion induced. The C@sub 2@H radical was identified as

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[1] **AVS 50th Anniversary Invited Speaker**

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

the main growth precursor for hard (14 GPa) diamond-like a-C:H films. It was shown that under conditions where most of acetylene molecules are decomposed into C, CH and C@sub 2@ radicals, the a-C:H films are soft and polymer-like. Furthermore it was observed that good a-C:H films can be grown also under conditions when C@sub 4@H@sub 2@ molecules are the main plasma chemistry product and when reactive radicals as C@sub 2@H has already reacted away with acetylene in the gas phase. The mass spectrometry measurements of C@sub 4@H@sub 2@ molecule in the background of the plasma shows that C@sub 4@H@sub 2@ density depends on the wall condition (argon plasma activated or hydrogen plasma passivated) suggesting that C@sub 4@H@sub 2@ is one of the contributors to the film growth. C@sub 2@H and C@sub 4@H@sub 2@ as possible precursors for a-C:H growth is confirmed by recent Molecular Dynamics simulations which reveal reaction probabilities close to one for both species.

9:40am **PS+TF-TuM5 Characterization of TaN Diffusion Barrier Layers Prepared by Chemical-Enhanced Physical Vapor Deposition (CEPVD)**, ***N. Li***[1], *D.N. Ruzic,* University of Illinois, Urbana-Champaign

CEPVD of TaN is a novel process attempting to deposit diffusion barrier layers with both high conformal step coverage (as in CVD) and superior quality (as in PVD). The experiments are performed by sputtering a Ta target in a modified conventional PVD instrument and simultaneously adding a certain amount of chemical precursor, TBTDET, in the vicinity of the substrate at elevated temperature (330@degree@C) in combination with a carrier gas (N2), reducing agent (H2), non-reactive sputtering gas (Ar) and a RF-powered secondary ionization plasma. Different combinations of RF power, N2, H2, Ar flow and bias voltage result in distinct resistivity regimes. Increasing H2 flow rate from 5 sccm to 10 sccm allows more hydrocarbon formation and thus results in significant resistivity variation. The addition of 10sccm Ar increases target sputtering and more Ta flux, producing film with relatively lower resistivity (5200 Î¼ -cm compared to 62,000 Î¼ -cm). The addition of Ar also produces a more columnar and porous structure. N2 flow rate determines precursor residence time and so controls growth density and deposition rate. Biasing the substrate with -60 V drops resistivity one order of magnitude. Patterned wafers with various trench aspect ratios are lined to compare the step coverage under different processing conditions. Four point probe, SEM, AES, XRD and XPS are utilized to characterize the film properties and the analysis reveals the balance between energetic Ta flux, TBTDET breakup and impurity volatilization. The synergy between PVD and CVD is clearly demonstrated.

10:20am **PS+TF-TuM7 Anisotropic Cu Deposition using Plasma Chemical Vapor Deposition**, ***M. Shiratani***, *K. Takenaka, M. Takeshita, M. Kita, K. Koga, Y. Watanabe,* Kyushu University, Japan **INVITED**

We have demonstrated complete filling of trenches by anisotropic Cu deposition, in which Cu is filled preferentially from the bottom of the trenches, using plasma chemical vapor deposition.@footnote 1@ The key to realize the anisotropic deposition is kinetic energy and flux of ions irradiating on the surface, since the deposition rate increases with increasing the kinetic energy and fluxes. Previously, by using H-assisted plasma CVD we have realized conformal deposition of smooth 20 nm thick Cu films in trenches as well as conformal filling of trenches.@footnote 2@ Although the Cu films have a low as-deposited resistivity of of 1.85 µ@ohm@cm and a strong adhesion strength above 10 MPa to the TiN layer, conformal filling results in a small crystal grain size below half of the trench width and in a seam where impurities of high concentration remain. The anisotropic deposition offers a possibility to overcome such shortcomings for the conformal filling together with two additional interesting features. One is the fact that deposition rate increases with decreasing the width of a trench. The other is a self-limiting deposition by which deposition stops automatically just after filling completely a trench. This feature may realize a LSI fabrication processes without the chemical mechanical polishing, being attractive for the Cu-porous low-k interconnects. @FootnoteText@@footnote 1@ K. Takenaka, et al., Matr. Sci. Smiconductor Processing 5, 301 (2003).@footnote 2@ M. Shiratani, et al., Sci. and Technol. of Adv. Mater. 2, 505 (2001).

11:00am **PS+TF-TuM9 Pulsed-plasma Deposition of Silicon Dioxide in a High Density Oxygen Discharge**, ***Y. Qi***, *T.D. Mantei,* University of Cincinnati

Hard clear silicon dioxide films have been grown from octamethylcyclotetrasiloxane (OMCTS) at low substrate temperatures in a pulse-modulated high density electron cyclotron resonance (ECR) oxygen plasma. The input microwave power at 2.45 GHz was pulse-modulated with repetition frequencies from 20 Hz to 20 kHz, duty ratios (on-time/period) from 5% to 100%, and peak microwave power levels from 800 W to 2400 W. The resulting films were SiO@sub 2@-like with Si-O bonds and Si:O ratios close to 1:2. The deposition growth rates were almost independent of frequency for all pulse repetition frequencies from 20 Hz to 20 kHz. The growth rates increased strongly as the peak pulse power was increased; with a 50% duty ratio, the growth rate was 0.5 - 0.6 mm/min with 800 W peak power, increasing to 0.8 - 0.9 mm/min at 1600 W peak power. The coating hardness values decreased with pulsed operation as the average input microwave power decreased. Deposition substrate temperatures were significantly lowered as the duty ratio (and thus the average power) decreased, e.g., substrate temperatures were 140°C - 150°C after 10 minutes of deposition with 1600 W of continuous microwave power, dropping to 90°C with a 50% pulse duty ratio and 1600 W peak power. Results from current experiments on pulsed low temperature growth of metal nitride and teflon coatings will also be discussed.

11:40am **PS+TF-TuM11 Secondary Plasma Based Debris Mitigation for Next-Generation 13.5nm EUVL Sources**, ***B. Jurczyk***, *D.N. Ruzic, E. Vargas-Lopez, M. Neumann, M. Williams, C. Chrpbak, S. Taj,* University of Illinois at Urbana-Champaign

Next-generation EUV photolithography machines (>25kW-class) require order of magnitude improvements in debris removal for component lifetime and stable operation. Discharge plasma light sources, such as the dense plasma focus, are leading candidates for EUV. The Illinois Debris-mitigation Experiment and Applications Laboratory (IDEAL) consists of a dense plasma focus discharge source operating on order of 25 J/pulse, 100 Hz rep rate, and 4 kV. Argon and Helium gases have been tested to generate plasma environmental conditions similar to that experienced by industry. The secondary-plasma-based debris mitigation technique is presented; a concept pioneered from iPVD reactors at the University of Illinois. Sputtered electrode and chamber component debris is re-ionized in the secondary plasma region and removed with the application of electric fields prior to the collection optics. A helical resonator inductive coil generates the secondary plasma with minimal coil self-biasing for decrease erosion. A dual-channel foil trap, with independently biased plates (0-1kV), collects debris from the secondary plasma region. The foil trap is positioned to vary aspect ratios from 1:1-to-16:1 to correlate with gas pressure effects. Results from in-situ high-precision quartz-crystal-oscillators, ex-situ surface characterization (XPS, Auger, Profilometry, etc.), secondary plasma characterization, and collection optic protection factors are presented for a series of mitigation schemes.

Plasma Science and Technology
Room 314 - Session PS-TuM

Plasma Diagnostics: Processing

Moderator: H. Sugai, Nagoya University, Japan

8:20am **PS-TuM1 Attractive Interactions Between Negatively Charged Dust Particles in a Plasma**, ***G.A. Hebner***, *M.E. Riley,* Sandia National Laboratories

Plasma dust particle interactions, charges, and screening lengths are derived from measurements of time-dependent particle positions in a simplified geometry. The magnitude and structure of the ion wakefield potential below a negatively-charged dust particle levitated in the plasma sheath region were measured as functions of the pressure and interparticle spacing. Attractive and repulsive components of the interaction force were extracted from a trajectory analysis of low-energy dust collisions between different mass particles in a well-defined electrostatic potential that constrained the dynamics of the collisions to be one dimensional. Typical peak attractions varied between 60 and 230 fN while the peak particle-particle repulsion was on the order of 60 fN. Random thermal motion of the particles contributed to observable rates for transitions between different equilibrium configurations of vertically separated particles. We also observed a slight potential barrier that impeded the formation of vertically aligned pairs. The influence of nearest- and non-nearest-neighbor interactions on calculated particle parameters are examined using several methods. Implications for plasma / surface interactions and plasma dielectric charging will be discussed. This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the

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

United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:40am **PS-TuM2 Measurement of Electrical Fields Around Dissimilar Materials Exposed to a Discharge***, **E.V. Barnat**, G.A. Hebner,* Sandia National Laboratories

The nature of a surface/plasma boundary can have an important impact on the processes that occur both in the plasma and on the bounding surface. In this work, fluorescence-dip spectroscopy is used to study the surface dependant sheath structure at the boundary of an argon glow discharge. The two laser technique monitors the variation in the fluorescence from an intermediate state caused by laser excitation from this intermediate state to Stark-shifted Rydberg levels sensitive to the electric fields present in the sheath. To demonstrate the effectiveness of the dip-spectroscopy technique, half of a conducting electrode is covered with an insulating surface and both spatially and temporally resolved measurements of the structure of the sheath are made around both the conducting and the non-conducting surfaces. The fields through the sheath above the two surfaces, the potential drops across the sheath, and the fields near the surface along the electrode are discussed for various discharge conditions. Future applications of fluorescence-dip spectroscopy will be discussed as well. @FootnoteText@ This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. .

9:00am **PS-TuM3 Plasma Processing Diagnostic Methods and Studies: A Historical Perspective***, **V.M. Donnelly***[1], University of Houston **INVITED**

In the late 1970's, plasma etching emerged as a breakthrough method for pattern transfer in silicon integrated circuits. Soon after, it became apparent that, to further develop this technology, it was important to understand the mechanisms responsible for anisotropic plasma etching. Researchers in industry, national laboratories and universities began applying well established diagnostic techniques, and inventing new methods, for elucidating the chemical and physical processes underlying plasma etching, as well as plasma assisted deposition. Experiments were designed to either measure parameters of the plasma (species concentrations and velocities), or to simulate plasma-surface interactions under less complex conditions (high-vacuum / beam experiments, discharge flow tubes, etc). This talk will review the history of diagnostic methods for plasma processing. An admittedly incomplete survey of plasma diagnostic techniques will begin with several methods that greatly predate the microelectronics era. Electrical, optical and beam methods will be discussed and selected key experiments will be highlighted.

9:40am **PS-TuM5 Absolute SiCl@sub X@ Densities in Silicon Gate Etching Plasmas Determined by Broad Band UV Absorption***, **M. Kogelschatz,*** CNRS/LSP, France*; G. Cunge,* CNRS/LTM, France*; N. Sadeghi,* CNRS/LSP, France*; O. Joubert, L. Vallier,* CNRS/LTM, France

Broad band UV absorption spectroscopy has been used to measure the absolute gas phase concentration of SiCl@sub X@ and SiF@sub X@ etch products (X = 0-2) during silicon gate etching in high density HBr/Cl@sub 2@/O@sub 2@ plasmas and their mixture with fluorocarbon gases. The silicon atom concentration in the ground and metastable states has also been measured. To convert the absorption rates to the Si atom density, the instrumental width of the monochromator had to be taken into account. Typical concentrations of etch products are about 10@super 11@cm@super -3@, and their behavior with the plasma conditions (RF power, O@sub 2@ gas flow) will be discussed. Vibrationnally resolved absorption spectra of SiCl@sub 2@ and SiBr, observed for the first time in etching plasmas, will also be presented. However, due to the lack of absorption cross sections, the absolute concentration of SiBr can not be deduced. A particular emphasize will be given on correlation between these etch products and the composition of the films deposited on the plasma chamber walls. This composition was determined from the analysis by OES and mass spectrometry of products introduced in the gas phase of a weak Ar-SF6 plasma from the chamber walls. The deposit of the silicon oxychloride layers on the walls is at the origin of process drifts as it changes the chemical composition of the surfaces exposed to the plasma. A large change of the recombination rate of Cl atoms as a function of the reactor walls composition has been observed by measuring the variation of the Cl/Cl@sub 2@ concentration ratio in the gas phase, as well as the absolute Cl@sub 2@ concentration by UV absorption.

10:20am **PS-TuM7 In-situ Processing Memory Effects for Confined vs. Unconfined Plasmas***, **E.A. Hudson**, R. Annapragada, D. Keil, K. Takeshita,* Lam Research Corp.

In the fabrication of integrated circuits there is a growing trend towards performing several etch steps in a single pass through an etch tool. This in-situ processing approach reduces production costs and cycle times, but presents technical challenges because it requires the sequential use of very different plasma chemistries in the same reactor. An important example is the use of a polymerizing fluorocarbon-based plasma to etch patterns into silicon dioxide or organosilicate films, followed by oxidizing plasmas to remove the remaining photoresist film. Residual fluorocarbon polymer, left on chamber surfaces by the etch step, is attacked under oxidizing conditions, releasing fluorine-containing species which may have harmful effects on the wafer structures. This paper compares the "fluorine memory" effect for unconfined vs. mechanically confined capacitively-coupled RF discharges. Diagnostic measurements focused on plasma properties, chamber surface cleaning efficiency, and wafer-level results. Optical emission spectroscopy was used to detect atomic fluorine in the plasma during the photoresist strip step. Fluorine was found to persist much longer in the case of the unconfined plasma. The impact of residual byproducts at the wafer was evaluated from silicon dioxide loss and from changes in feature dimensions. Results indicate that use of a mechanically confined plasma greatly reduces "fluorine memory" effects during the photoresist strip step, compared to the unconfined configuration. This is attributed to the reduced gas residence time and more efficient cleaning of chamber surfaces in the confined configuration.

10:40am **PS-TuM8 Plasma Diagnostics and Thin Film Characterization in Dielectric Etching: Understanding the Role of Fluorine Chemistry***, **B. Ji**, S.A. Motika, P.R. Badowski, S. Dheandhanoo, E.J. Karwacki, J.R. Stets,* Air Products and Chemicals, Inc.*; C. Timmons, D.W. Hess,* Georgia Institute of Technology*; E.C. Benck,* National Institute of Standards and Technology*; Y. Ye,* Applied Materials, Inc.

Plasmas of fluorine-containing gases have for many years been utilized to etch dielectric materials such as silicon dioxide. Maintaining the balance between the anisotropic dielectric etch rate and formation of the protective passivation films on top of the photoresist surface and on the feature sidewalls is critical in assuring desired etch features and critical dimensions. In recent years, the semiconductor industry have adopted heavier molecular weight and lower fluorine to carbon ratio gases, such as c-C@sub 4@F@sub 8@, C@sub 5@F@sub 8@, and C@sub 4@F@sub 6@ for anisotropic dielectric etching. We performed a fundamentals study to better understand the relationship between etch gas compounds and the species formed within both capacitively and inductively coupled plasmas. UV Absorption Spectroscopy, Sub-millimeter Wave Absorption Spectroscopy, Optical Emission Spectroscopy, Mass Spectrometry, and X-ray Photoelectron Spectroscopy were employed to evaluate the gas phase and surface chemistries of these three etching molecules.

11:00am **PS-TuM9 Loss Kinetics of CF@sub x@ Radicals and F Atoms in the Afterglow of Inductively Coupled Pulsed Plasmas***, **X. Wu**, J.L. Cecchi,* University of New Mexico

We have studied the time evolution of the concentrations of CF, CF@sub 2@, and F in inductively coupled pulsed (ICP) plasmas after the termination of the discharge. The feed gases included CHF@sub 3@ and C@sub 2@F@sub 6@, with additions of H@sub 2@and O@sub 2@, to vary the amount of radicals and F produced in the discharge. Our observations were made over the pressure range from 10 to 60 mTorr and for inductively coupled powers of 300 to 900 W. Concentrations were determined by time-resolved wavelength modulated diode laser absorption spectroscopy for the radicals and by time-resolved actinometry for F. The latter measurements were facilitated by maintaining a small amount of power on the wafer chuck after the termination of the ICP power pulse. CF and F both exhibited first order exponential decays. The decay rates of CF increased with increasing pressure, suggesting the presence of gas phase loss processes in addition to losses at surfaces. The decay rates of CF varied linearly with F concentration, indicating that the gas phase reaction is likely due to the recombination with F atoms. CF@sub 2@ exhibited second-order decay. Possible mechanisms for this will be discussed.

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[1] **AVS 50th Anniversary Invited Speaker**

11:20am **PS-TuM10 Effect of an Applied-phase of Bias Pulse on a Charge Reduction on a SiO@sub 2@ Hole Exposed to Plasma Etching in a Two-frequency CCP***, **T. Ohmori,** T.K. Goto, T. Makabe,* Keio University, Japan

In a top-down nano-meter scale etching, it will be essential to develop in-situ diagnostics for plasma damage in the interface under close and complementary cooperation between optical and electric procedure. In our previous paper@footnote 1@ we have applied an emission selected computerized tomography close to the wafer exposed to plasma etching, in order to investigate the polarity and the phase of high energy charged particles incident on the wafer deeply biased by a low frequency source in RIE. A reduction in charging voltage on a contact hole bottom of SiO@sub 2@ was measured in the pulsed plasma power source in the 2f-CCP in CF@sub 4@/Ar by using a dual measurement system consisting of a temporal emission CT and a contact hole charging. In the present work, detailed correlational results of the reduction in the charging voltage are shown as a function of phase and amplitude of the single bias pulse at 500 kHz. Discussion is focused both on the injection mechanism of energetic negative charges to the wafer and on the magnitude of the negative charges. As a result, during the off-period 10 µs of VHF power source it is confirmed in the present pulsed 2f-CCP system that:(1)the magnitude of the injected negative charge increases with increasing the threshold time of the single bias pulse, and at the same time a strong reduction in the charging voltage is performed, (2)secondary a strong negative self-bias-voltage is always kept to have an efficient RIE with energetic positive ions on the wafer except for the period of the single bias pulse. @FootnoteText@ @footnote 1@T.Ohmori, T.K.Goto, T.Kitajima, and T.Makabe, Proc.of Dry Process Symposium 165(2002)Tokyo, Appl.Phys.Lett.(submitted).

11:40am **PS-TuM11 Analysis of Downstream Etch Chemistry in Ion-Ion and Electron-Ion Cl2 Discharges***, **A.K. Jindal,** A.J. Prengler, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

It has been shown that ion-ion plasmas can significantly reduce substrate charging damage. This study clearly shows that ion-ion plasmas also influence the etch chemistry. This knowledge may facilitate improvements in plasma processing or environmental control. Here, we use FTIR spectroscopy to examine the volatile etch products downstream of the turbo pump resulting from the etching of C-Si, SiO2, and photoresist in electron-ion and ion-ion Cl2 discharges. RF power is either pulsed to produce ion-ion plasmas or continuous to produce electron-ion plasmas. An independently controlled chuck is rf biased to produce an alternating flux of negative and positive ions or a combination of electrons, negative ions, and positive ions at the substrate. Changes in etch chemistry are studied and compared as functions of biasing schemes and substrate chuck voltages. Continuous wave (electron-ion), asynchronous, and synchronous, biasing regimes are all subjected to peak to peak chuck biases of 25, 50, 75, and 100 V via a 300 kHz waveform. Asynchronous and synchronous (ion-ion) modes apply to 1 kHz, 50 percent duty ratio pulsed regimes of the discharge in which the former implies continuous biasing throughout the entire pulse cycle and the latter to only the afterglow, where an ion-ion plasma exists. Clear distinctions in etch chemistry are evident solely based upon the biasing scheme. For example, CO2 is observed for all chuck biases in both pulsed regimes during photoresist etch, but no signal is apparent at lower biases in the continuous mode. Not only is there an undeniable difference in etch chemistry, but we can affect our emission by varying the biasing scheme. This work was funded in part by a grant from NSF/DOE, contract number CTS-0078669 and a grant from NSF, contract number CTS-0079783.

Semiconductors
Room 321/322 - Session SC-TuM
Narrow Gap Semiconductors

Moderator: P. Desjardins, École Polytechnique de Montréal, Canada

8:20am **SC-TuM1 Antimonide-Based Compound Semiconductors: From Interfaces to High-Speed Transistors***, **B.R. Bennett**, R. Magno, J.B. Boos,* Naval Research Laboratory*; R. Tsai, A. Gutierrez,* Northrop Grumman Space Technology **INVITED**

Future high-speed analog and digital systems that will benefit from reduced power consumption and high data transmission rates include wireless applications, space-based, and micro-air-vehicles used for communications, imaging, and sensing. The development of Sb-based electronics for use in low-noise high-frequency amplifiers, digital and mixed-signal circuits could provide the enabling technology to address these needs. Our group has been using MBE to grow heterostructures for Sb-based high electron mobility transistors (HEMTs), resonant tunneling diodes (RTDs) and heterojunction bipolar transistors (HBTs). In this talk, I will discuss the design, growth, and performance of these devices. Growth issues include interface formation, doping, and composition control of alloys containing both As and Sb. The attractive material properties of this system have been demonstrated by our development of high-speed, low-power AlSb/InAs HEMTs with an intrinsic f@subT@ value of 250 GHz at V@subDS@ = 600 mV and an f@subT@ of 90 GHz at 100 mV. Current work is focused on making the technology viable by reducing leakage currents and developing MMIC-compatible processing. We have also fabricated RTDs with InAs contacts, Al(Ga)Sb barriers, and GaSb wells. For barriers that are 9 Å thick, peak currents exceed 10@super4@A/cm@super2@ with peak-to-valley ratios of 10:1 at biases near 100 mV. Other HEMT and RTD technologies (e.g. GaAs and InP) cannot achieve comparable performance at such low voltages. HBTs using InGaSb for the base and InAlAsSb alloys for the collector and emitter are also being explored. The InGaSb base is attractive due to its narrow bandgap and good hole transport characteristics. In addition, a wide range of heterojunction design flexibility is available because of the various InAlAsSb alloys that can be used. Good diode characteristics with an ideality factor of 1.1 have been obtained for InGaSb/InAlAsSb p-n heterojunctions grown with a 6.2 Å lattice constant.

9:00am **SC-TuM3 Understanding the Electronic Properties of Diluted Nitrides Relevant to Optoelectronic Applications***, **W.M. Chen,*** Linköping University, Sweden*; I. Buyanova,* Linkoping University, Sweden **INVITED**

Dilute nitride semiconductors exhibits unusual physical properties, like a giant bowing in the bandgap energy, forming an attractive new material system promising for long wavelength light emitters operating within the optic-fiber communication wavelength window. A full exploration of the alloys potential in device applications requires, however, detailed knowledge of their fundamental physical parameters and material issues. In this talk we shall provide an overview of our present understanding of basic electronic properties of the dilute nitrides such as Ga(In)NAs alloys and some key material-related problems relevant to optoelectronic device applications, such as determination of dominant mechanism for carrier recombination, potential fluctuation and localization effect, identification and formation of non-radiative defects, effects of post-growth thermal annealing and hydrogenation, compositional dependence of the electron effective mass and band alignment in Ga(In)NAs/GaAs heterostructures.

9:40am **SC-TuM5 Nitrogen Incorporation and Strain Relaxation Mechanisms during Metalorganic Vapor Phase Epitaxy of GaAsN Layers on GaAs (001)***, **J.-N. Beaudry,*** École Polytechnique de Montréal, Canada*; G. Bentoumi,* Université de Montréal, Canada*; S. Guillon,* Bookham Technology, Canada*; R. Leonelli,* Université de Montréal, Canada*; R.A. Masut, P. Desjardins,* École Polytechnique de Montréal, Canada

GaAs@sub 1-x@N@sub x@ epilayers (x @<=@ 0.04), nominally 200-nm-thick, were grown on GaAs (001) by metalorganic vapor-phase epitaxy using trimethylgallium, tertiarybutylarsine (TBAs), and dimethylhydrazine (DMHy). We carried out a systematic investigation of N incorporation as a function of the J@sub DMHy@/J@sub TBAs@ flow rate ratio for growth temperatures T@sub s@ varying from 500 to 650°C. Quantitative secondary ion mass spectrometry measurements indicate that N incorporation increases initially linearly with J@sub DMHy@ with a temperature-dependent incorporation probability that decreases from 0.0036 at 500°C to 0.0005 at 600°C to nearly zero at 650°C. The use of very large DMHy flow rates results in larger incorporation probabilities but lower growth rates. High resolution x-ray diffraction (HR-XRD) shows that the GaAs@sub 1-x@N@sub x@ lattice parameter decreases approximately linearly with increasing x up to about 0.02, with a strain coefficient corresponding to a linear interpolation between the lattice constants of GaAs and cubic GaN. At higher N fractions, the lattice parameter decreases more rapidly. Films with x up to approximately 0.02 are perfect single crystals with smooth interfaces as judged by HR-XRD and cross-sectional transmission electron microscopy (XTEM). Atomic force microscopy and cross-sectional imaging by transmission electron microscopy of a 230 nm thick layer with x = 0.0375 show that crack formation is the most important tensile strain relief mechanism although extrinsic stacking faults and misfit dislocations were also observed. Optical absorption and photoluminescence analyses reveal that higher crystalline quality and lower impurity concentrations were obtained for growth between 575 and 600°C.

10:00am **SC-TuM6 Stress Evolution and Nitrogen Incorporation in GaAsN Films Grown by Reactive Molecular Beam Epitaxy*, M. Reason,*** *W. Ye, X. Weng, G. Obeidi, V. Rotberg, R.S. Goldman,* University of Michigan

Narrow gap nitride semiconductors have shown significant promise for a wide range of applications including long-wavelength light-emitters, high performance electronic devices, and high efficiency solar cells. A consequence of the large N-As size difference is a predicted limited miscibility on the anion sublattice, which often leads to the formation of GaN-rich nanostructures.@footnote 1,2@ In the case of dilute GaAs@sub 1-x@N@sub x@, conflicting results have been reported regarding the mechanism of N incorporation, and recent optical studies have suggested that the shear deformation potential and/or the binary elastic constants have an unusual composition dependence.@footnote 3@ To date, studies of stress evolution in GaAsN have been limited to x-ray rocking curves (XRC), typically interpreted using a linear interpolation of elastic constants. We have investigated stress evolution in GaAsN films, using a combination of in-situ and ex-situ measurements. A comparison of Nuclear Reaction Analysis and Rutherford Backscattering Spectrometry in channeling and non-channeling conditions suggests significant composition-dependent incorporation of N into non-substitutional sites. Furthermore, a comparison of stresses measured via in-situ wafer curvature measurements, with those determined using a Vegard's Law interpretation of XRC, suggests a change in the mechanism of N incorporation for x@>=@0.015. The observed stress differences are likely the signature of significant bowing of the elastic properties of GaAsN. This work was supported in part by the DOE (Photovoltaics Beyond the Horizon Program), the Air Force Office of Scientific Research (MURI Program), and the TRW Foundation. @FootnoteText@@footnote 1@R.S. Goldman et al., Appl. Phys. Lett. 69, 3698 (1996), J. Electr. Mater. 26, 1342 (1997). @footnote 2@X. Weng, S.J. Clarke, W. Ye, R.S. Goldman, et al, J. Appl. Phys. 92, 4012 (2002). @footnote 3@Y. Zhang, A. Mascarenhas, H.P. Xin, and C.W. Tu, Phys. Rev. B 61, 4433 (2000).

10:20am **SC-TuM7 Electronic and Optical Properties of GaAsN/GaAs Quantum Wells*, N. Shtinkov,*** *S. Turcotte, J.-N. Beaudry, P. Desjardins, R.A. Masut,* École Polytechnique de Montréal, Canada*; G. Bentoumi, R. Leonelli,* Université de Montréal, Canada

We present a theoretical and experimental investigation of the electronic structure and optical properties of GaAs@sub 1-x@N@sub x@/GaAs (001) quantum wells (QWs) with x < 0.045. The electronic structure is calculated using a recently developed empirical tight-binding (ETB) model, taking strain into account, for values of the GaN/GaAs valence band offset (VBO) from -4 to 4 eV. The valence band structure is found to be strongly influenced by the VBO and the strain-induced heavy hole-light hole splitting. At zero VBO only one heavy-hole and one light-hole state are observed. For VBO < 0 the ground hole state is localized in the barrier, but quasi-bound QW-localized heavy-hole states are observed in the continuum. For VBO > 0, the ground state is always a light-hole state localized in the QW, but there exist a number of excited heavy- and light-hole states. In spite of the significant influence of the VBO on the valence band structure, our results show that its effect on the transition energies is rather small for positive VBO. For example, changing the VBO from 0 to 4 eV in a QW with x = 0.04 shifts the ground state transition energy by only 16 meV. Therefore in simple rectangular QWs only the sign but not the value of the VBO can be unambiguously deduced from measurements of the transition energies. In order to compare our predictions with experimental results, we have measured low-temperature optical absorption spectra from fully coherent 7-period 7-nm-GaAs@sub 1-x@N@sub x@/15-nm-GaAs multiple quantum wells with x up to 0.04. We found that the measured ground-state and excited-state transitions are in good agreement with our ETB calculations when considering a positive GaAsN/GaAs VBO.

10:40am **SC-TuM8 Growth of InN and Related Compounds by RF Plasma Molecular Beam Epitaxy*, W.J. Schaff,*** *H. Lu,* Cornell University **INVITED**

InN is of interest for small bandgap, low effective mass applications. InN is grown with a remote RF plasma source of nitrogen using molecular beam epitaxy at substrate temperatures near 500C. GaN or AlN buffers on c-plane sapphire substrates are required for best InN quality. More than 200 wafers have been grown. All exhibit a direct bandgap near 0.7eV which is frequently measured for MBE grown InN@footnote 1@ and agrees with theoretical calculations.@footnote 2@ Bandfilling effects explain observations of increased energy of optical transitions at increased electron density.@footnote 3@ Control of electrical conductivity is limited. Undoped InN is n-type with electron densities that are usually high enough to be degenerate. Electron density falls with InN layer thickness and can be as low as 3E17cm-3 in layers beyond 5 microns thick. 300K mobility is beyond 1000 cm2/Vsec in 1 micron layers and is above 2000 in 5-7 micron thick layers.@footnote 4@ Dislocation density also decreases with InN layer thickness. A cause-effect relationship between electron and dislocation density is not established yet. Si is introduced as a shallow donor while unintentional shallow donors have not been identified. InN has not been made p-type. Mg and Be doping affects electron density and mobility, but net p-type conductivity has not been seen. InN can be grown in the a-plane direction when a-plane GaN or AlN buffers are used on r-plane sapphire.@footnote 5@ In contrast, direct growth on r-plane sapphire without a buffer layer creates predominantly a cubic form of InN.@footnote 6@ Mobility is lower and carrier density is higher in InN in the forms which are not c-plane wurtzite. @FootnoteText@ @footnote 1@V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, et al, phys. stat. Sol. (b), 229, R1 (2002).@footnote 2@ F. Bechstedt, J. Furthmüller, M. Ferhat, L. K. Teles, L. M. R. Scolfaro, J. R. Leite, V. Yu. Davydov, O. Ambacher, and R. Goldhahn, phys. stat. sol. a 195, 628 (2003).@footnote 3@ V. Cimalla, Ch. Förster, G. Kittler, I. Popa, R. Kosiba, G. Ecke, O. Ambacher,R. Goldhahn, S. Shokhovets, A. Georgakilas, H. Lu, W. Schaff, Proc. ICNS-5 submitted to phys. stat. sol (a) 195, No. 1, 3-10 (2003).@footnote 4@ H. Lu, W.J. Schaff, L.F. Eastman, GaN and Related Alloys - 2001. Symposium (Materials Research Society Symposium Proceedings Vol.693) Mater. Res. Soc, 2002, xv+860 p. (9-14).@footnote 5@ H Lu, W.J. Schaff L F. Eastman, J. Wu, Wladek Walukiewicz, Volker Cimalla, Oliver Ambacher, submitted to Applied Physics Letters.@footnote 6@ V. Cimalla, J. Pezoldt, O. Ambacher, L. Spiess, and G. Teichert, H. Lu and W. J. Schaff, submitted for publication.

11:20am **SC-TuM10 Electronic Band Structure Ge(1-x)Sn(x) Alloys Grown on Silicon*, C.S. Cook,*** Arizona State University*; S. Zollner,* Motorola*; M. Bauer, J. Kouvetakis, J. Menendez, J. Tolle,* Arizona State University*; C. Bungay,* J. A. Woollam Co., Inc.

The development of manufacturable direct band gap materials on Si is crucial for optoelectronic devices integrated with silicon circuits. Ge-Sn alloys with varying metastable compositions ranging from 2% - 18% were grown by UHV-CVD using a newly developed deuterium-stabilized Sn hydride with digermane. We use deep ultra violet and infrared spectroscopic ellipsometry to determine the optical properties of this new class of Si-based infrared semiconductors in the Ge1-xSnx system. Optical analysis of the energy derivatives in comparison with analytical lineshapes shows a Ge-like bandstructure that is substantially red-shifted compared that of elemental Ge. Tunability of these gaps with composition could have interesting optoelectronic applications.

Advanced Surface Engineering
Room 323 - Session SE-TuM

Nanostructured, Nanocomposite, and Functionally Gradient Coatings

Moderator: Y.W. Chung, Northwestern University

8:20am **SE-TuM1 Influence of Sputtering Condition and Target Material on the Microstructure and Properties of Ti-Si-N Coatings Prepared by r.f.-reactive Sputtering*, M. Nose,*** Takaoka National College, Japan*; Y. Deguchi,* Toyama University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; E. Honbo,* Toyama Industrial Research Center, Japan*; W.A. Chiou,* University of California, Irvine*; K. Nogi,* Osaka University, Japan

Since Veprek et al. presented a theoretical concept to design super-hard nano-crystalline composite materials on the TM-Si-N (TM = transition metal) systems consisting of nano-crystalline transition metal nitrides embedded in amorphous Si@sub 3@N@sub 4@, many studies on these kinds of films deposited by PVD have been reported. Although most of them used r.f.- or d.c.-reactive sputtering in an Ar/N@sub 2@ gas mixture, the results were not always consistent with each other. This suggests that the structure of films depends sensitively on the deposition conditions. Hence, we decided to examine the effect of sputtering condition and target material on the microstructure and mechanical properties of Ti-Si-N coatings prepared by r.f.-reactive sputtering. We used the composite targets conisting of Ti (99.99%) plate and Si@sub 3@N@sub 4@ chips as well as the target consisting of Ti plate and Si chips. Thin films were synthesized by r.f. sputtering machine in a facing target-type (FTS) on the substrates of high speed steel. During the deposition, the substrate was heated from room temperature up to ~300 °C and a d.c. bias up to -100V was applied. In the case of films deposited from the Ti-Si target without bias application, the hardness of high Si films (containing ~20 at %Si) showed the lower value of 20 GPa. The hardness of the films increased and reached to a maximum value of 40 GPa around at a bias of -30V, but the crystallite size of the film increased to ~30nm. On the other hand, the hardness of the films (containing ~20 at %Si) deposited from the Ti-Si@sub 3@N@sub 4@ target increased with increasing negative bias voltage, being saturated at a level of ~40 GPa over -80V. Although the crystallite size of the films increased gradually with increasing negative bias, it still remains about 7nm at -80V. The characteristics of the latter film could be attributed to the formation of nano-composite structure defined by Veprek et al.

8:40am **SE-TuM2 Growth and Physical Properties of Epitaxial CeN and Nanocrystalline Ti@sub 1-x@Ce@sub x@N Layers***, **T.-Y. Lee,*** University of Illinois at Urbana-Champaign, United States*; D. Gall,* Rensselaer Polytechnic Institute*; C.-S. Shin,* Hynix Corporation*; N. Hellgren,* Intel Corporation*; J.G. Wen, R.D. Twesten, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

While NaCl-structure transition-metal nitrides have been widely studied over the past two decades, little is known about the corresponding NaCl-structure rare-earth nitrides. Polycrystalline CeN, for example, has been reported by different groups to be both a wide bandgap semiconductor and a metal. To address this controversy, we have grown epitaxial CeN layers on MgO(001) and measured their physical properties. CeN is metallic with a positive temperature coefficient of resistivity and a temperature-independent carrier concentration of 2.8±0.2x10@super22@cm@super-3@ with a room temperature mobility of 0.31 cm@super2@ V@super-1@-s@super-1@. At temperatures between 2 and 50 K, the resistivity remains constant at 29 µ@ohm@-cm, while at higher temperatures it increases linearly to reach a room-temperature value of 68.5 µ@ohm@-cm. The hardness and elastic modulus of CeN(001) were determined from nanoindentation measurements to be 15.0±0.9 and 330±16 GPa. We further explore the possibility to alter the microstructure evolution in metastable Ti@sub1-x@Ce@subx@N quasi-binary alloys by controlling, using low-energy ion irradiation, the kinetics of phase separation driven by the large lattice mismatch of the two components (a@subCeN@ = 0.504 nm, a@subTiN@ = 0.424 nm). We observed nanophase films with x > 0.1. During reactive sputter-deposition of alloys, we observe nanophase films with x>0.1. Under conditions of low ion-irradiation, the nanostructure consists of equiaxed nanometer-size grains which form due to continuous renucleation induced by CeN segregation, which is analogous to the one observed in the nanocomposites of TiN/Si@sub3@N@sub4@. In contradistinction, a nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with J@subi@/J@subMe@ ~ 15 and E@subi@ = 45 eV. The intense ion mixing in the near surface area allows sufficient adatom mobility to form local TiN- and CeN-rich areas that propagate along the growth direction.

9:00am **SE-TuM3 Fabrication of Nanostructured Metallic Thin Films by Femtosecond Pulsed Laser Ablation***, **M. Jaime Vasquez,** T. Fiero, G.P. Halada, C.R. Clayton,* State University of New York at Stony Brook

Pulsed laser ablation is a well-known technique used for deposition of a variety of thin films for various applications. A major disadvantage of the use of excimer lasers has been the deposition of irregular melted droplets on the deposited film attributed to heterogeneities of the target, fluctuations in the laser fluence and other difficulties of process control. The extremely short pulse duration of femtosecond lasers results in reduction or complete prevention of lateral thermal damage as well as lower and more precise threshold fluences of ablation. This presentation focuses on both the mechanism of material ablation using femtosecond lasers as well as a number of examples of nanostructured metallic films of significance to analytical surface studies and catalysis. The femtosecond laser deposition process involves a high intensity laser pulse (10@super -15@ s range) that passes through an optical window of a vacuum chamber (10@super -6@ torr) and is focused onto the target, which can be a single metal, a mix of powders or a reactively arc melted coin. The partially ionized ejected material or ablation plume is then allowed to settle and form a thin film on a Si substrate. The plume itself was studied through analysis of the kinetics of ejected material from a Pt target and through charge screening methods to aid in determination of ionic character. In addition to Pt films, a nanostructured Al@sub 2@CuMg intermetallic thin film was formed (to study corrosion issues in Al aerospace alloys). Films were characterized by Secondary Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Thin films were polyscrystalline and of the same composition as targets and chemically homogeneous. Observations of the morphological and structural features of the ablated films indicate that the technique can be used to reliably create nanostructured thin films.

9:20am **SE-TuM4 Self-adaptation Processes in Nanostructured Hard Coatings***, **C. Mitterer,** P.H. Mayrhofer,* University of Leoben, Austria*; E. Badisch, M. Stoiber, G. Gassner,* Materials Center Leoben, Austria **INVITED**

Hard coatings deposited by plasma-assisted vapor deposition are widely applied to reduce tool wear. In the last decade, nanocomposite coatings have attracted increasing interest, due to the possible design of superhard coatings. Recently, it has been shown that nanostructured coatings also allow the realization of self-adaptive properties. This work summarizes recent developments in this field. The unavoidable Cl impurities in TiN coatings deposited by PACVD using TiCl@sub4@ as precursor is known to deteriorate mechanical coating properties when exceeding several at.-%. However, small and tolerable Cl concentrations of about 3 at.-% cause a reduction of the friction coefficient against various steels and alumina from 0.8 to 0.15. This is due to the formation of an interfacial lubricant film on top of the coating caused by Cl-stimulated rutile formation in humid air. These coatings have been shown to improve the lifetime of metal forming tools significantly. Low-friction behavior at elevated temperatures, which is a pre-requisite for dry cutting operations, can be achieved by liquid oxide lubrication. This can be realized by various nitride phases, e.g. VN, WN, Mo@sub2@N or MoN, which form low-melting oxides in the temperature range between 400 and 550°C. Melting of these phases occurs between 650 and 850°C. Using a nanoscaled arrangement of these phases in a hard matrix results in a self-adaptation of the friction coefficient to values of 0.18-0.4 at 700°C. Self-hardening to increase the wear resistance can be observed in metastable (Ti,Al)N coatings due to spinodal decomposition into fcc TiN and AlN domains. These nanoscaled coherent domains introduce additional stresses into the coating resulting in a hardness increase in the temperature range between 600 and 1000°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

10:00am **SE-TuM6 Design of Functional Coatings***, **D. Hegemann,*** Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland, Germany*; A. Fischer,* Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland

Since materials are commonly chosen with respect to their bulk characteristics, availability, mechanical properties, and costs, their surface characteristics often do not meet the demands for special applications. The plasma technology is an appropriate method to tailor surface properties selectively and offers a convenient way to design even functionally gradient surface coatings. Using low pressure plasmas, various materials and geometries can be treated in batch or reel-to-reel reactors. When long-term stable surface properties such as wettability are of great interest, well-adherent, stable coatings can be provided minimizing aging effects. Using low power inputs in the course of chemical vapour deposition (CVD) processes, monomer structures can be retained in the gas phase yielding dense and homogeneous functional gradient films. The evaluation of the deposition rate of these radical-dominated plasmas was proven to be an appropriate way to design functionally gradient coatings, since also hints for the optimum deposition conditions are given. Chemicals containing functional groups such as amino, carboxy or epoxy are used to mediate the adhesion between substrate and coating. Siloxane-based plasma coatings enable the deposition of hydrophobic, polymer-like layers or hydrophilic, quartz-like films. Gradient layers are suitable to enhance the adhesion of the functional coatings e.g. by adaptation of the mechanical properties, when an inorganic coating is deposited on a polymeric substrate or an organic coating on a non-polymeric material. These gradient layers can be designed considering the reaction parameters power per gas flow and plasma potentials, which control deposition rate, chemical composition, and mechanical properties. Finally, an example of a physical vapour deposition (PVD) process is given, in which a nm-thin silver film has been coated continuously onto the surface of multifilament yarns to enhance the dischargement of a textile surface.

10:20am **SE-TuM7 Functional Profile Coatings and Film Stress***, **C. Liu,** R. Conley, A.T. Macrander,* Argonne National Laboratory

In recent years we have developed a profile-coating technique to obtain functional thickness-profiled thin films and multilayers. This technique uses a linear motion of the substrate in a dc magnetron sputter system and a contoured mask to obtain the desired profile perpendicular to the substrate-moving direction. The shape of the contour is determined according to the desired profile and the knowledge of the film-thickness distribution at the substrate level. Applications of this technique include laterally graded multilayers and elliptical x-ray Kirkpatrick-Baez (KB) mirrors. An elliptical shape is essential for aberration-free optics. The use of profile coating to make x-ray-quality elliptical KB mirrors overcomes the obstacle of polishing asymmetrical mirror surfaces and provides the x-ray community with a practical way to obtain monolithic KB mirrors for microfocusing. Previously we have used gold as a coating material and cylindrical Si mirrors as substrates to obtain elliptical KB mirrors. More recently we are using flat Si substrates to fabricate elliptical KB mirrors. Substantially thicker and steeper gradients of Au films are needed to obtain an elliptical profile from a flat substrate. The Au films may relax to droplets when the stress in the film is too large. The challenges and solutions for this problem will be discussed.

10:40am **SE-TuM8 The Effect of Surface Finish on Field Emission in Nitrogen-implanted, Silicon Dioxide-Coated Stainless Steel***, **N.D. Theodore**, D. Manos,* College of William and Mary*; C. Hernandez, T. Wang, H.F. Dylla,* Jefferson Lab*; R. Moore,* University at Albany Institute for Materials

The purpose of this study was to assess the changes in tunneling parameters associated with field emission from processed stainless steel surfaces, as a function of their prior surface finish. According to Fowler-Nordheim theory (FNT), field emission from a material is governed by two parameters, alpha and beta, which relate to the work function of the material and to its surface morphology. Thus surface roughening may lead to large changes in field emission due to geometrical enhancements associated with sharp features. In this paper, six 304 stainless steel disks were hand-polished to different finishes, ranging from 1 micron to 30 microns rms roughness. These disks were then coated with a nitrogen-implanted silicon dioxide layer. @footnote1@ Depth Auger electron spectroscopy revealed that the thickness of the coating is approximately 240 nm. Field emission spectroscopy maps, STM maps, and AFM and DekTek scans were also taken of each sample. Data from these scans as well as the compositional character of the coating will be presented. Results show that despite surface morphology, each sample possessed 1-3 emission sites, producing current of 2nA at each emitter at threshold electric fields above 85 MV/m. The coated samples have comparable field emission I-V curves. An interpretation of these data in terms of a total electron energy FNT model will be discussed.@footnote 1@C. Sinclair, et al. Proccedings of the 2001 Particle Accelerator Conference. Chicago, IL, 2001.

Surface Science
Room 327 - Session SS1-TuM

Catalysis II: Hydrocarbons at Metal Surfaces

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

8:20am **SS1-TuM1 Adsorption Energies of Small Alkane Molecules on MgO(100) and on Pd Nanoparticles on MgO by Temperature Programmed Desorption***, **S.L. Tait, Jr.,*** University of Washington*; Z. Dohnalek, B.D. Kay,* Pacific Northwest National Laboratory*; C.T. Campbell,* University of Washington

Catalysts consisting of Pd nanoparticles supported on oxides are active in a variety of important reactions involving small alkanes. Molecular beams and temperature programmed desorption (TPD) were used to study the adsorption of small alkane molecules, C@sub n@H@sub 2n+2@ (n=1-10), on the MgO(100) surface and on Pd nanoparticles on MgO(100) at low temperatures (24 K), a regime little explored for such well-defined model catalysts. High quality MgO films are grown on the Mo(100) surface, producing an MgO(100) surface with defect densities comparable to those obtained by UHV-cleavage of MgO crystals. Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined kinetic energy. King and Wells style sticking measurements are made by quadrupole mass spectrometer (QMS) during deposition. The initial sticking probability increases with alkane chain length until it reaches unity for octane (n=8). The sample is heated at a controlled rate and desorption products are observed by line-of-sight QMS. The adsorption energies and kinetic prefactors for desorption are extracted from these TPD data. Adsorption energy increases non-linearly with alkane chain length. The alkanes bind more strongly to Pd particles than to MgO(100). We plan to present preliminary results also concerning Pd particle size effects in alkane adsorption and dissociation. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

8:40am **SS1-TuM2 Reactions of Aliphatic Alcohols on WO@sub3@(001) Surfaces***, B.G. Frederick, **S. Ma,*** University of Maine

Interactions of ethanol and isopropanol with WO@sub3@(001) thin film surfaces, epitaxially grown on a sapphire substrate, were studied with calibrated thermal desorption spectroscopy (CTDS). The reactivity of reduced and oxidized WO@sub3@ surfaces, as characterized by XPS and UPS, were compared in order to understand the surface structure dependence. Coverage dependent desorption spectra show that alcohol molecules diffuse rapidly on the WO@sub3@ thin film surfaces. Ethanol and isopropanol desorb molecularly between 200 and 450 K with evolution of water. The remaining alkoxy intermediates decompose via @BETA@-H elimination, followed by C-O bond scission, to produce ethylene and propylene, respectively. We suggest that diffusion and competition between reaction rates of dehydroxylation vs. associative molecular desorption of alcohol control the alkoxy coverage that determines the selectivity toward alkene under these low coverage conditions.

9:00am **SS1-TuM3 Dissociative Adsorption of Cyclohexene on Pt(111) at 300 K studied by Single-Crystal Microcalorimetry and Sticking Probability Measurements***, **H. Ihm**, H.M. Ajo, D.E. Moilanen, C.T. Campbell,* University of Washington

The dehydrogenation reaction of cyclohexene to benzene on platinum surfaces is of fundamental interest due to the importance of the surface chemistry occurring in hydrocarbon conversion. There have been many studies to understand its reaction, mechanism, energetics, and kinetics using experimental and theoretical methods. They agree that cyclohexene on Pt(111) converts to cyclohexenyl between 200-250 K and further converts to benzene between 300-350 K.@footnote 1,2@ There have been studies to estimate reaction (activation) energies from cyclohexene to cyclohexenyl or benzene, but these were in a limited coverage regime and either by indirect experimental measurements or by theoretical calculation.@footnote 1,3@ Here, we report direct calorimetric measurements of the heats of reactive adsorption of cyclohexene on Pt(111) at 300 K as a function of coverage. These calorimetry measurements were performed by using a pyroelectric detector and a pulsed cyclohexene molecular beam impinging onto a 1 µm thick Pt(111) sample. We also measured the sticking probability as a function of coverage. The sticking probability is initially high (0.86) and stays constant up to 0.7 ML then decreases linearly to 0 at 1 ML. The flux of the cyclohexene molecular beam was measured with a liquid-nitrogen cooled quartz crystal microbalance. Work supported by NSF. @FootnoteText@@footnote 1@ F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala, and C.T. Campbell, J. Phys. Chem. 1992, 96, 5965-5974. @footnote 2@ W.L. Manner, G. S. Girolami, and R.G. Nuzzo, J. Phys. Chem. B 1998, 102, 10295-10306.@footnote 3@ B.E. Koel, D.A. Blank, and E.A. Carter, J. Molecular Catal. A: Chemical 131 (1998) 39-53.

9:20am **SS1-TuM4 The Reaction of 1-chloro-2-methyl-2-propanol (Cl@super t@BuOH)on Oxygen-covered Ag(110): C-Cl Bond Cleavage in Epoxide Formation***, **H. Piao**, K. Adib,* Brookhaven National Laboratory*; M. Enever,* University of Delaware*; Z. Chang,* Brookhaven National Laboratory*; D.R. Mullins,* Oak Ridge National Laboratory*; J. Hrbek,* Brookhaven National Laboratory*; M.A. Barteau,* University of Delaware

Synchrotron-based Temperature Programmed X-ray Photoelectron Spectroscopy in combination of Temperature Programmed Desorption has been used to explore the C-Cl scission in the reaction of Cl@super t@BuOH on oxygen-covered Ag(110) surface to produce isobutylene oxide (IBO). Although the C-Cl bond cleavage is involved in the rate-determining step for the evolution of IBO, the mechanism was not fully understood. This motivated the surface reaction mechanism study to determine whether the surface chlorohydrin reaction follows an S@sub N@1 reaction or a concerted S@sub N@2 path. Using experimental data we also developed a kinetic model for surface reaction chemistry. The combination of experimental and theoretical results indicates that Cl@super t@BuO decomposition does not occur by an S@sub N@2 process that releases IBO directly into the gas phase. Instead, C-Cl scission deposits organic intermediates or products on the surface, and that the appearance of these products in the gas phase lags the appearance of atomic chlorine on the surface. Therefore, we can conclude that the production of IBO is the result of a process involving two kinetically significant steps: C-Cl scission that deposits Cl atoms and IBO molecules on the Ag(110) surface followed by desorption of molecularly adsorbed IBO. Low barrier and pre-exponential for the second step on the high coverage surface indicate that the rate of

C-Cl scission may be influenced by other factors, e.g., the availability of surface adsorption sites for Cl adatoms.

9:40am **SS1-TuM5 Surface Chemistry of Hydrocarbon Fragments on Transition Metals: Towards Understanding Catalytic Processes***, **F. Zaera,*** University of California, Riverside **INVITED**

An overview of our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. Particular emphasis will be placed on the similarities and differences between surface and organometallic systems, and on the relevance of this chemistry to catalysis. The methods developed in our laboratory for the clean production of catalytically-relevant but unstable surface moieties on well-characterized metal surfaces will be described, and the main thermal decomposition pathways of those intermediates will be discussed. An argument will be presented for the definition of catalytic selectivities based on subtle changes in the regioselectivity for early dehydrogenation rates. For instance, the unique ability of platinum in promoting isomerization and cyclization reactions appears to correlate with its preference to catalyze gamma-hydride elimination steps; nickel, in contrast, facilitates dehydrogenation at the alpha position, and catalyses hydrogenolysis instead. The additional mechanistic complications in hydrocarbon reforming under catalytic conditions introduced by the presence of strongly bonded carbonaceous deposits on the surface of the active catalyst will be addressed. The working reforming metal catalyst is likely to display a bifunctional character, with rapid hydrogenation-dehydrogenation steps taking place on the hydrocarbon-covered surface and more demanding skeletal rearrangement steps occurring on patches of bare metal. Finally, some details behind the imparting of enantioselectivity to metal catalysts via the adsorption of chiral modifiers will be introduced.

10:20am **SS1-TuM7 Fluorinated Carboxylic Acids Deprotonation on the Cu(100) Surface***, B. Immaraporn,* Fritz-Haber Institute, Germany*; **P. Ye**, A.J. Gellman,* Carnegie Mellon University

The kinetics of acid deprotonation on the Cu(100) surface have been studied using four different fluorinated carboxylic acids (CF@sub 2@HCO@sub 2@H, CF@sub 3@CO@sub 2@H, C@sub 2@F@sub 2@HCF@sub 2@CO@sub 2@H, and CF@sub 3@CF@sub 2@CO@sub 2@H). All four acids adsorb molecularly on Cu(100) at 90 K and then undergo deprotonation to form carboxylates during heating below 300 K. Temperature programmed reaction spectroscopy and x-ray photoemission spectroscopy were used to verify that the acids deprotonate on the Cu(100) surface. Work function measurements were used to study the deprotonation kinetics during heating and estimate the activation energy barriers (@DELTA@E@super â€¡@@sub OH@) to deprotonation. The nature of the transition state to acid deprotonation on Cu(100) was probed by analysis of linear free energy relationships (LFER) or correlations of with @sigma@@sub F@. The field reaction constant, @rho@@sub F@, or the slope of the LFER was found to be @rho@@sub F@ = 57 ± 9 kJ/mol in the limit of zero coverage and @rho@@sub F@ = 22 ± 2 kJ/mol at 0.5 ML coverage. These values of @rho@@sub F@ can be compared to the values of @rho@@sub F@ = 104 kJ/mol for acid deprotonation in the gas phase. This comparison suggests that the transition state for acid deprotonation on Cu(100) must be anionic with respect to the reactant (RCO@sub 2@H@sub (ad)@@super â†”@[RCO@sub 2@@super delta@@super -@@super â€¦@H@super delta@@super +@]@super â€¡@.

10:40am **SS1-TuM8 Enantioselective Reactivity of R-2-bromobutane on Cu(531)***, **D.M. Rampulla**, A.J. Gellman,* Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. The difficult aspect of enantioselective reactions is that they require chiral media such as solvents, surfaces, or catalysts. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(531)@super R@ and Cu(531)@super S@ surfaces. R-2-bromobutane debrominates to produce a chiral R-2-butyl intermediate. The R-2-butyl group decomposes by @beta@-hydride elimination to form cis- and trans-2-butene and 1-butene. The hydrogen released by @beta@-hydride elimination can also hydrogenate the R-2-butyl intermediate to form butane. In addition to reaction temperatures that are indicative of enantioselective kinetics, the reaction yield is influenced by the chirality of the Cu(531) surfaces.

11:00am **SS1-TuM9 Coupled Experimental and Theoretical Study of Weakly Adsorbed Molecules on Metal Surfaces***, **H. Ogasawara**, H. Ostrom, B. Brena,* Stockholm University, Sweden*; D. Nordlund,* Uppsala University, Sweden*; M. Nyberg, L. Petersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Linear Accelerator Center

The heat of adsorption is often treated as an indicator of the strength of adsorbate-substrate interaction. We present the combined experimental and theoretical study of weakly adsorbed systems on metal surfaces. We studied the electronic structure of water and hydrocarbons which are often considered as weakly bound species. We observed significant electron sharing between the adsorbate and metal surface and involvement of both bonding and antibonding molecular orbitals in the molecule-metal bond. These findings are a key to understand the O-H or C-H bond activation mechanism. We also present computational details how we computed the adsorption structure of these systems.

11:20am **SS1-TuM10 H@sub 2@ Production from Ethanol Over Au-Rh/CeO@sub 2@ Catalysts***, **H. Idriss**, P.Y. Sheng,* The University of Auckland, New Zealand

The reactions of ethanol over oxides and metal-oxides surfaces are receiving increasing attention because of the potentially efficient production of hydrogen by oxidation and steam reforming.@footnote 1,2@ Ethanol (now viewed as a bio-fuel with potential for making hydrogen) has received considerable attention in the past because it is a simple probe molecule in studying surface reactions on metals@footnote 3@and oxides.@footnote 4@ We have previously investigated the decomposition of ethanol on M/CeO@sub 2@surfaces (M = Rh, Pt, Pd and Au).@footnote 1,5@ In this work we show that the addition of Au to Rh, for the reaction of ethanol, enhances both the production of H@sub 2@ and the total oxidation to CO@sub 2@. The reaction of ethanol was conducted by TPD, IR and in steady state catalytic conditions, while catalysts were investigated by XRD and XPS. Among the key results of this work are the following. 1. Addition of Au resulted in the total suppression of adsorbed CO when compared to Rh/CeO@sub 2@ catalyst (IR), at low temperatures. 2. The presence of Rh enhanced the production of H@sub 2@ and the total decomposition of ethanol when compared to Au/CeO@sub 2@ catalyst (steady state reactions). The CO@sub 2@ to CO ratios were found equal to 25 for Au/CeO@sub 2@, 5.6 for Rh-Au/CeO@sub 2@, and 1.8 for Rh/CeO@sub 2@, catalysts (TPD). The reaction pathway for ethanol on the bimetallic system will be discussed and compared to that on the mono-metallic catalysts. @FootnoteText@ @footnote 1@ Sheng, P.-Y., Yee, A., Bowmaker, G. A., Idriss, H. J. Catal. 2002, 208, 393; and references therein. @footnote 2@ Cavallaro, S. Freni, S. Int. J. Hydrogen Energy, 1996, 21, 465.@footnote 3@ Gates, S.M., Russell, J.N., Yates, J.T., Surf. Sci., 1986, 171, 111.@footnote 4@ Idriss, H., Seebauer, E.G., J. Mol. Catal. A, 2000, 152, 201.@footnote 5@ Diagne, C., Idriss, H., Kiennemann, A., Catal. Commun. 2002, 3, 565.

Surface Science

Room 328 - Session SS2-TuM

Nucleation and Growth

Moderator: J.F. Wendelken, Oak Ridge National Laboratory

8:20am **SS2-TuM1 The Dynamics of Crystallite Shape Transformations***, **J.E. Reutt-Robey**, D.B. Dougherty,* University of Maryland **INVITED**

At the nanoscale, the shape of a crystallite is remarkably sensitive to the local chemical potential. While much is known about equilibrium crystal shapes (ECS), the mechanism and rate by which a crystallite morphology evolves in response to abrupt changes in temperature and gaseous environments are largely unknown. Using variable temperature STM as our experimental probe, we have investigated the reshaping dynamics of submicron lead crystallites prepared in their near-ECS on Ru(OOO1). In the case of chemical (oxygen) adsorption, we observe a dramatic particle reshaping into a heavily faceted structure.@footnote 1@ We show that this reshaping is triggered by surface impurities, which are needed to nucleate lead oxide grains. Once nucleated, an oxide grain grows laterally on the crystallite surface in an apparent autocatalytic process. Although nucleation is temperature insensitive, subsequent oxide grain growth rates depend on temperature, presumably due to limiting lead mobility at our temperature of investigation. These results are consistent with independent measurements of step fluctuation kinetics. We show how temperature reduction leads to a "flattening" of supported neat crystallites through a monolayer-by-monolayer peeling mechanism.@footnote 2@ From the step peeling kinetics, and simulations with continuum models, we find that the kinetics of monolayer peeling is limited by multi-layer relaxations. Atomistically, these relaxations represent limited mass transfer across the curved facet boundary. Within the thermal window of our measurements, we show that particle reshaping is not reversible and discuss the limiting nucleation barriers.@footnote 3@ @FootnoteText@ @footnote 1@K. Thurmer, E. Williams, and J.E. Reutt-Robey, Science 297, 33-35 (2002). @footnote 2@K. Thurmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Edmundts, H.P. Bonzel, Phys. Rev. Lett. 87 (2001) 186102. @footnote 3@K. Thurmer, J.E. Reutt-Robey, E.D. Williams, Surf. Sci., in press.

9:00am **SS2-TuM3 Fluctuations of Islands on Anisotropic Surfaces@footnote 1@**, ***F. Szalma,*** *T.L. Einstein,* University of Maryland, College Park

We have performed kinetic Monte Carlo simulations to model the decay and edge-fluctuations of islands containing hundreds to thousands of atoms on (111) crystal surfaces. Investigating the dispersion of the Fourier modes@footnote 2@ of the fluctuations as a function of wavevector, we observe anomalous dispersion due to the geometrical fact that the equilibrium island shapes are anisotropic because of the intrinsic anisotropy of crystal surfaces. Contrary to results for the isotropic approximation,@footnote 3@ the Fourier modes are not eigenmodes of the system; however, they can be transformed into an eigensystem, which provides a means to determine the anisotropic line tension of the island. In recent experiments observing how small crystallite droplets approach their equilibrium state, these fluctuations are intimately related to their decay,@footnote 4@ and the line tension is a factor in determining their ultimate shape. Finally, comparison of theoretical and experimental configurations allows gauging of the suitability of the calculated energies used in the simulations. @FootnoteText@ @footnote 1@Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. FS also supported by OTKA D32835, Hungary.@footnote 2@S.V. Khare et al., Surf. Sci. 522 (2003) 75.@footnote 3@S.V. Khare and T.L. Einstein, Phys. Rev. B 54 (1996) 11752.@footnote 4@T.J. Stasevich, F. Szalma, and T.L. Einstein, submitted to SS17.

9:20am **SS2-TuM4 The Importance of Substrate Steps on the Ripening of 3D Particles: Ag and Cu on Ru(0001)**, ***W.L. Ling,*** *T. Giessel, K. Thürmer, R.Q. Hwang, N.C. Bartelt, K.F. McCarty,* Sandia National Laboratories

Many hetero-epitaxial systems grow in the Stranski-Krastanov mode, in which material added to a wetting layer results in 3D islands. Once nucleated, and after growth has stopped, these 3D islands can minimize surface and interfacial free energy if they grow taller. However, there can be large free-energy barriers to this vertical growth because of the apparent necessity of nucleating new layers on top of these islands. In fact, Mullins and Rohrer have shown that it is unlikely that such nucleation would occur during ripening.@footnote 1@ In this work, we have studied the evolution of 3D islands of Ag and Cu on Ru(0001) using low-energy electron microscopy. We find that vertical growth does not occur at all during ripening when the Ag or Cu film does not overlay substrate steps. On stepped sufaces, on the other hand, we find vertical growth readily occurs. Using real-time observations, we find that the vertical growth occurs by an unexpected route that does not require nucleation. Islands, which adopt flat tops in an early stage of growth, gain a layer when they descend a monatomic Ru step. In this manner, they maintain the flat tops throughout ripening but grow taller as they migrate downhill on the substrate. We have investigated the vertical growth rate as a function of step spacing and island height. We find that thin islands shrink and tall islands grow, and the growth rate increases with the step density. @FootnoteText@@footnote 1@W.W. Mullins and G.S. Rohrer, J. Am. Ceram. Soc. 83, 214 (2000).

9:40am **SS2-TuM5 Geometry-Based Simulation Algorithm for Island Formation during Submonolayer Film Growth**, ***J.W. Evans,*** Iowa State University; *M.C. Bartelt,* Lawrence Livermore National Laboratory; *M. Li,* Iowa State University

A current challenge is to develop efficient new coarse-grained simulation strategies which reliably predict the morphology of growing films. We present a geometry-based simulation (GBS) algorithm which avoids explicit treatment of the terrace diffusion of adatoms and their aggregation with islands - a computationally expensive component of either atomistic KMC simulation or continuum formulations. GBS characterizes island growth in terms of capture zones (CZ's), and implements simple but realistic geometric rules to incorporate crucial spatial aspects of the island nucleation process, i.e., nucleation nearby CZ boundaries. This approach reliably predicts island size distributions and spatial correlations, and is especially efficient for highly reversible island formation.

10:00am **SS2-TuM6 Pyramidal Faceted Ni Nanocrystals on W(111)**, ***Q. Wu,*** *J. Kolodziej, H. Wang, T.E. Madey,* Rutgers University

Nanoscale features formed by nucleation of ultrathin Ni films on W(111) are studied by means of ultrahigh vacuum-STM, soft X-ray photoemission spectroscopy (SXPS) using synchrotron radiation, LEED, and AES. Whereas a single monolayer (ML) of Ni covers planar W(111) uniformly, we find that multilayers of Ni (~5 ML) follow the Stranski-Krastanov growth mode, and form clusters and islands on the Ni-covered W(111). Upon heating to ~600K, Ni clusters are found to aggregate into nanoscale pyramidal facets, which coexist with planar regions of Ni-covered W(111). This type of faceting is different from the monolayer-induced faceting of W(111) seen for Pt, Pd, Ir, and Rh: a single ML of Ni does not cause faceting of W(111). Thermal stability of Ni films on W(211) and W(111) is studied by SXPS and AES, which indicates that alloy formation between Ni and W occurs at temperatures @>=@700K. Further annealing of faceted Ni nanocrystals also leads to Ostwald ripening. Reactivity of Ni nanoclusters with adsorbates (e.g. oxygen and thiophene) is also investigated. The nucleation and growth of nanocrystals are discussed in terms of overlayer strain due to lattice mismatch.

10:20am **SS2-TuM7 Growth and Stability of Bi Films on Si(111) Studied by LEEM**, *G.E. Thayer,* IBM T.J. Watson Research Center; *J.T. Sadowski,* Tohoku University, Japan; ***R.M. Tromp,*** IBM T.J. Watson Research Center

The structural and electronic properties of ultra-thin metal films on semiconductor surfaces have attracted much recent interest primarily due to the dominating dependence of novel device performance on metal contacts. Since contacts are interfaces, contact issues are real problems where surface science can provide insightful solutions. Understanding the factors governing heteroepitaxial growth, such as surface free energies and stress relaxation effects are important, and in situ electron microscopy can play a unique role in investigating the processes involved. Using low-energy electron microscopy (LEEM) we observed real-time growth of Bi on Si(111). With the surprisingly large lattice mismatch of 17% between bismuth and silicon, one might expect growth of Bi/Si(111) to be almost certainly dominated by strain, and therefore three dimensional. Up to about five monolayers, the Bi film grows with small grain (012) oriented islands on top of a uniform wetting layer. Above five monolayers, the crystal orientation dramatically flips from (012) to (111), from a four-fold symmetry to a three-fold symmetry, into a flat single crystal film (grains are approximately 100µm@super 2@ in size). The transition occurs very quickly with grains transitioning at a rate of 1µm@super2@s@super -1@. After the transition into a (111) oriented epitaxial film, the growth continues in a two-dimensional layer-by-layer mode of bi-layers. The thermodynamic stability of Bi/Si(111) films was also investigated by annealing the films to temperatures of up to 150°C (melting temperature of Bi is 220°C), where dewetting becomes important, even prior to melting.

10:40am **SS2-TuM8 Nucleation Kinetics during Homoepitaxial Growth of TiN(001) by Reactive Magnetron Sputtering**, ***M.A. Wall***[1], *D.G. Cahill, I. Petrov,* University of Illinois at Urbana-Champaign; *D. Gall,* Rensselaer Polytechnic Institute; *J.E. Greene,* University of Illinois at Urbana-Champaign

Polycrystalline TiN is extensively used as a diffusion barrier in microelectronics, as a hard wear resistant coating on cutting tools, and as a corrosion and abrasion resistant layer on optical components. The performance of TiN in all these applications is dependant on the texture of the layer, which is in turn a function of the film growth parameters and nucleation kinetics. To gain an atomic-scale understanding of the processes which govern TiN nucleation, we grow epitaxial layers on TiN(001) via reactive magnetron sputtering in an ultra-high vacuum (UHV) system and employ in-situ scanning tunneling microscopy (STM) to investigate the dynamics. In addition, we perform density functional calculations in order to guide the interpretation of our experimental results. The characteristic island size R@sub c@ necessary to nucleate a new layer on a growing island is measured as a function of growth temperature T@sub s@ and nitrogen fraction f@sub N2@ in an Ar/N@sub 2@ mixture. By applying nucleation rate theory to temperature dependant R@sub c@ data obtained from layers grown with f@sub N2@ = 1, we extract a diffusion activation energy E@sub s@ = 1.4±0.1 eV for T@sub s@ @<=@ 865 °C

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

where nucleation is diffusion limited. For T@sub s@ @>=@ 910 °C, nucleation becomes limited by the formation of unstable clusters, and we extract an adspecies formation energy E@sub f@ = 1.4±0.2 eV. When f@sub N2@ is reduced from 1 to 0.1, E@sub s@ = 1.1±0.2 eV which results in a factor of two increase in R@sub c@ at a given T@sub s@. The activation energy we calculate for Ti diffusion on TiN(001) is 0.4 eV, significantly smaller than E@sub s@ extracted from our experiment, indicating that Ti is not the dominant diffusing species. Based on calculated binding energies of TiN@sub x@ clusters, the dominant diffusing species is likely TiN@sub x@, with 1 @<=@ x @<=@ 3.

11:00am **SS2-TuM9 Pt Adsorption on Chiral SrTiO@sub3@ Surfaces*, A. Asthagiri*,** *D.S. Sholl,* Carnegie Mellon University

The existence of intrinsically chiral surfaces provides many opportunities related to the catalytic chemistry and separation of chiral molecules. A key difficulty in realizing the potential of this approach has been the production of surfaces with reasonable surface area. We describe results that underpin efforts to epitaxially deposit ultra-thin films of metal on metal oxide substrates. The success of these efforts requires careful control of the film morphology of the underlying substrate and knowledge of the growth modes of metal on these surfaces. To this end, we have performed extensive plane wave Density Functional Theory (DFT) calculations to describe the bonding of Pt on a variety of SrTiO@sub3@ surfaces. These calculations include both terminations of all three low Miller index surfaces, (100), (110), and (111), and two representative stepped surfaces, (620) and (622). Our results show that epitaxial growth of Pt on the substrates can be expected, and that step flow growth should be feasible for the stepped substrates. Our results provide quantitative insight into the experimental observations made by our collaborators for these systems, including the existence of inversion domains for Pt films on SrTiO@sub3@(111). We will discuss the implications of our calculations for the practical growth of chiral metal films on SrTiO@sub3@ substrates.

11:20am **SS2-TuM10 High-Temperature Low Energy Electron Microscopy Studies of Spiral Dislocation Dynamics on TiN(111) Terraces*, S. Kodambaka*,** *S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

We have grown epitaxial TiN(111) layers by reactive evaporation onto Al@sub 2@O@sub 3@(0002) substrates and used in situ high-temperature low-energy electron microscopy to study surface morphological evolution on large (> 4 µm) atomically-smooth TiN(111) terraces during annealing at temperatures T@sub a@ in the range 1500 and 1750 K (T@sub a@ = 0.47-0.55T@sub m@, where T@sub m@ is the melting point in K). At each annealing temperature, we observe rotation of screw dislocation segments lying in the surface slip plane around the immobilized segment of the dislocation lying out of the slip plane resulting in a spiral with steps oriented along . Step heights are proportional to the number of revolutions in the slip plane. We find that the total length of the dislocation line increases with annealing time as the spirals undergo a shape-preserving anti-clockwise motion with a constant angular velocity. From the temperature-dependent angular velocity measurements, we determine an activation barrier of 5.0±0.2 eV, with a prefactor of 10@super 14+/-0.5@ s@super -1@, for spiral rotation. Studies of this process, a single-ended Frank-Read source, provide insight into understanding dislocation multiplication mechanisms occurring in highly refractory, technologically important transition-metal nitride layers.

11:40am **SS2-TuM11 Conversion from Nanowire to Epilayer: Epitaxial Growth of Bi on Si(114)-2x1***, S. Cho,* ***J.M. Seo,*** Chonbuk National University, Korea

The Bismuth (Bi) adsorption on the reconstructed Si(114)-2x1 has been studied using STM under UHV. Among 1-D features of Si(114)-2x1, such as Tetramer, Dimer and Restatom rows parallel to [-110] direction, Bi atoms preferentially adsorbed on the Tetramer rows and formed 1-D wires whose separation is 1.6 nm. The periodic structure in the Bi wire along [-110] has been converted to 3a (a=0.38 nm) from 2a of clean Si(114). The Bi wire of the second layer adsorbs between the Bi wires of the first layer, and shifts by 1.5a along the row. The Bi wires of subsequent layers also adsorb between the previously formed Bi wires in the same fashion. Such epitaxial growth continues unless the defects like substrate vacancies interfere. The packing unit is a Bi-dimer and the hexagonal packing has been confirmed by the hexagonal pattern of the facet near the ledge. It has been concluded that the reasons for 2-D epitaxial growth of Bi on Si(114) are the followings; the first, the existence of preferential adsorption site on Si(114), and the second, the adjustable lattice-matching between the Bi-dimer row and the substrate along as well as perpendicular to the wire.

Thin Films

Room 329 - Session TF-TuM

Thin Films on Organic, Polymeric and Biological Substrates

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

8:20am **TF-TuM1 Low Cost Thin Film Electronics on Flexible Polymeric Substrates*, T.N. Jackson*,** Penn State University **INVITED**

Silicon microelectronics has been spectacularly successful at providing increasingly complex digital processing and large-capacity digital memory with continually improving performance/$. It has been less successful at providing simple function at very low cost and in providing electronic function over large areas or on arbitrary surfaces. Thin film transistors (TFTs), based on either inorganic or organic semiconductors, are of interest for lowcost flexible and arbitrary substrate applications. Inorganic amorphous silicon (a-Si:H) TFTs are widely used as pixel access devices in displays and large area sensors on glass substrates. It is also possible to fabricate these devices on polymeric or other unconventional substrates and we have demonstrated a-Si:H TFTs on high temperature polymeric substrates (for example, polyimide) with performance very similar to that obtained on glass substrates. Organic semiconductors are of particular interest because they can be deposited and processed at very low temperature (often less than 100°C). Organic thin film transistor (OTFT) device performance now rivals or exceeds that of a-Si:H devices, and low OTFT process temperatures allow fabrication on a range of surfaces including cloth, paper, or polymeric substrates. Using small molecule organic semiconductors we have fabricated TFTs with field effect mobility > 1 cm2/V-sec on flexible polymeric substrates with good uniformity and yield. Devices of either type (organic or inorganic) are of particular interest for applications where their switch characteristics can be used for selection or isolation of arrays of devices. This approach, widely used for display addressing, allows many thousands or even millions of sensor, actuator, or other elements to be controlled with simple, low-cost electronics and the flexible processing used for thin film active devices allows direct integration with a wide range of materials and devices.

9:00am **TF-TuM3 Ultra-high Barrier Coating Deposition on Polycarbonate Substrates*, M. Schaepkens*,** *K.W. Flanagan, T.-W. Kim, M. Yan, A.G. Erlat, C. Heller, P.A. McConnelee,* General Electric

The use of polycarbonate film substrates enables fabrication of new applications, such as flexible display devices, lighting devices, and other flexible electro-optical devices, using low cost, roll-to-roll fabrication technologies. One of the limitations of bare polycarbonate material in these applications is that oxygen and moisture rapidly diffuse through the material and subsequently degrade the electro-optical devices. This paper summarizes recent results obtained at GE Global Research to solve the oxygen and moisture diffusion issue. It will be shown that through the application of thin, dense, plasma-based inorganic coatings one can significantly reduce the oxygen and moisture permeation rate through polycarbonate films. However, as a result of defects that are commonly present in these inorganic coatings there is a limit to the performance of such barrier coatings. To further improve the barrier performance, advanced barrier coatings comprising both inorganic and organic materials have been developed. Both modelling and experimental results will be presented that explain why these hybrid material barrier coatings are capable of reaching ultra-high barrier performance.

9:20am **TF-TuM4 Organic Thin Film Transistors based on Fluorene-Arylene Copolymers for Printed Electronics*, M.G. Dibbs*,** *P. Townsend, D. Brennan, S. Kisting, J. Shaw,* The Dow Chemical Company **INVITED**

During the last 50 years polymeric materials have played an important role in semiconductor fabrication, interconnect, packaging and displays. They have usually played a passive role and have not been involved in the active generation, amplification, and switching of current or voltage. This is now changing. Research efforts on polyanalines, conjugated thiophene oligomers and polymers and pentacene and thiophene oligimers have led to improvements of mobility by 5 orders of magnitude over the last 15 years. Polymeric semiconductors offer a means to create unique, low cost electronic devices since they can be readily fabricated into thin, mechanically robust films onto a variety of substrates by low cost processing techniques. Recently new generations of polymeric semiconductors have been developed. All plastic chips based entirely on organic materials have been demonstrated. Materials based on fluorene-arylene copolymers are under development for this purpose. This paper describes recent work with this family of materials, compares results obtained by different research groups, and discusses issues related to the interplay of device construction and material characterization with a focus toward printed electronics.

10:00am **TF-TuM6 Elastic Metal Interconnects***, **J.E. Jones**, S.P. Lacour, S. Wagner, Z. Suo,* Princeton University

Stretchable, elastic metal interconnects are a key to the fabrication of 3-D conformal circuits and electrotextiles. The basic concept for reversibly stretchable, elastic metallization is a corrugated stripe of thin-film metal that is expanded by stretching. The maximum elongation is reached when the stripe is stretched flat. We prepared wavy metal stripes by evaporating gold onto pre-stretched strips of the elastomer, poly-dimethyl siloxane (PDMS). We experimented with gold metal line width and thickness and substrate elongation. We measured the film structure, amplitude, and wavelength, as well as electrical resistance in relaxed and various stretched states. So far we have reached elastic strains of 15% while maintaining the initial resistance and 80% with a rise in the resistance. We discovered a rich macroscopic and microscopic film morphology. Presented are the fabrication, electro-mechanical performance, and data on the film structure of these wavy metal interconnects.

10:20am **TF-TuM7 Properties of Indium Zinc Oxide Thin Films on Heat Withstanding Plastic Substrates***, **H. Hara**, T. Hanada, T. Shiro, T. Yatabe,* Teijin Ltd., Japan

Accompanying with downsizing and improving of resolution of various display devices, a heat withstanding plastic substrates with low resistivity of transparent conductive oxide (TCO) films have been demanded. We succeeded in development of optical anisotropy transparent plastic substrates with high glass transition temperature over 200 degC. However, tin doped indium oxide (ITO) films used as the transparent conductive electrode have high resistivity about 5E-4 ohm cm because the deposition of ITO films was carried out by sputtering at room temperature to avoid the out gassing from the plastic substrate. This kind of ITO films arise the amorphous/crystal transformation (a/c transformation) at 150 degC. The a/c transformation makes the ITO films crack with increase in resistivity. Then, we have been investigated new transparent conductive oxide films with low resistivity for our heat tolerance plastic substrate. We found that 7.5 wt% ZnO doped indium oxide (IZO(7.5)) films are suitable for the plastic substrates by surveying the ZnO content preciously. IZO(7.5) films deposited at room temperature by conventional dc-magnetron sputtering exhibited the low resistivity, 2.9E-4 ohm cm, keeping the high transparency, over 86 %. By using XRD and TEM, it is revealed that IZO(7.5) films were remained the structure in amorphous after annealing. Moreover, the result of thermal properties of IZO(7.5) films by DSC was elucidated that the a/c transformation was occured at 350 degC. The etching rate to 3.5 wt% HCl of IZO(7.5) films were 2 nm/sec. It is almost as same as or quicker than that of amorphous ITO films. The durability to 5 wt% KOH solution is also good for practical use. We have already succeeded in deposition of IZO(7.5) film on our heat withstanding plastic substrate with 1000 mm width and 500 m length. This substrate with IZO(7.5) film can remain the all properties after 180 degC annealing.

10:40am **TF-TuM8 Interface and Bulk Charge in Low Temperature Silicon Nitride Dielectrics on Plastic Substrates***, **K.J. Park**, G.N. Parsons,* North Carolina State University

Silicon nitride is a common gate dielectric for thin film transistors (TFT's) on plastic substrates, but the effect of processing temperature on charged defects in the film bulk and at the semiconductor/dielectric interface is not well known. For this work silicon nitride was deposited using various NH@sub3@/SiH@sub4@ gas ratios at temperatures between 50° and 300°C and the effect of process conditions on current vs. voltage (IV) and capacitance vs. voltage (CV) measurements was evaluated. For some conditions, CV was measured as a function of film thickness, and values for bulk and interface charge were extracted from the measured trends. We find that the apparent leakage current decreased with increasing NH/SiH ratio, but CV showed that increasing NH/SiH also leads in an increase in the flat band voltage shift, consistent with fixed charge in the films. Thickness dependence of CV indicates that increasing NH/SiH results in an increase in positive fixed charge at the interface, and an increase in negative fixed charge in the film bulk. When the NH/SiH ratio is fixed at 10, changing the substrate temperature from 50 to 250°C results in an increase in positive interface charge, and an increase in negative bulk charge, leading to charge compensation at higher temperatures. Internal charge can lead to a built in field which opposes the applied field, leading to a decrease in leakage current under high internal field conditions. Fixed charge is important to control threshold voltage and may affect transconductance in TFT devices. Results of amorphous silicon TFT's fabricated on polyimide substrates at various temperatures will be discussed.

11:40am **TF-TuM11 Effect of Swift Heavy Ions on the Structural and Optical Properties of RF Plasma Polymerized Aniline Thin Films***, S. Saravanan, C. Joseph Mathai, **M.R. Anantharaman**,* Cochin University of Science and Technology, India*; S. Venkatachalam,* Vikram Sarabhai Space Centre, India*; D.K. Avasthi,* Nuclear Science Centre, India

Organic and polymer thin films have been receiving a great deal of attention due to their interesting properties. They find extensive applications in making devices such as Light Emitting Devices, rechargeable batteries, super capacitors, intermetallic dielectrics and EMI shielding. Polyaniline thin films prepared by plasma polymerization are cross-linked, pinhole free and their permittivity lie in the ultra low k regime. Electronic and photonic applications of polyaniline thin films attracted the attention of various researchers. Modification of polymer thin films by swift heavy ions is well established and ion irradiation of polymers can induce irreversible changes in their structural, electrical and optical properties. Polyaniline thin films prepared by RF plasma polymerization were irradiated with 92 MeV silicon ions for various fluences of 1 x 10@super 11@ ions/cm@super 2@, 1 x 10@super 12@ions/cm@super 2@ and 1 x 10@super 13@ ions/cm@super 2@ using the pelletron facility at Nuclear Science Centre, New Delhi, India. FTIR and UV Vis NIR measurements were carried out on the pristine and silicon ion irradiated polyaniline thin films for structural evaluation and optical bandgap determination. In this paper the effect of swift heavy ions on the structural and optical properties of plasma polymerised aniline thin film is investigated. Their properties are compared with that of the pristine sample. The FTIR spectrum indicates that the structure of the irradiated sample is altered. The optical bandgap of these irradiated thin film is considerably modified.

Applied Surface Science
Room 324/325 - Session AS+BI-TuA

Biomaterials Characterization

Moderator: J.E. Fulghum, University of New Mexico

2:00pm **AS+BI-TuA1 Spatially Defined Immobilization of Biomolecules on Microstructured Polymer Substrate****,* ***A. Hozumi,*** *N. Shirahata,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan*; Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology, Japan

â€€The spatial arrangement of biomolecules on solid surfaces with artificial control in the micro~nanometer scale has attracted attention in biotechnical and biomedical applications. Here we report a simple method by which a number of biomolecules can be immobilized onto positions spatially defined in micrometer-scale. Our approach demonstrated here is based on the photodecomposition and hydrophilization of polymeric material using vacuum ultraviolet (VUV) light of 172 nm radiated from a Xe@sub 2@@super *@ excimer lamp. Each poly (methyl methacrylate) (PMMA) substrate was irradiated for 30 min at 10@super 3@ Pa with VUV light through a photomask contacting the PMMA surface. As confirmed by atomic force microscopy, after VUV-irradiation, microwell arrays composed of about 2 nm in diameter and 350 nm in depth were successfully formed on the PMMA substrates. Next, using such microstructured PMMA substrates, we demonstrated spatial arrangement of biomolecules. The microstructured sample was immersed into a solution containing antibodies labeled with fluorescence for 30 min. The antibodies were selectively adsorbed on the microwells in which the surfaces were photooxidized, while the surrounding regions where they were not unirradiated regions remained free of adsorption, as evidenced by fluorescence microscopy. This specific adsorption was probably due to the differences in chemical properties between the VUV-irradiated and unirradiated regions, as well as due to the geometrically effect. Indeed, according to water-contact angle measurements and X-ray photoelectron spectroscopy analysis, the VUV-irradiated PMMA surface became highly hydrophilic with its water-contact angle changing from 80Ã…Ã£ to 25Ã…Ã£ due to the formation of polar-functional groups, such as C=O and O-C=O, on the surface. Such chemically and geometrically defined microwells are expected to serve as spatially arranged active sites for the immobilization of a wide variety of biomolecules.).

2:40pm **AS+BI-TuA3 Low-Temperature STM Manipulation of Single Bio Molecules***,* ***J.J. Benson,*** *V. Iancu, A. Deshpande, S.-W. Hla,* Ohio University, Athens

Single porphyrin molecules adsorbed on Cu(111) surface are investigated by using a variety of manipulation procedures and spectro/microscopy measurements with a low temperature UHV STM at 6 K. The tunneling I/V and dI/dV spectroscopy techniques are used to probe the electronic properties of the single molecules with atomic level precision.@footnote 1@ Mechanical stability of single molecules is also examined using 'lateral manipulation' techniques with the STM-tip.@footnote 2@ In this procedure, the STM-tip is brought very close to the molecule to increase tip-molecule interactions (approximately one angstrom from the molecule). Then the tip is moved across the surface. Due to the tip-molecule interaction, the molecule is pushed across the substrate to relocate it to specific surface sites. Detailed internal conformation changes of the molecule can be directly monitored through the corresponding STM-tip height signals during the lateral manipulation process. These combined STM manipulation/spectroscopy investigations elucidate detailed information about the electronics and mechanical properties of the porphyrin molecules at sub-nanometer level resolutions. @FootnoteText@@footnote 1@F. Moresco et al, Phys. Rev. Lett. 86, 672-675, (2001). @footnote @@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330, (2003). .

3:00pm **AS+BI-TuA4 Base-dependent Displacement of Thiolated DNA Films by Mercaptohexanol (MCH)***,* ***H. Kimura-Suda,*** National Institute of Standards and Technology*; D.Y. Petrovykh,* University of Maryland & Naval Research Laboratory*; L.J. Whitman,* Naval Research Laboratory*; M. Tarlov,* National Institute of Standards and Technology

The immobilization of DNA on surfaces is the basis for DNA microarrays and many emerging nanotechnology applications. It has been demonstrated that the attachment of thiolated DNA probes to gold surfaces is an effective approach for construction of DNA-based sensors and diagnostics. One challenge with the use of thiolated DNA is reproducibly controlling the surface coverage and hybridization activity of adsorbed probes. A two-step method, where first the gold substrate is exposed to a solution of thiol-modified single-stranded DNA (HS-DNA), followed by exposure to a solution of mercaptohexanol (MCH), is a common approach for controlling the coverage and orientation of DNA probes. In this protocol, MCH both passivates the surface against nonspecific adsorption of DNA targets and "activates" DNA probes by displacing adsorbed nucleotides from the gold surface. The MCH treatment also displaces DNA probes from the gold surface resulting in less steric hindrance for hybridization. Nonetheless, the displacement of thiolated DNA by MCH remains poorly understood. In this study, we focused on base-dependent displacement of HS-DNA films from gold upon MCH exposure. Self-assembled monolayers of thiolated homo-oligonucleotides [HS-(dA), HS-(dT), HS-(dC), HS-(dG)] on gold surfaces were produced and characterized before and after exposure to MCH with FTIR and XPS. Surprisingly, we find that the displacement of HS-DNA on gold by MCH is strongly base-dependent. For example, most HS-(dT) is removed or displaced, whereas most HS-(dC) remains on the surface. In this talk we will present a selectivity series for the base dependent displacement of homo-oligonucleotides by MCH and discuss the origin of this effect. We will demonstrate that base dependent displacement effects can account for dramatic variations in probe coverage for probes of different base composition.

3:20pm **AS+BI-TuA5 Neuron Pathfinding and Surface Chemistry, Patterning and Reactions***,* ***T.P. Beebe, Jr.,*** University of Delaware **INVITED**

Biomaterials interfaces are at the heart of new approaches to control cell-surface interactions, and modern surface analytical techniques can now provide molecular-scale information about surface modifications, coverages and patterning or relevant ligands and proteins. These approaches can inform our understanding of the relationship between surface chemistry, surface structure and biological function. Using the biomedical problem of repair to damaged central nervous system tissue as the motivation for biomaterials interface characterization and cell-surface interactions, we will present several approaches to surface modification and surface characterization in conjunction with cell-surface biophysical measurements. The tools for these studies are AFM, XPS, TOF-SIMS and fluorescence microscopy and labeling.

4:00pm **AS+BI-TuA7 In-situ Spectroscopic Study of Thermal Phase Transition of Supported Hybrid Bilayer Membranes***,* ***C.S.-C. Yang,*** *K.A. Briggman, J.C. Stephenson, L.J. Richter,* National Institute of Standards and Technology

Hydrated phospholipid structures (Langmuir-Blodget films, supported bilayers, vesicles, etc.) have been widely studied as model systems for biological membranes. We report a study of the thermal phase transitions of fully hydrated hybrid bilayer membranes, i.e. phospholipid monolayers self-assembled onto a Au surface previously modified by a self-assembled monolayer of octadecane thiol (ODT). Using Sum Frequency Generation, a non-destructive interface-sensitive nonlinear optical probe, the structure and conformation of both the ODT and phospholipid alkyl chains have been characterized as a function of temperature from 25 to 60 °C. There is very little change in the ODT alkyl chain order over the temperature range studied. There are significant changes in the lipid chain order that are attributed to the transition from the ordered gel phase to disordered fluid phase, allowing us to determine the phase transition temperatures of the two-dimensional lipid layer. The gel-fluid phase transitions for a series of saturated phospholipids in the hybrid bilayers are observed at ~ 10 °C higher temperatures than those in corresponding multilamellar vesicles.

4:20pm **AS+BI-TuA8 Spectroscopic Quantification of Covalently Immobilized Oligonucleotides***,* ***A.V. Saprigin,*** *C.W. Thomas, C.H. Patterson, M.S. Spector,* Naval Research Laboratory

Quantitative determination of surface coverage, film thickness, and molecular orientation of DNA oligomers covalently attached to aminosilane monolayers has been obtained using complementary infrared and photoelectron studies. Spectral variations between the different nucleic acids are observed in surface immobilized oligomers for the first time. Carbodiimide condensation was used to covalently attach phosphorylated oligonucleotides to silanized aluminum substrates. Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the surfaces after each modification step. Infrared reflection-absorption spectroscopy of covalently bound DNA provides orientational information. Surface density and layer thickness are extracted from XPS data. The surface density of immobilized DNA, 2-3Ã—10^13 molecules/cm^2, was found to depend on base composition. Comparison of antisymmetric to symmetric phosphate stretching band intensities in reflection-absorption spectra of immobilized DNA and transmission FTIR spectra of DNA in KBr pellet indicates that the sugar-phosphate backbone is predominantly oriented with the sugar-phosphate backbone lying parallel to the surface, in agreement with the 10-20 Ã… DNA film thickness derived from XPS intensities.

4:40pm **AS+BI-TuA9 Photoionization for Trace Measurement of DNA on Surfaces***, **J.F. Moore**, W.F. Calaway,* Argonne National Laboratory*; B.V. King,* University of Newcastle, Australia*; J.W. Lewellen, S.V. Milton, M.J. Pellin,* Argonne National Laboratory*; M. Petravic,* Australian National University*; I.V. Veryovkin,* Argonne National Laboratory*; G.L. Woloschak,* Northwestern University

Recent developments in vacuum ultraviolet (VUV) lasers allow new photoionization techniques to be applied to surface and interface analysis problems. Single photon ionization of laser desorbed nucleosides and DNA was performed using a molecular F@SUB 2@ laser (wavelength 157 nm, pulse energy 8 mJ, pulse length 10 ns) and a tunable free electron laser (wavelength 120 - 265 nm, pulse energy 0.1 mJ, pulse length 300 fs). Results including detection limit and degree of fragmentation are compared for several systems including guanosine and single-stranded DNA of 10-30 base pair lengths. The tunability of the free electron laser to a wavelength just above the ionization potential of the analyte molecule can be used to enhance selectivity and sensitivity of the analysis. There are clear applications of this sensitive, selective, spatially resolving technique that is capable of identifying mutated or adducted DNA with little sample preparation. These uses will be elaborated on in the context of our results and plans for further technique development, and operational experience with the free electron laser. @FootnoteText@ This work is supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

5:00pm **AS+BI-TuA10 Utilization of Polyatomic Primary Ion Sources for Analysis of Drug Delivery Systems by Secondary Ion Mass Spectrometry (SIMS)***, **C.M. Mahoney**, G. Gillen,* National Institute of Standards and Technology

The utilization of cluster primary ion beams in SIMS has become very popular in the last decade due to the increased secondary ion yields as compared to monoatomic sources.@footnote 1-4@ In particular the analysis of organic materials has gained considerable interest as these cluster primary ion beam sources (in particular SF@sub 5@@super +@) have resulted in the enhancement of characteristic molecular secondary ion yields and have decreased the beam induced damage.@footnote 4@ Furthermore, the increased sputter rate with decreased beam damage has allowed for depth profiling in organic films and polymers for the first time with limited success.@footnote 4@ Here we explore the applicability of cluster SIMS in the analysis of various materials utilized in drug delivery. The effects of SF@sub 5@@super +@ bombardment on molecular secondary ion yields will be explored in various biodegradable polymers (polylactic acid, polyglycolic acid and polycaprolactone) as well as several model drugs (theophylline, 4'-hydroxyacetanilide, amyloid probe). The enhancement in the sensitivity will then be applied to imaging applications where it will be shown that imaging with SF@sub 5@@super +@ enhances the signal intensity as compared to Ar or Cs primary ions resulting in more sensative imaging capabilities. This will be useful in many systems where the concentration of drug is very low (e.g. biological samples, ppb-ppm range). Dynamic SIMS analysis (utilizing SF@sub 5@@super +@) of a series of polylactic acid films doped with varying concentrations of 4'-hydroxyacetanilide will also be discussed. @FootnoteText@ @footnote 1@ Kotter, F.; Benninghoven, A. Applied Surface Science 133 (1998) 47.@footnote 2@ Appelhans, A.D.; Delmore, J. Anal. Chem. 61 (1989) 1087.@footnote 3@ Gillen, G.; King, R.L.; Chmara, F. J. Vac. Sci. Technol. A 17(3) (1999) 845.@footnote 4@ Gillen, G.; Roberson, S.; Rapid Commun. Mass Spectrom. 12 (1998) 1303.

High-k Gate Dielectrics and Devices Topical Conference
Room 317 - Session DI-TuA

High-k Dielectric Characterization

Moderator: E.L. Garfunkel, Rutgers University

2:40pm **DI-TuA3 Invited Paper***, **E. Cartier**,* IBM T.J. Watson Research Center **INVITED**

3:20pm **DI-TuA5 Enhanced Tunneling in Symmetric Stacked Gate Dielectrics with Ultra-thin HfO@sub 2@ Layers (0.5-10. nm) Sandwiched between Thicker SiO@sub 2@ Layers (1.5 nm)***, **C.L. Hinkle**, C. Fulton, G. Lucovsky, R.J. Nemanich,* North Carolina State University

A novel method for obtaining the tunneling mass, m@sub eff@, and conduction band offset energy with respect to Si, E@sub B@, for high-k gate dielectrics is presented. It is based on a quantum mechanical WKB-approximation that explains large bias dependent increases in tunneling in symmetric stacked devices with ultra-thin HfO@sub 2@ layers (~0.5 nm) sandwiched between thicker SiO@sub 2@ layers (~1.0-1.5 nm) as compared with reference devices with homogenous SiO@sub 2@ dielectrics. J-V traces for substrate injection indicate a marked departure from the approximately exponential bias dependence of homogenous dielectrics for V@sub ox@ = V@sub g@ - V@sub fb@ >1 V. This correlates with differences between the tunneling attenuation factors, @alpha@@sub i@t@sub i@ = 4@pi@t@sub i@(2m@sub effi@E@sub Bi@)@super 0.5@/h, in the constituent layers, i, where t@sub i@ is the i@super th@ layer thickness. For V@sub ox@ >1 eV, small decreases in @alpha@t(SiO@sub 2@) compared to larger decreases in @alpha@t(HfO@sub 2@) result in a marked increase in their ratio. For V@sub ox@ > 1.5 V, there is minimal attenuation in the HfO@sub 2@ layer, so that the tunneling current is determined predominantly by the SiO@sub 2@ layer. At V@sub ox@ = 3V, the relative current with respect to the reference Si device is >1000. By analyzing these data, and increasing the thickness of the HfO@sub 2@ layer beyond 2 nm to determine the thickness at which relative tunneling begins to decrease due to increased attenuation in that component of the stack, values of m@sub eff@ = 0.15±0.05 m@sub o@ and E@sub B@ = 1.4±0.2 eV are obtained for HfO@sub 2@.

3:40pm **DI-TuA6 Observation of Bulk HfO@sub 2@ Defects by Spectroscopic Ellipsometry***, **H. Takeuchi**, D. Ha, T.-J. King,* University of California at Berkeley

HfO@sub 2@ (hafnium oxide) is a promising candidate to replace SiO@sub 2@-based films as the gate dielectric in ultra-scaled MOSFETs, due to its thermal stability in contact with Si, compatibility with a conventional CMOS process flow, and moderately high dielectric constant (20-25). The electrical characteristics of HfO@sub 2@ films, such as equivalent SiO@sub 2@ thickness (EOT), leakage current density, hysteresis in capacitance vs. voltage curves, fixed charge density and resultant field-effect carrier mobilities, have been extensively investigated. However, the physical mechanism for deviation from ideal behavior is not yet well understood. In particular, not much is known about bulk defects inside HfO@sub 2@ and their impact on electrical characteristics and the thermal stability of HfO@sub 2@. In this study, we report a bulk defect in HfO@sub 2@ which can be detected as an optical absorption peak by spectroscopic ellipsometry (SE). 12.5nm-thick HfO@sub 2@ films were formed by oxidation of pure Hf films in a cold-wall rapid thermal annealing (RTA) reactor. Absorption coefficients near the absorption edge were extracted by the data inversion method, in which the optical constants for short wavelength were calculated using the thickness obtained from long wavelength data. The obtained optical bandgap of 5.7eV matches very well with theoretical calculation and VUV measurement reported by other groups, and a shift due to crystallization was also detected. In addition, an extra absorption peak was observed in 4.5~5.0eV range. The energy difference between this absorption peak and the bandgap corresponds well to the trap energy extracted from measurement of the temperature dependence of Poole-Frenkel current. Hence, the peak is associated with electron transition from the valance band to the trap energy level inside the bandgap. This peak reduces with oxidation annealing time, indicating that the defects can be attributed to oxygen vacancies in the HfO@sub 2@ film.

4:00pm **DI-TuA7 Chemically Abrupt Interfaces between Lanthanum Aluminate and Silicon for Alternative Gate Dielectric Applications***, **L.F. Edge**, D.G. Schlom,* Pennsylvania State University*; S.A. Chambers,* Pacific Northwest National Laboratory*; C.L. Hinkle, G. Lucovsky,* North Carolina State University

LaAlO@sub 3@ is one of the most promising alternative gate dielectrics for the replacement of SiO@sub 2@ in silicon MOSFETs. Single crystalline LaAlO@sub 3@ is known to have a dielectric constant of 24 and an optical bandgap of 5.6 eV. The band offsets between LaAlO@sub 3@ and Si have been predicted to be in the range 2.1 to 3.5 eV for electrons and 1.0 to 1.9 eV for holes. It will be shown that LaAlO@sub 3@ is stable in contact with silicon under standard MOSFET processing conditions. Epitaxial Si has been grown by MBE on single crystals of LaAlO@sub 3@ and annealed at 1026C, which is a standard implant activation anneal for MOSFETs, and the interface remained stable and free of SiO@sub 2@. A major challenge in the growth of alternative gate dielectrics on Si is the formation of unwanted SiO@sub 2@ at the interface. One technique to prevent the formation of SiO@sub 2@ is to grow in a low temperature and excess oxidant regime. We have investigated the oxidation kinetics of Al and La, both individually and together (codeposition), to determine the minimum oxygen partial pressure required to achieve fully oxidized LaAlO@sub 3@. Using these optimized conditions, amorphous LaAlO@sub3@ films as thin as 1.0 nm have been grown on silicon by MBE. AES and XPS analyses indicate that the films are fully oxidized and show no SiO@sub 2@ at the interface, even after prolonged exposure of the films to air.

4:20pm **DI-TuA8 Medium Energy Ion Scattering Studies of the Structure and Composition of Epitaxial SrTiO@sub 3@ Films on Silicon***, **L.V. Goncharova**, D.G. Starodub, E.L. Garfunkel, T. Gustafsson,* Rutgers University*; D.G. Schlom,* Pennsylvania State University

Thin crystalline oxide films on silicon show a wide range of new electronic, optical, and magnetic properties with potential impact on novel devices. Precision control of the composition, stoichiometry and structure of such films and the ability to characterize the films and their interfaces are therefore of central importance. We have used high-resolution medium energy (~ 100 keV) ion scattering (MEIS) to investigate the composition and structure as a function of depth of thin (40-250 Å) crystalline SrTiO@sub 3@ films on Si (100). As ion beams are penetrating, and the ion-solid interaction is well understood, this technique allows us to get quantitative information both about the film/vacuum and about the film/substrate interface structure. Different channeling and blocking geometries have been utilized to distinguish epitaxial/amorphous regions, to characterize the chemical composition of the SrTiO@sub 3@/Si interface and also to give information about structural parameters. Thin SrTiO@sub 3@ films were grown epitaxially on Si(001) at the low temperatures in an excess of oxygen.@footnote 1@ Our MEIS results show that films grown by this method have A-site (SrO) termination. We further show that submonolayer amounts of strontium silicide, used in the initial stages of growth, are fully eliminated from the interface after growth is completed and that instead Ti has diffused into the interface region. The SrTiO@sub 3@/Si interface was confirmed to be crystalline; however the geometrical structure deviates significantly both from the 'bulk' epitaxial film and from the substrate. Possible structural models for the transition region and mechanisms of titanium incorporation in the interface region will be discussed. @FootnoteText@ @footnote 1@ J. Lettieri, J.H. Haeni, and D.G. Schlom, J.Vac.Sci.Technol. A 20 (2002) 1332.

4:40pm **DI-TuA9 In-situ and Ex-situ Characterization of Barium Strontium Titanate Thin Films on Thermal SiO@sub 2@/Si Substrates***, **N.A. Suvorova**, C.M. Lopez,* University of North Carolina, Chapel Hill*; A.A. Suvorova, M. Saunders,* University of Western Australia*; E.A. Irene,* University of North Carolina, Chapel Hill

Alternative materials with high dielectric constant (k) are in demand for replacement of SiO2 in MOSFET devices. Barium strontium titanate (BST) is one of possible candidate for DRAM applications. The most important requirement for the incorporation of an alternative gate dielectric is to maintain a high quality interface with Si comparable to that of SiO2 /Si. Similar to other high k materials for BST this is a major problem due to interface reaction with Si. One potential solution is the use of a thermal SiO2 ultra thin underlayer, which helps to minimize the reaction between high k dielectric and Si as well as maintain the high interface quality. However this solution degrades the k values of the two film gate stack. The present study is aimed toward optimizing the SiO2 underlayer thickness in order to maintain the interface quality yet minimize the effect on k. The results from this optimization study are presented with emphasis on the key process parameters that improve the dielectric film stack. For in-situ growth characterization of BST film grown on thermally oxidized Si substrates spectroscopic ellipsometry has been used. Studies of material properties have been complemented with analytical electron microscopy. Electrical characterization has been employed for ex-situ studies of Pt/BST/SiO2/Si structures. From conductance-voltage analysis, the interface trap density Dit was observed to significantly decrease for the capacitors grown on oxidized Si substrates and annealed in forming gas.

5:00pm **DI-TuA10 Band Offsets at Ba- SrTiO@sub 3@ / Si Interfaces***, **F. Amy**, A. Wan, A. Kahn,* Princeton University

The continuous drive toward faster electronics and scaling down of MOSFET device dimensions requires alternatives to SiO@sub 2@ for gate dielectrics. High-k dielectrics have therefore received considerable attention from industry and the scientific community. Crystalline perovstike oxides such as SrTiO@sub 3@ and BaTiO@sub 3@ are of special interest and offer several advantages. First, they can be MBE-grown lattice-matched to Si (or Ge) substrates with very low interface state density.@footnote 1@ Second, they can serve as a buffer layer for the growth of semiconductors, opening possibilities for integrating Si electronics and III-V optoelectronics. However, several issues concerning these materials remain to be fully addressed, among which band offsets with Si and other semiconductors. In this work, we use a SrTiO@sub 3@(100 Å)/BaSrO(11 Å)/Si structure grown by MBE, and X-ray and UV photoemission spectroscopy to study core levels and valence band respectively. Depending on surface preparation, including ex-situ UV ozone, O@sub 2@ or UHV annealing, the valence band maximum position shifts by more than 2 eV, whereas very little if any shift is observed on core levels. These findings indicate that surface composition and morphology are of paramount importance in the UPS determination of electronic structure, and may explain discrepancies between results reported in the literature. Our investigation of clean and stoichiometric SrTiO@sub 3@ surface indicates that its conduction band minimum is located 0.4 eV (± 0.4) below the one of silicon. An in-depth investigation of the role of surface preparation is being pursued, and results on BaTiO@sub 3@/SrTiO@sub 3@/Si samples will be reported. @FootnoteText@ @footnote 1@ . R. A. McKee, F. J. Walker, and M. F. Chisholm, Phys. Rev. Lett. 293, 468 (2001)

Electronic Materials and Devices
Room 310 - Session EM+SC-TuA

50th Anniversary Sessions: Electronic Materials

Moderator: L.J. Brillson, Ohio State University

2:00pm **EM+SC-TuA1 Electronic Materials Growth: A Retrospective and Look Forward***, **C.W. Tu**,* University of California, San Diego **INVITED**

This article reviews the development of electronic materials, primarily III-V compound semiconductors, from substrates to epitaxy and in situ monitoring to heterostructures, quantum wells and superlattices, that are important to various device applications. As the current research direction leads to the immediate future, the article then summarizes some of the recent advancement in quantum wires, nanowires, and quantum dots.

2:40pm **EM+SC-TuA3 Electronic Materials Theory: Interfaces and Defects***, **C.G. Van de Walle**,* Palo Alto Research Center **INVITED**

The experimental advances in electronic materials over the past decades have been accompanied by a remarkable increase in the ability to predict structural and electronic properties from first principles. Basic theory, along with modeling and simulation, has always been instrumental in understanding materials. Only recently, however, has the capability emerged to accurately predict properties based solely on the composition of the material, without any fitting to experimental quantities. Such a description must be based on a quantum-mechanical treatment, i.e., a solution of the Schrödinger equation for the system of atomic constituents. The seemingly impossible task of solving this vast many-body problem was rendered feasible by the development of density functional theory (DFT), an achievement for which Walter Kohn received the Nobel Prize in Chemistry in 1998. Other important developments that have greatly enhanced the ability to tackle large systems include pseudopotentials, the simultaneous optimization of electronic and atomic degrees of freedom as embodied in the Car-Parrinello method, and the tremendous increase in available computer power. In this talk I will focus on two areas in which these theoretical and computational advances have had a major impact, namely heterojunction interfaces and defects in semiconductors. Both are intimately connected to the high-quality growth techniques that have enabled a host of novel electronic devices. In the area of defects I will describe the effects of point defects and impurities on doping, specifically highlighting the role of hydrogen. A recently discovered universal alignment for the electronic level of hydrogen in semiconductors and insulators reveals a surprising link with the problem of heterojunction band lineups.

3:20pm **EM+SC-TuA5 Progress in Electronic Materials Characterization***, **P.H. Holloway**,* University of Florida **INVITED**

Progress in characterization of electronic materials over the past 50 years will be illustrated by selected examples of determination of the atomistic reconstruction and formation of electronic states at surfaces and interfaces of semiconductors using surface sensitive characterization techniques. The same techniques have been used to characterize reactions at interfaces and determine the mechanisms by which charge carrier transport is changed from that controlled by Schottky rectifying to contacts with ohmic characteristics. Seconday ion mass spectrometry (SIMS) has been used to measure dopant profiles over dimensions <10 nm below the surface, and optical characterization techniques have been used for real time control of semiconductor growth. Finally, areas of future development in electronic materials characterization techniques will be the subject of speculation.

4:00pm **EM+SC-TuA7 Making Contact - The Evolution of Materials for Silicon Device Contacts and Interconnections*, J.M.E. Harper,*** University of New Hampshire*; S.M. Rossnagel, F.M. d'Heurle, L. Clevenger, C. Lavoie, C. Cabral, Jr.,* IBM T.J. Watson Research Center **INVITED**

The evolution of silicon device technology during the 50-year history of the AVS required not only the constant miniaturization of the transistor, but the concurrent miniaturization of contact metallurgy and interconnection structures. With decreasing area and thickness came a series of materials challenges related to deposition processes, interdiffusion, compound formation and phase stability. These challenges were overcome with a steady stream of innovations in alloy metallurgy, deposition methods, diffusion barriers and understanding of phase formation that apply far beyond the field of microelectronics. Many of these advances were developed by active AVS members and award winners, since the AVS has provided a fertile professional arena for bringing together the necessary scientific and engineering perspectives. Examples will be taken from the development of aluminum-copper and copper interconnections and from the evolution of titanium, cobalt and nickel silicide contact metallurgy.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI+NS-TuA

Self Assembly and Nanomagnetism

Moderator: S.D. Bader, Argonne National Laboratory

2:00pm **MI+NS-TuA1 Many-spin Hamiltonian for the Single-molecule Magnet Mn12-Ac*, K. Park,*** Naval Research Laboratory and Howard University*; M.R. Pederson,* Naval Research Laboratory*; S.L. Richardson,* Howard University and Naval Research Laboratory

Nanoscale single-molecule magnets recently received great attention due to scientific and practical reasons: macroscopic quantum phenomena and possible utilization as magnetic storage devices or quantum computing. A single-molecule magnet (SMM) is a three-dimensional array of identical molecules, each of which consists of several transition metal ions surrounded by organic ligands and is independent of neighboring molecules. Among many kinds of SMMs, Mn12-Ac has been the most extensively studied for the past decade. Although the low-energy features of Mn12-Ac have been well understood by considering each molecule as an effective ground-state spin of S=10, there is still a big controversy over the energy gap between the first excited-state manifold and the ground-state manifold as well as the internal structure of the single molecule. To provide a guide to understanding the controversial many-spin features, we investigate the intramolecular exchange couplings and the projected single-ion anisotropies using density-functional theory (DFT). We use all-electron Gaussian-orbital-based Naval Research Laboratory Molecular Orbital Library (NRLMOL) within Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA). Based on the calculated exchange couplings and anisotropy parameters, we construct a model many-spin Hamiltonian which reproduces calculated single-spin results and allows for the extraction of many-spin features.

2:20pm **MI+NS-TuA2 Magnetic Interaction in Assemblies of Nanometer-sized Fe Dots on Cu (111)*, M.A. Torija,*** *J. Pierce,* University of Tennessee, Knoxville*; J.F. Wendelken,* Oak Ridge National Laboratory*; E.W. Plummer,* University of Tennessee, Knoxville*; J. Shen,* Oak Ridge National Laboratory

Assemblies of separated iron quantum dots can be prepared on the Cu(111) surface via a buffer-layer-assisted growth process. First, an inert Xe layer is frozen onto a Cu(111) substrate that is held below 30 K. Then, Fe atoms are dosed from a typical evaporation source and form clusters on the Xe layer. Finally, the sample is warmed above 90 K, allowing the buffer layer to evaporate and the formed quantum dots to land on the surface. Scanning tunneling microscopy has shown us that we can control the average spacing and size of the dots by changing the Xe layer thickness and/or the amount of Fe deposited. Surprisingly, the dot arrays show non-zero remanent magnetization that is stable with the passage of time. To distinguish the roles of the magnetic interactions vs. the magnetic anisotropy in stabling the remanent magnetization, measured by SMOKE, we compare the ordering temperature of dot assemblies that have equal size distribution but different density. At fixed dot size distribution, varying the density of the Fe dots from 0.003 to 0.015 leads to an enhancement of ordering temperature from 153 K to 363K. This clearly indicates that magnetic interactions play an important role in stabling the remanent magnetization. Another interesting phenomena that we observed is a spin reorientation induced by the dot size. that for a fixed nominal thickness, the easy axis of magnetization is perpendicular for lower Xe thickness (small dots), and becomes in-plane for higher Xe thickness (big dots). It may be explained by the interplay between surface and bulk anisotropies.

2:40pm **MI+NS-TuA3 Contribution of Orbital Magnetism to the Magnetism of Monodisperse Nanoparticles*, M. Farle,*** Universitaet Duisburg-Essen, Germany **INVITED**

Self-organized magnetic nanoparticles with diameters of less than 10 nm are interesting for technological applications and for the investigation of interface properties due to their high surface-to-volume atom ratio. One of the most important magnetic properties, the magnetic anisotropy energy (MAE) is strongly influenced by the local structure and size of the particles, since on the atomic level MAE is related to the anisotropy of the orbital magnetic moment. Well-known techniques to measure the orbital contribution to the total magnetic moment are ferro-/paramagnetic resonance (FMR/EPR) and x-ray magnetic circular dichroism. Two examples will be discussed: a)disordered 3 nm FePt with different Fe contents, b)11.4 nm CoO@Co (a 2nm CoO shell surrounding a 8 nm Co core). For the FePt particles with different Fe concentration we find a linear increase of the g-factor measured by FMR/EPR , i.e. of the ratio of orbital-to-spin magnetic moment for larger Pt contents. This indicates that the presence of Pt induces an enhanced orbital magnetic moment in the nanoparticle. In the case of CoO@Co we find by FMR a bulk- like g factor g = 2.15 of fcc Co, while XMCD yields a 300 % enhanced ratio of orbital-to-spin moment. A quantitative comparison taking the different sampling depths of both techniques into account reveals the presence of uncompensated large magnetic Co moments at the interface of the antiferromagnetic CoO shell to the ferromagnetic Co core . Supported by EC contract no. HPRN-CT-1999-00150 and Deutsche Forschungsgemeinschaft.

3:20pm **MI+NS-TuA5 Self-assembly of FePt Nanoparticles on Si(100) Surface*, N. Shukla*,** *J. Ahner, D. Weller,* Seagate Research

Chemically synthesized monodispersed FePt nanoparticles are of great interest due their high magnetic anisotropy. The self-assembly and uniform coating of these nanoparticles on substrates is crucial for enabling high-density magnetic recording media. We have studied various parameters, potentially influencing the uniformity of FePt nanoparticle coatings. In particular, we report on the effects of excess surfactant concentration, type of surfactant, solvents and substrates. Films are fabricated using dip-coating and spin-coating methods. A narrow range of surfactant concentration is identified that leads to long range (~ 1x 1 mm@super2@) uniformity. Outside this concentration range the nanoparticle coatings form clusters with local self-assembly. In addition, the type of solvent and type of surfactant has a profound impact on the self-assembly of FePt. Decreasing the size of surfactant chain length changes the self-assembly from uniform to ring structures. Polarity and viscosity of the solvents also impact the self-assembly. Polar solvents give poor uniformity. Low viscous solvents have a similar impact.

3:40pm **MI+NS-TuA6 Submicron Cobalt Particle Fabrication by Ion Beam Induced Chemical Vapor Deposition (IBICVD)*, Y. Kageyama*,** *T. Suzuki,* Toyota Technological Institute, Japan

Nanometer-sized patterned structures for high density data storage have recently become of great interest. It has been demonstrated that the ion-beam induced chemical vapor deposition (IBICVD) technique has a potential benefit for fabrication of nano-dots.@footnote 1,2@ Characterization of IBICVD-synthesized Co particles was performed, and the result is presented in this paper. The submicron Co particles were deposited on Si@sub 3@N@sub 4@ substrates by a focused Ga@super +@ ion beam (FIB) system equipped with a source reservoir filled with precursor of octacarbonyl dicobalt [Co@sub 2@(CO)@sub 8@] powders. Vapor of the precursor was introduced though a feeding nozzle (0.5mm diameter) above the substrate separated by 0.5 mm. The base pressure of the deposition chamber was about 10@super -5@ Pa. The ion current and the pressure during deposition were 14 pA and 0.7 - 1.4 x 10@super -4@ Pa, respectively. The in-situ image of Co particles was taken by SEM of the FIB system. Under the condition of irradiation of ion beams, the particle formation process is rather complicated due to concurrence of competitive processes (etching and deposition), therefore the morphology of Co particles strongly depends on the ion beam dwell time (5 to 120 µms) and the partial pressure of Co@sub 2@(CO)@sub 8@ precursor, as revealed by AFM analysis. The smallest size of Co particle obtained is about 150 nm so far. They exhibit ferromagnetic behaviors. Further studies on modification of properties by heating substrates, and on formation of alloys by introducing a second deposition source, are in progress. @FootnoteText@@footnote 1@ A. Lapicki, E. Ahmad, and T. Suzuki, J. Magn. Magn. Mat. 240 (2002) 47@footnote 2@ A. Lapicki, K. Kang, and T. Suzuki, IEEE Trans. Magns. 38 (2002) 2589.

4:00pm **MI+NS-TuA7 Magnetic Nanostructures Made by Self-assembled Block Copolymer Lithography***, **C.A. Ross**, J.Y. Cheng, H.I. Smith, E.L. Thomas,* Massachusetts Institute of Technology*; G. Vancso,* University of Twente, The Netherlands **INVITED**

The fabrication and magnetic properties of thin-film particles with diameters of 35 nm and periodicity of 50 nm made using block copolymer nanolithography will be described. Such particle arrays may be used in magnetoelectronic and magnetic storage devices, where it is important to control the magnetization state, switching field, and uniformity of the particles and to understand their size-dependent magnetic behavior. Arrays of single-layer Co and NiFe particles with thicknesses of 5, 10, 15 and 20 nm, and Co/Cu/NiFe multilayer particles have been made. The Co and NiFe particles show an increase in coercivity and a decrease in switching field distribution with thickness. The particles exhibit thermally-assisted reversal, with switching volumes larger than the physical particle volume due to strong magnetostatic coupling between the particles. The multilayer particles show hysteresis behavior consistent with interlayer magnetostatic coupling, and measurable giant magnetoresistance despite the small dimensions of the particles. These arrays have short-range close-packing, but no long-range order. To impose long-range order the substrates have been patterned with shallow grooves, which induce alignment of the rows of polymer features parallel to the steps creating an ordered array. The polymer domain spacing conforms to the dimensions of the templating features leading to a quantized number of rows of domains within each groove. It is also possible to confine the polymer to certain regions of the substrate using soft printing methods, which also leads to a limited degree of ordering. Results from these templated self-assembly processes will be discussed. This work was supported by NSF. Refs: Cheng et al, Adv. Mater. 13 1174 (2001); Appl. Phys. Letts. 81 3657 (2002); IEEE Trans. Magn. 38 2541 (2002).

4:40pm **MI+NS-TuA9 Magnetic Properties of Low-dimensional Nanostructures on an Insulator***, **Z. Gai**, J.R. Thompson, J. Pierce, J. Shen,* Oak Ridge National Laboratory

Magnetic nanostructured materials are attracting much attention because of the dramatic changes in their magnetic, electronic and transport properties compared with conventional bulk materials. In previous work, iron zero-dimensional dots, one-dimensional nanowires and two-dimensional films have been successfully prepared on top of a commonly used insulating NaCl (001) single crystal surface. In-situ atomic force microscopy images show that the sizes of the dots and the widths of the wires are very uniform; the films are atomically flat and are formed due to a high nucleation density. In the present work, the magnetic properties of the dots, wires and films are measured by Superconducting Quantum Interference Device (SQUID) magnetometer X-ray magnetic circular dichroism (XMCD). The wires have an out-of-plane easy magnetization axis, and surprisingly show ferromagnetic stability even at room temperature. The magnetic behaviors of the dots and films are very different from the wires. The detailed comparison will be discussed in the talk. Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

5:00pm **MI+NS-TuA10 Magnetic Reversal of Co/Pd Multilayer Films and Sub-100nm Islands***, **G. Hu**, T. Thomson, M.E. Best, B.D. Terris,* Hitachi San Jose Research Center*; C.T. Rettner, S. Raoux, G.M. McClelland, M.W. Hart,* IBM Almaden Research Center

Patterned arrays of Co/Pd multilayer islands with perpendicular anisotropy are one approach to increasing magnetic recording density towards 1Tbit/in@super 2@. To realize this technology arrays consisting of single domain islands with sufficient anisotropy for thermal stability and a narrow switching field distribution will be required. In order to understand the reversal properties of islands we have compared the reversal mechanism and anisotropy of patterned arrays to nominally identical unpatterned, continuous films. The island arrays were fabricated by creating an etch mask using electron beam lithography and nano-imprinting followed by etching of a SiO@sub 2@ substrate. Multilayer films of Co/Pd were then sputter deposited onto the topographically patterned substrates. We found that for the continuous films, the magnetic anisotropy is only sensitive to the Co and Pd layer thicknesses while coercivity and magnetization reversal mechanism can be easily tuned by varying the deposition conditions. However, for small, single domain islands, the coercivity is much less sensitive to deposition conditions and more sensitive to composition than for the continuous films. The coercivity of these islands is generally significantly greater than that of the continuous films. Moreover, the switching behavior of the islands does not exhibit any correlation with the film reversal mechanism, but rather follows the film magnetic anisotropy closely. Systematic studies have been carried out to adjust the magnetic anisotropy of the multilayer films by varying the cobalt and palladium layer thicknesses. Unlike the continuous films, the measured coercivity of the islands agrees well with the reversal field calculated based on the measured anisotropy of the film and the Sharrock equation.

Microelectromechanical Systems (MEMS)
Room 320 - Session MM-TuA

Fabrication and Characterization of MEMS Devices

Moderator: C.B. Freidhoff, Northrop Grumman

2:00pm **MM-TuA1 Development of a Deep Phase Fresnel Lens in Silicon***, **B. Morgan**, C.M. Waits,* University of Maryland, College Park*; J. Krizmanic,* NASA - Goddard Spaceflight Center*; R. Ghodssi,* University of Maryland, College Park

Astronomical observations at Gamma and hard X-ray energies are presently hindered by instruments with low sensitivity and poor angular resolution. Fresnel Zone Plates and their derivatives, could achieve higher sensitivity and greater angular resolution.@footnote 1@ For ground testing of a Phase Fresnel Lens (PFL), lateral dimensions of each lens feature must be on the order of 10 µm, while vertical dimensions must be >20 µm, both a natural fit for MEMS processing. Silicon, the standard material used in MEMS, has low absorption of Gamma and X-ray radiation, making it a good material choice for the fabrication of a PFL for ground testing. Gray-scale technology was selected as the fabrication method for developing such a lens because of two main advantages: (1) the multiple heights required for increased efficiency may be fabricated without alignment, and (2) Deep Reactive Ion Etching (DRIE) with precise selectivity control enables the fabrication of deep (>20 µm) silicon lenses. Multiple PFL's, with diameter >1.6mm and varying heights, have been successfully fabricated in silicon. The optimization of gray-scale lithography processing for large-scale structures was realized through the use of a custom calibration mask. Advanced gray-scale optical mask design allows the fabrication of small gray level geometries over a large area, enabling precise profile control to maximize lens efficiency. Depending on target photon energy, etch depths required to produce the appropriate phase shift in silicon have been between 20 and 100 µm. Highly accurate vertical dimension control is also necessary to ensure the proper interference pattern at the lens focus. Therefore, PFL height was controlled by finely tuning etch selectivity during DRIE, which adjusts the scaling factor between photoresist and silicon, and provides the appropriate PFL profile in silicon. @FootnoteText@ @footnote 1@G.K. Skinner, Astronomy & Astrophysics, v.375, no.2, 2001, p.691-700.

2:20pm **MM-TuA2 Fabrication and Characterization of a Capacitive Micromachined Shunt Switch***, **S.L. Firebaugh**,* United States Naval Academy*; H.K. Charles, Jr., R.L. Edwards, A.C. Keeney, S.F. Wilderson,* Johns Hopkins University

Microelectromechanical switches offer many advantages over solid-state devices, including greater linearity, increased isolation and lower insertion loss.@footnote 1-5@ One disadvantage of such switches is that they require high actuation voltages (20-100 V), leading to problems with dielectric charging and system integration. Furthermore, when reducing the actuation voltage one must consider the dependence of power handling capability on actuation voltage.@footnote 6@ This paper describes the design, fabrication and testing of a shunt switch@footnote 3,4@ based on a bridge suspended over a coplanar waveguide. When a sufficient DC voltage is applied the bridge pulls down towards the signal line, creating a high-frequency short circuit and causing the signal to reflect back towards the source, blocking transmission. The switch is used as a test vehicle to explore the effects of bridge shape on performance, as well as to investigate the limits of micromachined switches. A common problem for MEMS switch developers is obtaining equipment to test device characteristics such as power handling limits on a wafer probe station. In this work, standard microwave connectors and equipment are facilitated by a custom test fixture. The pull-in effect is studied in detail, as well as methods for switching the device while avoiding dielectric charging effects and maintaining reasonable power handling levels. @FootnoteText@ @footnote 1@ C.T.C. Nguyen et al., Proc. IEEE, vol. 86, no. 8, pp. 1756-1768, August 1998.@footnote 2@ J.J. Yao, J. Micromech. Microeng., vol. 10, pp. R9-R38, 2000.@footnote 3@ Z.J. Yao et al., IEEE J. Microelectromech. Syst., vol. 8, no. 2, pp. 129-134, 1999. @footnote 4@ J.B. Muldavin and G.M.Rebeiz, IEEE Trans. Microwave Theory and Tech., vol. 48, no. 6, pp. 1045-1052, June 2000.@footnote 5@ D. Hyman et al., Electron. Lett., vol. 35, no. 3, pp. 224-226, February 1999.@footnote 6@ B. Pillans et al., 2002 IEEE MTT-S Int. Microwave Symp. Dig., pp. 329-332.

2:40pm **MM-TuA3 Design and Process Integration of an Electric Induction Micromotor***, **C. Livermore**, J.L. Steyn,* Massachusetts Institute of Technology*; J.U. Yoon, A. Forte,* MIT Lincoln Laboratory*; R. Khanna,* Massachusetts Institute of Technology*; T. Lyszczarz,* MIT Lincoln Laboratory*; S.D. Umans, J.H. Lang,* Massachusetts Institute of Technology **INVITED**

We present the development of a millimeter-scale electric induction machine designed to output Watt-level power for portable power applications. The micromotor comprises a stack of five micromachined silicon wafers. A 4 mm spinning silicon rotor disk is encapsulated within the stack; facing the spinning rotor is a six-phase electric stator. Mechanical-electrical power conversion is accomplished by the interaction of the stator potential with induced charges on the rotor. To operate at high power levels, the micromotor must operate under extreme conditions: high speed rotation (near one million rpm), high voltages (300 V across 3 µm to 4 µm gaps), and high electric frequencies (about 1.5 MHz). These requirements in turn place stringent requirements on the device design and fabrication flow: low electric losses, excellent resistance to electric breakdown, and essentially leak-free wafer bonds among the five silicon wafers. This presentation describes the approaches that are used to meet these requirements simultaneously in a complete, functional device. A thick oxide liftoff process is used to embed islands of oxide in the silicon substrate under the electric elements to reduce stray capacitance and electric losses. The island structure also minimizes overall bow from the stressed films, making wafer bonding possible. The stator's two-level interconnected electric elements are made of platinum and fabricated by a liftoff process. The platinum electrodes and interconnects reduce line resistance, minimize ohmic losses, and provide a smooth, break-down resistant line shape.@footnote 1@ @FootnoteText@ @footnote 1@ The Lincoln Laboratory portion of this work was sponsored by the Defense Advanced Research Projects Agency. Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the Department of Defense.

3:20pm **MM-TuA5 Microfabrication of a Pressure Sensor Array Using 3D Integration Technology***, M. Khbeis,* Laboratory for Physical Sciences*; **X. Tan**,* University of Maryland*; G. Metze,* Laboratory for Physical Sciences*; R. Ghodssi,* University of Maryland

A novel microfabrication approach that enables successful integration of a piezoresistive pressure sensor array on an airfoil for detection of micro-scale turbulent vortices is presented. These sensor arrays will be used to study the dynamics of turbulent air flow with the ultimate goal of reducing drag on aircraft. Minimization of surface undulations on the sensor is required to avoid generating additional air turbulence. Therefore it is essential to implement an enabling fabrication approach that eliminates the dependence on topside electrical connections. We have developed a 3D integrative process to provide backside interconnections, while maintaining the specified 200µm sensor element pitch. This 3D fabrication effort incorporates several advanced process technologies including: low temperature SiO@sub 2@-to-Si wafer bonding (<250°C), bulk wafer thinning (to 20µm), high-aspect ratio (HAR 20:1) Si and SiO@sub 2@ etching using m=0 resonant induction (M0RI), and HAR (10-15:1) metallization using high pressure Aluminum reflow. This integrative process will facilitate vertical stacking of multiple device components on different layers, allowing the integration of MEMS and microelectronic devices for the realization of Small Smart Systems (SSS). Process developments and preliminary experimental results are presented.

3:40pm **MM-TuA6 Simulation of Field Emission-based Pressure Sensors***, **A.M. Nair**, N. Badi, A. Bensaoula,* University of Houston

This paper reports on simulating the moving part of a field emission-based pressure sensor. The device is comprised of a membrane made of silicon or other stiffer materials acting as the anode of a device comprised of a fixed flat cold cathode emitter. This is achieved by modeling the deflection and mechanical stress of a diaphragm of varying geometry under selected input pressures. Realistic field emission characteristics from our boron nitride and carbon nitride cold cathodes@footnote 1@ were used to model the current density distribution in the deflected diaphragm. The total current output was achieved by integrating the current density over the entire diaphragm area as a function of membrane bending due to external pressure. Results show that simple and reliable field emission devices can be designed to yield extremely sensitive pressure sensors but their characteristics are critically dependent on the specific geometry. Simulation data will be presented for devices with geometries similar to those being fabricated in our laboratory. @FootnoteText@@footnote 1@N. Badi, A. Tempez, D. Starikov, A. Bensaoula, V.P.Ageev, A. Karabutov, M.V. Ugarov, V. Frolov, E. Loubnin, K. Waters and A. Shultz, "Field Emission from as-grown and Surface Modified BN and CN Thin Films" J. Vac. Soc.Technol. A 17, 1191 (1999). Acknowledgment: This material is based upon work supported by the National Science Foundation under Grant No. 0010100

4:00pm **MM-TuA7 Nanotribological Characterization of Digital Micromirror Devices using Atomic Force Microscopy***, **H. Liu**, B. Bhushan,* Ohio State University

Texas Instruments' Digital Micromirror Device (DMD) comprises an array of fast digital micromirrors, monolithically integrated onto and controlled by an underlying silicon memory chip.@footnote 1@ It is one of the few success stories in the emerging field of microelectromechanical systems (MEMS). In this study, atomic force microscopy (AFM) has been used to characterize the elements of the mirror structure of the DMD. AFM images of the mirror, hinge and yoke, and metal arrays are characterized. An AFM methodology was developed to identify and remove mirrors of interest. The surface roughness and adhesion properties of contacting surfaces were extensively studied. The influence of relative humidity and temperature on the behavior of the DMD was also investigated. Potential mechanisms for stiction accrual@footnote 2@ are discussed in light of the findings. @FootnoteText@ @footnote 1@L.J. Hornbeck, MRS Bulletin, 26, 325(2001) @footnote 2@B. Bhushan, (ed.), Tribology Issues and Opportunities in MEMS, (Kluwer Academic, Dordrecht, Netherlands, 1998).

4:20pm **MM-TuA8 PZT Dry Etching using ICP Etcher for MEMS Devices***, **M. Dubey**, R.G. Polcawich, E. Zakar, J. Pulskamp, A.E. Wickenden, L.J. Currano,* U.S. Army Research Laboratory

Piezoelectric Lead Zirconate Titanate (PZT) thin films deposited on platinized silicon substrates were reactively ion etched using an inductively coupled plasma (ICP) etching system. Etch rates for PZT, Pt, and silicon dioxide were determined from room temperature to 90 °C using Ar, He, Cl@sub 2@, CF@sub 4@, C@sub 2@H@sub 4@, C@sub 4@F@sub 8@, and SF@sub 6@ gases at RF powers from 500 to 1400 W. Measured etch rate for PZT varied from 500 to 2600 Å/min, for Pt from 940 to 1750 Å/min, and for oxide from 50 to 300 Å/min. Experimental results will be presented on selectivity and etched profile of PZT, Pt, and silicon dioxide films at different operating pressures and bias voltages. MEMS (microelectromechanical systems) test structures fabricated using ICP etchers will also be described.

4:40pm **MM-TuA9 Integration of Silicon Anisotropic Wet Etching and BCB Processes***, **N. Ghalichechian**, A. Modafe, R. Ghodssi,* University of Maryland, College Park

We have developed a fabrication process for integration of Benzocyclobutene (BCB) dielectric film and anisotropically etched deep silicon v-grooves in potassium hydroxide (KOH) solution for development of MEMS actuators such as an electrostatic micromotor supported on microball bearings. BCB is a low dielectric constant polymer (k=2.65) with several advantages over silicon dioxide for dielectric insulation such as simple deposition process, low-temperature cure, and low residual stress that are desired in a reliable, efficient electrostatic micromotor. KOH solution is used for fabrication of silicon v-grooves that form a bearing structure to house the micro-balls. We have used gold (Au) film as the etch mask and chromium (Cr) film as the adhesion layer that bonds the Au to the underlying BCB. It was initially observed that the metal films lost adhesion and no longer protected the BCB film during long KOH etching (7 hours in 20 %w solution) process. A fabrication process is developed to improve the adhesion between the BCB and the metal films during the silicon anisotropic bulk micromachining using KOH. This is achieved through several unit process experiments to investigate (a) the effect of cure temperature (210-250 °C), (b) surface treatment of BCB, (c) adhesion improvement at the interface between thin film metals and BCB by applying an adhesion promoter, AP3000, prior to metallization, and (d) the required Cr and Au thickness that results in a robust adhesion to BCB and reliable etch mask for KOH. The optimized experimental results in this work have enabled successful and repeatable fabrication of deep v-grooves (280 µm wide, 220 µm deep) in silicon with BCB (1 µm thick) and Cr/Au (20/500 nm thick) multilayer etch mask. The detailed process parameters and experimental results for this integrative process technology will be presented.

5:00pm **MM-TuA10 Optical Characterization of Poly-Dimethyl Siloxane (PDMS) during Inductively Coupled Plasma Processing for Implementation in a PDMS-based Photonic Crystal***, *E.A. Joseph, L.J. Overzet, M.J. Goeckner,* ***D.S. Park****, M. Tinker, J.B. Lee,* University of Texas - Dallas

Poly-dimethyl siloxane (PDMS) is a silicone elastomer quickly gaining popularity in MEMS and EUV lithography markets. Material etch rates and plasma susceptibility however are not yet fully understood and may significantly effect optical MEMS device performance. In this work, PDMS etch susceptibility is studied in oxygen and CF4 inductively coupled plasma mixtures with in-situ spectroscopic ellipsometry. Initial etch rates as high as 40 µm/hr using a 3:1 mixture of CF4:O2, nearly double that of optimized conventional RIE@footnote 1@ have been obtained, while pure oxygen plasma exposure has been found to increase the refractive index by 7%. A more detailed study of etch rate and dielectric constant dependence on gas flow will be presented along with the implications of using PDMS in a photonic crystal MEMS device. @FootnoteText@ *This work is supported by grants from NSF / DOE, CTS-0079783 & CTS-0078669 and NSF ECS-0296018.@footnote 1@J. Garra, T. Long, J. Currie, Schneider, R. White, and M. Paranjape, J. Vac. Sci. Technol. A 20(3), May/June 2002.

Manufacturing Science and Technology
Room 309 - Session MS-TuA
Directions in Semiconductor Device Scaling for the Next Decade

Moderator: S. Shankar, Intel Corporation

2:00pm **MS-TuA1 The Future of Chip Making Is Different --- Or Is It?**, ***R. Puhakka,*** VLSI Research **INVITED**

During this downturn chip making industry has seen numerous arguments that Moore’s Law has to slow down and no one can afford to continue as before. The fab cost is over $3B for leading edge fab, steppers are forecasted to cost more than $30M each, and new materials like copper, Low-K and High-K are creating new failure modes that are not well understood. In essence, the future of chip making is different. Or is it? Data shows that cost per transistor still continues to drop at historical rates. The number of transistors manufactured continues to grow fast, which shows world’s appetite for technology. Simultaneously, chip industry continues to shrink the critical dimensions at a very regular rate of node per two years. All of this is more difficult and expensive. This means it’s becoming more of a big company game - - a long term trend that’s been in place since the eighties. The analysis, however, also shows evidence that long term growth for chips and equipment is fundamentally lower. The future is different, but not as dramatically as has been argued.

2:40pm **MS-TuA3 Technology and Manufacturing Challenges in High Tech**, *R.L. Wisnieff,* IBM Corporation; ***S.M. Rossnagel,*** IBM T.J. Watson Research Center **INVITED**

Semiconductor technology is currently going through a fundamental transition, for the last forty years the active device has been the primary limitation in circuit performance, however today the wiring that interconnects the active devices is rapidly becoming the largest factor in determining the maximum speed the circuit will operate at. The search for high performance interconnects led to the widespread adoption of copper wiring to lower the resistance and, more recently, to the introduction of low dielectric constant materials to lower the capacitance of the interconnect circuit. The research and development of copper wiring spanned a period of roughly 12 years with much of this time was spent in refining the technology to achieve high reliability and yield. The research and development of lower dielectric constant materials is being undertaken at a much faster pace over a period of 5 years materials have been developed and applied to product. This accelerated schedule has left substantial room for improvement in the materials and processes that are being used. It is likely that there will be a series of incremental improvements ultimately culminating in a wiring technology that will use air gaps.

3:20pm **MS-TuA5 The Future of Semiconductor Lithography**, ***W.J. Trybula,*** International SEMATECH **INVITED**

The technology acceleration of the semiconductor industry has placed tremendous pressures on both equipment suppliers and manufacturers. Reviewing the International Technology Roadmap for Semiconductors (ITRS) readily demonstrates this advance in technology through acceleration. By examining the market pressures, an understanding of the forces driving the semiconductor manufacturers can be obtained. The result of these pressures is demonstrated by the Lithographic exposure tools that are currently under development. 193nm tools are being introduced into widespread manufacturing. 157nm lithography is being developed for introduction in late 2005 or early 2006 with production insertion slated for 2007. Extreme UltraViolet (EUV) is also under development for with plans manufacturing insertion in 2009. In addition, Electron Projection Lithography (EPL), Maskless Lithography (MML), and nano-Imprint Lithography are all being pursued. This paper provides an overview of the technologies being developed. Details of each are provided, which encompass the methods of operation, the key drivers for each technology, the mask requirements, the advantages of the technology, and projected insertion timing based on the exposure tool manufacturers' estimates. A summary will be provided that shows the time scale of each of the technologies for insertion. The key challenges for the technologies will highlight the areas of prime consideration. A final table will be provided that estimates the total industry cost to develop the technologies that are under primary consideration for insertion in the next few years.

4:00pm **MS-TuA7 CMOS Scaling Limits and Opportunity for Nanoelectronics**, ***Y. Nishi,*** Stanford University **INVITED**

Moore’s Law and the scaling principle have guided IC technology and products development in the past 3.5 decades, which has led us to sub 100nm era today. At the end of each decade IC technology community anticipated some sort of slowing down in the pace of geometry shrink, i.e.; in late 70’s it was 1um as the limit of practical scaling, and in late 80’s it became 0.1um as the ultimate limit. Now we are discussing 10-20nm as the ultimate limit. In the past cases, a set of technology break through allowed us further scaling, such as stepper technology and later excimer laser technology coupled with rapid thermal processing. At the same time we did not have physics driven limits in small geometry devices in the past, but now it seems there will be fundamental changes in transport phenomena in MOS transistors as geometry shrinks. The question today should be, "Do we have another break through which may bring us to sub-20nm in terms of performance, power consumption, cost and manufacturability?" If the answer is "no", we need to look into other options to partially, if not fully, replace scaled CMOS approach. This talk will cover the trends of CMOS scaling in the past, today and tomorrow, and discuss technical bottle neck and challenges mainly from device physics and technology point of view, followed by looking into several opportunities of nanoelectronic devices such as nanowires, nanotubes from device physics integration point of view.

4:40pm **MS-TuA9 John Bardeen and Transistor Physics**, ***H.R. Huff,*** International SEMATECH **INVITED**

The point contact transistor and the discovery of transistor action by Bardeen and Brattain on Dec 16, 1947,@footnote 1,2@ which evolved from studies on Shockley's field-effect principle, was the first solid-state electronic device to utilize both free-electrons and free-holes and resulted in Bardeen and Brattain receiving a patent on Oct 3, 1950.@footnote 3@ Shockley was not a co-patent holder, however, since his scientific contribution of the field-effect principle had, in retrospect, already been anticipated through a previous patent awarded to Lilienfeld in 1930.@footnote 4@ The assessment as to whether the minority-carrier holes emitted into the large grained polycrystalline, n-type Ge (or Si) sample were mainly transported from the emitter to the collector through the p-type inversion layer@footnote 5@ or exhibited some non-trivial transport as minority-carriers through the n-type bulk sample, continues to be of interest and will be discussed. In that regard, Shive's experiment clearly illustrated the importance of the geometrical configuration in determining the percent of surface versus bulk transport@footnote 6@ while Shockley's p-n (bulk) junction theory and p-n junction transistor, originally an undisclosed notebook account, facilitated the mathematical description of Bardeen and Brattain's previously disclosed transistor action@footnote 1-3@ using a one-dimensional analysis.@footnote 7@

Bardeen also comprehended that it was not efficient to modulate the conductivity of a slab of semiconductor via the field effect@footnote 8@ and, thereby, patented the essence of the first modern (MOS) transistor.@footnote 9@ This was an insulating gate modulating an n-type inversion layer via the field effect, utilizing the inversion layer to confine the minority-carrier transport, in series with a reverse-biased n-p junction, and resulted in the first recorded power gain in a solid-state amplifier.@footnote 9@ The device, described by Sah as a sourceless MOS transistor,@footnote 10@ became the basis of, for example, subsequent MOS memory DRAM and CMOS microprocessor applications. Indeed, John Bardeen, the co-inventor of the bipolar and inventor of the MOS transistor, may rightly be called the father of modern electronics. Nevertheless, Shockley deservedly shared the Noble prize in 1956 with Bardeen and Brattain for his seminal contributions of injection over a barrier, p-n (bulk) junction theory and p-n junction transistor. The scientific background, personnel involved and intertwining of these historic 1940s events are described. @FootnoteText@@footnote 1@J. Bardeen and W.H. Brattain, Phys. Rev., 74, 230-231 (1948) @footnote 2@W.H. Brattain and J. Bardeen, Phys. Rev., 74, 231-232 (1948) @footnote 3@J. Bardeen and W.H. Brattain, U.S. Patent No.2,524,035 (filed June 17, 1948; issued Oct. 3, 1950) @footnote 4@J.E. Lilienfeld, U.S Patent No. 1,745,175 (filed Oct. 8, 1926; issued Jan. 18, 1930) @footnote 5@J. Bardeen, Phys. Rev., 71, 717-727 (1947) @footnote 6@J.N. Shive, Phys. Rev., 75, 689-690 (1949) @footnote 7@W. Shockley, Bell Sys. Tech. J., 28, 435-489 (1949) @footnote 8@W.Shockley and G.L. Pearson, Phys. Rev., 74, 232-233 (1948) @footnote 9@J. Bardeen, U.S. Patent No. 2,524,033 (filed Feb. 26, 1948; issued Oct. 3, 1950) @footnote 10@C.T. Sah, Proc. IEEE, 76, 1280-1326 (1988)

Processing at the Nanoscale
Room 308 - Session NS+MI-TuA

Nanoscale Patterning and Lithography

Moderator: B.D. Terris, IBM Almaden Research Center

2:00pm **NS+MI-TuA1 Patterning Magnetic Recording Media by Imprinting***,* ***G.M. McClelland****, M.W. Hart,* IBM Almaden Research Center*; M.E. Best,* Hitachi San Jose Research Center*; C.T. Rettner, K.R. Carter,* IBM Almaden Research Center*; G. Hu, B.D. Terris, M. Albrecht,* Hitachi San Jose Research Center **INVITED**

Patterning magnetic media is a promising strategy for increasing magnetic recording density beyond the current value of 15 Gbit/sq. cm. As proposed by Chou, imprinting is an attractive means for generating the small structures required. This application is not affected by some difficult aspects of imprinting: overlay is not required, long range distortion is accommodated by positioning of the recording head, and defects can be corrected by error correction during read out. We have developed a complete, cost effective process for patterning of 30-nm-dia. single-domain magnetic islands over a 65 mm disk. The process steps are: forming a flexible stamp from a master, imprinting a replica in resist, reactive ion etching SiO2 pillars into the substrate, and depositing a magnetic film by evaporation. To accommodate the roughness and curvature of the substrate, a 10-micon-thick polymer stamp on an acrylic backing plate is used. The stamp is formed by photocuring an acrylate mixture in contact with an SiO2 master made by e-beam lithography. The resist is formed from a 15-nm-thick prepolymer liquid acrylate film spun onto the glass substrate. The film is viscous, so that non-flatness in the substrate is accommodate by stamp deformation, rather than by flow of the resist. After UV exposure, the stamp is removed to leave 30-nm-high resist pillars on a 10-nm-thick base layer. A dozen repeated imprints show a defect rate of about 1 in 10,000 pillars. A CF4/CH4 etch transfers the resist pattern into 30-nm-high, 30-nm-dia. SiO2 pillars with a period of 60 nm. To form a magnetic film, a 10-nm CoPt multilayer is deposited by e-beam evaporation at 300 K. This method shows promise for large-scale manufacturing, because the stamp-making process can be repeated indefinitely from a single master, and many replicas can be formed from each stamp.

2:40pm **NS+MI-TuA3 Buffer Layer Assisted Laser Patterning of Metals at the Nanometer Scale***,* ***G. Kerner****, M. Asscher,* The Hebrew University of Jerusalem, Israel

Spatial patterning of thin films on surfaces is of great importance for basic physical sciences and technology. An innovative method is presented for a single pulse, macroscopic scale laser patterning of metallic thin film to form nanometer range variable width conducting wires. Employing laser induced thermal desorption (LITD) via interfering split low power beams- metallic gold and potassium coverage grating on top of multilayer Xe is formed over Ru and Si at 20K as a demonstration. Upon annealing to 80K, the Xe layer desorbs and the metallic pattern softly lands and strongly attaches to the substrate. This is a highly versatile patterning technique that can be employed with practically any element and chemical species. It may readily be utilized to prepare millimeters long, 30nm wide conducting wires using current laser technology. The structure and thermal stability of the metallic pattern has been studied by means of AFM, STM, optical second harmonic and linear diffraction. The metallic structures are composed of nanometer size clusters, their size and distribution depend on the buffer layer thickness. The technique presented here is potentially an attractive alternative method for the deposition of periodic and more complex spatial patterns of conducting wires at widths well below the current limits.

3:00pm **NS+MI-TuA4 Low-Temperature Nanolithography using Energetic Neutral Atoms***,* ***E.A. Akhadov****, A.H. Mueller, M.A. Hoffbauer,* Los Alamos National Laboratory

Neutral atomic beams with kinetic energies of a few eV are exploited for etching of nanoscale features in polymeric materials and for epitaxial thin film growth on substrates held near ambient temperature. A unique low temperature etching and thin film growth technique, called Energetic Neutral Atom Beam Lithography (ENABL), has been recently developed at LANL. Using a collimated atomic beam with a small de Broglie wavelength permits the fabrication of high-aspect-ratio (>25:1) nanoscale features in polymeric substrates without undesirable defects (undercutting, tapering etc.) common to conventional etching. The high flux (~10@super17@ atoms/cm@super2@sec) and high kinetic energies (1 to 5 eV) of reactive atomic species (O and N) allow etching of sub-100nm features at high rates and the growth of high-quality oxide films at ambient temperatures. The use of ENABL for etching and film growth opens new frontiers for materials synthesis and processing at the nanoscale at ambient temperatures. Future prospects and challenges for low-temperature ENABL-based nanoscale fabrication will also be addressed.

3:20pm **NS+MI-TuA5 Self-Assembling Circuits?***,* ***K.W. Guarini****, C.T. Black,* IBM **INVITED**

The aggressive dimensional and performance targets for future technology generations place severe demands on lithography, not only for feature size scaling but also pattern integrity, density, line edge roughness, and process control. Already today many process "tricks" are routinely employed to shrink the dimensions of lithographically-defined features, such as resist trim and sidewall image transfer, but there are limitations on the extendibility of such approaches. While the great potential of various so-called "next generation" lithography techniques has been well touted, these solutions are inherently complex, require new tooling infrastructure, and present throughput challenges. Self organizing materials offer an exciting prospect for overcoming many of these hurdles. The simplicity, reproducibility, and dimensional control inherent in self-assembling materials make them attractive for silicon nanofabrication. In the grandest vision, we might imagine integrated circuits that one day "organize themselves"-yielding the ultimate sizing and positional control, but this vision is still in the realm of science fiction. However, already today we can implement self-organizing materials for selective unit processes to complement or enhance conventional semiconductor processing. For instance, self-assembling polymer films provide an appealing alternative to photoresists for certain types of patterning at nanometer-scale dimensions. In particular, diblock copolymer thin films self assemble into uniform, densely-spaced nanometer-scale features over wafer-scale areas. These films are compatible with standard semiconductor fabrication processes, enabling their integration into device and circuit fabrication. Such self-organizing materials provide novel nanofabrication capabilities and may enable solutions to some challenges confronting integrated circuit fabrication.

4:00pm **NS+MI-TuA7 Fabrication and Electrical Characterization of 2D Dopant Nanostructures in Si***,* ***J.S. Kline****, J.C. Kim, S.J. Robinson, K.-F. Chen, R. Chan, M. Feng, J.R. Tucker,* University of Illinois at Urbana-Champaign*; J.-Y. Ji, T.-C. Shen,* Utah State University*; C. Yang, R.-R. Du,* University of Utah

Lithography and contact with external leads are the two major challenges in nanoscale electronic device fabrication. We attempt to address both of these issues by using an integrated approach. STM lithography on H-terminated Si surfaces routinely achieves 1nm resolution. P donors can be selectively deposited onto the H-desorption area by dosing phosphine gas onto the STM patterned device template. Subsequent Si low-temperature deposition and annealing allows epitaxial overgrowth and the dopant atoms are completely activated. The sheet resistance of the P-delta layer is in the range of 1-4k@Omega@/square and can be controlled by phosphine surface coverage. External contacts to the device are fabricated by As ion implantation. We present a method whereby differences in surface features and tunneling spectroscopy between the contact and device region allow the registration of the STM. Low temperature electrical measurements of nanowires and other more complex structures are currently in progress and will also be reported. This work is supported by NSF, ARO, and DARPA.

4:20pm **NS+MI-TuA8 Polymer Patterning using a Soft Inkpad**, ***Y.P. Kong,*** Institute of Materials Research and Engineering, Singapore*; L. Tan, L.-R. Bao,* University of Michigan, Ann Arbor*; X.D. Huang,* Institute of Materials Research and Engineering, Singapore*; S.W. Pang,* University of Michigan, Ann Arbor*; A.F. Yee,* Institute of Materials Research and Engineering, Singapore

We present a method of producing micrometer and submicrometer patterns of polymer on substrates. A patterned hard mold is pressed onto an 'inkpad' coated by a polymer. The inkpad consists of a polydimethylsiloxane (PDMS) layer backed by a hard substrate. The function of the PDMS layer is twofold. Oxygen plasma treatment of the PDMS layer allows a polar polymer solution to be spun coated on it. The hydrophobic recovery of the PDMS layer then lowers its surface energy and this allows the transfer of the polymer to the hard mold that has a higher surface energy. Secondly, the deformation of the PDMS layer during the pressing induces a large stress field gradient at the edges of the mold protrusions. It is this stress that leads to a localized rupture of the polymer layer. The pressing is carried out at temperatures close to the glass transition temperature of the polymer and under relatively low pressures to transfer the polymer onto the protrusions of the hard mold. After the hard mold is separated from the inkpad, it is brought into contact with a substrate under a suitable temperature and pressure to produce a positive replica of the mold. At the same time, a negative image of the mold is left on the inkpad and this negative pattern can be transferred to a substrate. With a 700 nm period silicon grating mold, we are able to produce both positive and negative polymeric gratings. We also demonstrate the transfer of multiple layers of polymer onto the protrusions of the mold thereby increasing the aspect ratio of the patterns. Transferring of different polymer layers leads to the possibility of making high-resolution polymer light emitting displays and organic circuits. The advantages of our patterning method over nanoimprint lithography are: lower process temperatures and pressures, no material transport related problems, absence of a residual layer that needs removal, and the possibility to create both negative and positive replicas of the mold.

4:40pm **NS+MI-TuA9 Influence of Stoichiometry and Structure on the Local Oxidation of Metal Films**, ***N. Farkas****, G. Zhang, K.M. Donnelly, E.A. Evans, R.D. Ramsier,* The University of Akron*; J.A. Dagata,* National Institute of Standards and Technology

Oxidation growth kinetics of sputter-deposited Zr and ZrN thin-films are studied on the local scale by atomic force microscope (AFM) -assisted lithography. The growth kinetics are found to depend strongly upon the nitrogen content of the deposition plasma. Mass transport of subsurface O, H, and N species also plays an important role in the growth of nanometer-scale oxide structures, producing feature heights up to an order of magnitude greater than those observed in other material systems such as silicon and titanium. The stoichiometric and structural differences in the films are investigated by X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and X-ray diffraction (XRD) techniques to account for solid-state reaction and transport mechanisms involved in oxidation driven by a highly localized electric field. These results demonstrate the potential of AFM lithographic techniques for characterizing oxidation kinetics in the presence of the rich chemical behavior exhibited by reactive metal films.

Organic Films and Devices
Room 318/319 - Session OF+EM-TuA

Molecular and Organic Films and Devices-Optoelectronics

Moderator: A.J. Makinen, Naval Research Laboratory

2:00pm **OF+EM-TuA1 OLEDs and Solid State Lighting**, ***A.R. Duggal,*** GE Global Research **INVITED**

OLED technology has improved to the point where it is now possible to envision developing OLEDs as a low cost solid state light source. In order to realize this, significant advances have to be made in device efficiency, lifetime at high brightness, high throughput fabrication, and the generation of illumination quality white light. In this talk, the research challenges for general lighting will be reviewed and approaches being pursued at GE to meet them will be outlined.

2:40pm **OF+EM-TuA3 Hybrid Electroluminescent Devices Based on Conjugated Polymers and CdS:Mn/ZnS Core/Shell Nanocrystals**, ***H. Yang,*** *P.H. Holloway,* University of Florida

Nanocrystals with a CdS:Mn/ZnS core/shell structure with a core crystal diameter of 2.3 nm and a shell thickness of 0.4 nm were synthesized via a reverse micelle route. Direct current (dc) electroluminescent (EL) devices were tested having a hybrid organic/inorganic multilayer structure of ITO//PEDOT-PSS//conjugated polymer//CdS:Mn/ZnS nanocrystal//Al, where two different conjugated polymers (poly(N-vinylcarbazole) (PVK) and poly(p-phenylene vinylene) (PPV)) were used. The poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS) layer was used for enhanced hole injection from the ITO electrode. In PVK-based nanocrystal devices, only orange emission from the CdS:Mn/ZnS nanocrystal layer was observed, with no emission from the PVK. However, only green EL emission was observed from the PPV layer in PPV-based nanocrystal hybrid devices, with no emission from the nanocrystal layer. EL emission from a single layer of a multilayer structure was concluded to result from radiative electron-hole recombination occurring predominantly in that layer. All of these data will be interpreted in terms of energy levels for the PVK, PPV, and quantum-shifted CdS:Mn/ZnS structures, where a charge transport through the device depends upon the valence and conduction band offsets at the interfaces between conjugated polymer and nanocrystal layer. In addition, PPV-only EL devices showed much smaller current flow and weaker EL emission than PPV-based nanocrystal hybrid EL devices, suggesting that the CdS:Mn/ZnS nanocrystal layer serves as an electron transport layer (ETL) in the hybrid device. These observations will be shown to be consistent with the energy level diagrams of the EL devices.

3:00pm **OF+EM-TuA4 Large Magnetic Field Effects in Organic Light Emitting Diodes (OLED) based on Alq3**, ***A.H. Davis****, K. Bussmann,* Naval Research Laboratory

A study of the spin statistics of exciton formation in organic semiconductors predicts that the amount of light produced by an organic light emitting diode (OLED) can be modulated by controlling the relative spin-polarization of the holes and electrons that combine to form excitons. Organic materials with intrinsically low spin-orbit coupling show long electron and hole spin lifetimes (tS > 1 ms), allowing for the possibility of spin-coherent transport from ferromagnetic electrodes to the recombination zone of a bilayer organic LED. It is important to distinguish this spin-dependent exciton formation and luminescence from other various magnetic field effects (MFE's) observed in the photoconductivity, photoluminescence, delayed luminescence and electroluminescence (EL) of certain organic crystals. We have grown a number of OLED's with magnetic and non-magnetic electrode materials based on a conventional Alq3/NPB organic bilayer and report two magnetic field effects that are present in all devices. The first is a low field effect (LFE) consisting of a one to seven percent increase in EL with an applied field that typically saturates below 1000 Oersteds (Oe). The second is a high field effect (HFE) consisting of an EL decrease by as much as 20+% at 1.8 Tesla (T). Unlike the LFE, the HFE is dependent on temperature, current density and electrode material. This suggests that the LFE and HFE are caused by separate mechanisms and that conditions near the electrode/organic interfaces are important to the HFE. We discuss these results in terms of several possible mechanisms, some of which should be sensitive to the spin-polarization of the injected holes and electrons.

4:00pm **OF+EM-TuA7 The Application of DLC Layer for Polymeric Electroluminescent Devices**, ***S.H. Choi***, Yonsei University, Korea*; D.W. Han,* Samsung SDI*; S.M. Jeong,* Yonsei University, Korea*; H.K. Baik,* Yonsei University, Korea, South Korea*; K.M. Song,* Kon Kuk University, Korea*; S.J. Lee,* Kyungsung University, Korea

The Polymeric electroluminescent devices (PLEDs), which are included with an diamond-like-carbon (DLC) layer between indium tin oxide (ITO) and poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT) have been fabricated. Indium diffusion, which is due to be etched ITO surface by acidic PEDOT solution into the hole transport layer can degrade the device. It has been used X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry (RBS) to measure indium contamination in PEDOT. DLC layer was deposited between hole transport layer and ITO anode by the using the Cs+ ion sputtered negative ion deposition system (CsISNIDS). It was found that device stability and efficiency were seriously affected by indium contamination in HTL and DLC layer could improve device stability. In addition it has been investigated the I-V, L-V characteristics, and Quantum efficiency as a function for a set of devices with and without DLC layer.

4:20pm **OF+EM-TuA8 Photonic Crystals and Nanocomposite Materials***, **J. Ballato**, D. Carroll, S. Foulger,* Clemson University **INVITED**

The promise (some fact and some fanciful) of nanotechnology has led to a well funded global race to develop new materials, components, and devices for use in a remarkably diverse range of applications. Towards the true realization of commercial- and defense-relevant devices, this talk will focus on highly promising results on passive and active photonic devices whose performance is markedly improved, with respect to traditional analogs, through the use of nanocomposite materials. Specifically to be discussed are highly efficient organic light emitting diodes (OLEDs) and photovoltaics (OPVs) fabricated using doped and undoped carbon nanotube-containing conjugated polymers. All-organic photonic crystals based on ordered arrays of nanoparticles encapsulated in elastomeric matrices also will be discussed. These nanocomposites exhibit bandstops that are highly tunable though stain generated by mechanical forces (mechano-chromism) or chemical affinity (chemo-chromism) which opens new doors for optical beam steering and chemical sensing.

Plasma Science and Technology
Room 315 - Session PS-TuA

Dielectric Etch

Moderator: M.L. Steen, IBM T.J. Watson Research Center

2:00pm **PS-TuA1 Dielectric Etch: Past, Present and Future***, **T.J. Dalton**[1],* IBM Research **INVITED**

Dielectric etch has grown in importance during the last decade with the emergence of single- and dual-damascene processing for semiconductor interconnect structures utilizing copper metallurgy, first in research and development and now in high-volume manufacturing. At the same time, the challenges of dielectric etch for semiconductor processing have changed significantly due to two factors. First, the materials of interest have evolved from silicon dioxide to "dense" low dielectric constant ("low-k") materials (both organic and silicate) to porous low-k materials (again, both organic and silicate). Second, the critical dimension (CD) has decreased to the sub 100-nm regime, forcing extreme control of feature sizes and sidewall profiles. This talk will focus on the evolution of dielectric etch for advanced logic integrated circuit fabrication in the last decade, specifically discussing dielectric materials, etch processes, and etching sources. Additionally, we will look ahead to issues with dielectric etch in the future.

2:40pm **PS-TuA3 Depth Dependent Spatial Frequency Analysis of Post-Etch Sidewall Roughness***, **S.A. Rasgon**, H.H. Sawin,* Massachusetts Institute of Technology*; A.P. Mahorowala, D. Goldfarb, M. Angelopoulos,* IBM T.J. Watson Research Center*; S.D. Allen,* IBM Microelectronics Division

For the patterning of sub-100 nm features, a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable. Until recently, LER studies have focused on the analysis of top-down SEM micrographs of post-developed photoresist lines. However, plasma etching processes often roughen the feature sidewalls and might form striations. This post-etch substrate LER is probably more relevant from a manufacturing perspective than the post-developed LER. The depth dependence of the post-etch sidewall morphology cannot be captured adequately by top down SEM techniques. A novel atomic force microscopy (AFM) technique developed by Reynolds and Taylor (JVST B 17(2), p. 334-344, 1999) was used to examine sidewall roughness (SWR) transfer through photoresist, BARC/hardmask, and oxide layers simultaneously. Dense line-and-space structures were cleaved parallel to the line patterns, and turned 90 degrees to access the exposed sidewall with the AFM tip. The images vividly highlight the resulting SWR structure, allowing one to observe roughness transfer through materials and determine any potential correlations. This paper studies the effect of etch chemistry, BARC/hardmask material, and resist thickness/type on the morphology and structure of SWR striation spatial frequency and spatial correlation, under conditions typically encountered during oxide etch processes. Quantitative data on RMS roughness and striation spatial frequency as a function of feature depth is collected using AFM-based techniques. Power spectral density (PSD) and correlation analysis of the sidewall AFM images allows us to track the evolution of sidewall striations through the various feature layers after each process step (lithography, BARC/hardmask open, and oxide etch). Finally, the impact of these sidewall striations on future processing steps (for instance, conformal liner deposition) is discussed.

3:00pm **PS-TuA4 Investigation of Bottom-emitted Particles and their Influence on the Etch Characteristics of Sidewall in the Fluorocarbon Plasma Etching***, **G.-R. Lee**, J.-H. Min, J.-K. Lee, S.H. Moon,* Seoul National University, Korea

When energetic ions impinge on the bottom of an etched pattern, various particles are emitted from the bottom surface, which constitute an additional source for modifying the composition of plasma gases besides collisions among gas-phase particles generated in a plasma. The effect of bottom-emitted particles on the composition of gas-phase radicals increases with a decrease in the distance from the bottom surface and, accordingly, the etch characteristics of sidewalls in proximity to the bottom of an etched pattern is strongly affected by the bottom-emitted particles. However, information about the bottom-emitted particles, including species and amount of the particles and their influence on the etch characteristics of sidewall, is limited largely due to the lack of experimental methods for observing the phenomenon in a larger scale. In this study, we have analyzed particles emitted from different bottom materials using mass spectrometry at various bias voltages. We also examined the effect of the bottom-emitted particles on the etch characteristics of a SiO@sub 2@ surface located vertically and in proximity to the bottom surface. Ions of high energy sputter the steady-state fluorocarbon polymer layer covering the bottom to generate heavy and unsaturated fluorocarbon radicals, which contribute to the etch characteristics of the sidewall. As a result, the effect of bottom-emitted particles on the sidewall etching is profound under the conditions of high bias voltages and those allowing the formation of a thick steady-state polymer layer on the bottom surface.

3:20pm **PS-TuA5 Bilayer Mask Process for sub-90 nm Patterning using a New 100MHz CCP RIE***, **H. Hayashi**, J. Abe, A. Kojima, J. Nishiwaki, A. Takase, K. Sho, E. Shiobara, I. Sakai, E. Shinomiya, T. Ohiwa,* TOSHIBA Corporation Semiconductor Company, Japan

Shrinkage of LSI design rule, especially to sub-90 nm nodes, necessitates the reduction of photoresist thickness to maintain the process window in deep UV lithography. However, thinning the resist layer leads to critical dimension (CD) loss in the subsequent etch process due to resist erosion. A bilayer mask process, in which patterns formed at the Si-containing resist layer are transferred to spun-on-carbon film having anti-reflective property, is a promising candidate for sub-90 nm patterning. However, this process can be used only if carbon film etching with high selectivity to the thin Si-containing ArF resist is realized. In this paper, a new reactive ion etching (RIE) employing 100 MHz capacitive coupled plasma (CCP) where the wafer is placed on the cathode, is proposed. By introducing the high frequency of 100 MHz, low ion energy and high selectivity could be expected. Self-bias voltages (Vdc) generated in the 100 MHz Ar plasma at 40 mTorr were 20 to 90 V depending on RF power, less than 1/3 those of the 13.56 MHz plasma which were 290 to 540 V under the same conditions. As a result, the carbon film etch process using the 100 MHz plasma in hydrogen based gas chemistry showed great improvement of selectivity, to more than 8. Etch rates of the carbon film were 200 to 300 nm/min at the pressures of 5 to 100 mTorr. Finally, the etch profile of a pattern with a resist thickness of 150 nm and carbon 300 nm thick was examined, and it was found that a vertical carbon etch profile was obtained, with less faceting of the Si-containing resist mask. The ArF bilayer mask process combined with the new 100 MHz CCP proves to be the most effective patterning process for devices of 90 nm and below.

3:40pm **PS-TuA6 Etching Bilayer Resists in Ammonia Based Plasmas***, **S. Panda**, R. Wise, A.P. Mahorowala,* IBM

Bilayer resist schemes (thin, silicon containing image layer over thick, organic transfer layer) can mitigate lithographic limitations associated with the smaller wavelengths and higher NA values required for patterning shrinking feature sizes. State of the art transfer etch processes utilize an oxygen based chemistry to oxidize Si in the image layer while etching the transfer layer beneath. Undercutting of the image layer, poor CD control, and LER can result from the use of oxidizing chemistry, and are exacerbated by more sensitive ArF materials. Commonly used SO2 addition (for sidewall passivation) can form undesirable byproducts leading to both tool and line contamination. In the present study we present an oxygen-free ammonia based transfer etch process. In addition to NH@sub3@; N@sub2@, H@sub2@, and C@sub2@H@sub4@ were examined as additives. It is hypothesized that selectivity to the underlayer arises from nitridation of

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[1] **AVS 50th Anniversary Invited Speaker**

the silicon containing image layer which becomes resistant to etch. XPS analyses of the etched samples, optical emission and mass spectroscopic studies were performed to understand the mechanisms involved.

4:00pm **PS-TuA7 Model for Dielectric Etching in C@sub 4@F@sub 6@ Based Inductively Coupled and Dual Frequency Plasmas***, **S. Rauf**, P.J. Stout, P. Ventzek,* Motorola Semiconductor Products Sector*; S. Adamson, A. Dementev, K. Novoselov, V. Kudrja,* Soft-Tec, Moscow, Russia

1,3 Perfluorobutadiene (C@sub 4@F@sub 6@) has recently received much attention in the microelectronics industry for etching of conventional and low-@kappa@ dielectrics. This consideration is motivated in part due to the environmentally benign nature of C@sub 4@F@sub 6@, and its desirable etching and polymerizing characteristics. This paper describes a model for etching of SiO@sub 2@ and Si in medium and high density Ar/C@sub 4@F@sub 6@/O@sub 2@ plasmas. The plasma chemical mechanism for C@sub 4@F@sub 6@ is assembled using measured dissociative ionization and attachment cross-sections, and first principle based computations of C@sub 4@F@sub 6@ neutral dissociation kinetics and cross-sections. The plasma surface interaction mechanism has been constructed empirically by correlating computed species characteristics with experimentally measured etching and deposition rates. Computational modeling of the plasma and surface processes is conducted using a combination of 2-dimensional plasma equipment models (HPEM@footnote 1@ from University of Illinois and IO)@footnote 2@ and feature scale simulations (BabyBean@footnote 3@ and Papaya).@footnote 4@ The paper discusses experimental validation of the model in two disparate plasma operating regimes, ICP@footnote 5@ and dual frequency.@footnote 6@ The model is also used to understand the differences in plasma chemistry of medium and high density C@sub 4@F@sub 6@ based plasmas, and how these differences impact dielectric etching characteristics. @FootnoteText@ @footnote 1@P. L. G. Ventzek et al., J. Vac. Sci. Technol. B 12, 461 (1994)@footnote 2@S. Rauf, to appear in IEEE Trans. Plasma Sci. (Aug. 2003)@footnote 3@S. Rauf et al., J. Vac. Sci. Technol. A 20, 1177 (2002)@footnote 4@P. J. Stout et al., J. Vac. Sci. Technol. A 21, 265 (2003)@footnote 5@X. Li et al., J. Vac. Sci. Technol. A 20, 2052 (2002)@footnote 6@F. Fracassi et al., J. Vac. Sci. Technol. A 21, 638 (2003).

4:20pm **PS-TuA8 A Computational Investigation of Plasma and Surface Chemistry During Fluorocarbon Plasma Etching of SiO@sub 2@ in Ar/c-C@sub 4@F@sub 8@/O@sub 2@/CO Magnetically Enhanced Capacitively and Inductively Coupled Plasmas@footnote 1@***, **A.V. Vasenkov**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Gas mixtures containing Ar, c-C@sub 4@F@sub 8@, O@sub 2@, O@sub 2@, and CO are often used for the plasma etching of silicon dioxide in order to optimize the fluxes of etching, polymerizing and activating species to the substrate. Reaction mechanisms, both gas phase and surface, are required for first principle modeling of these systems to both provide insights to the plasma chemistry and to help optimize the process. In this paper, we describe a refined gas-phase reaction mechanism for low-pressure and low-temperature plasmas sustained in mixtures initially consisting of Ar/c-C@sub 4@F@sub 8@/O@sub 2@/CO/N@sub 2@ or any combination, and its application to a computational investigation of plasma properties in magnetically enhanced inductively coupled plasmas (MEICPs) and magnetically enhanced capacitively coupled plasmas (MECCPs, or MERIEs). The systemmatic dependence of ion and radical fluxes, and ion energy distributions on gas mixtures, power and pressure will be discussed. Comparisons will be made between MEICPs and MECCPs. Predictions for ion saturation current were compared to experiments MEICPs sustained in Ar/c-C@sub 4@F@sub 8@ and O@sub 2@/c-C@sub 4@F@sub 8@ for validation. Principle differences between MEICPs and MERIES is the average molecular weight of both the radicals and ions, being higher in MERIES. @FootnoteText@ @footnote 1@ Work supported by Semiconductor Research Corporation, SEMATECH and the National Science Foundation.

4:40pm **PS-TuA9 Kinetic Study on SiO@sub 2@ Dry Etching Process by Chemical Reaction Engineering Approach***, **T. Tokimitsu**, Y. Shimogaki,* University of Tokyo, Japan

Kinetic study on plasma process to etch SiO@sub 2@ films using C@sub 4@F@sub 8@ was made by chemical reaction engineering approach. In the present study, we assumed that the reactor as a CSTR (continuously stirred tank reactor) and examined the residence time dependency of gaseous species concentration. This approach is quite effective to elucidate the reaction mechanism that governs the performance of plasma reactor. Ionization voltage controlled AMS (appearance mass spectrometry) was conducted and it was found to be possible to measure the absolute concentration of each molecule. The residence time dependency of C@sub 4@F@sub 8@, C@sub 2@F@sub 4@ and C@sub 2@F@sub 6@ concentrations were measured by this technique. It was found that the main species in plasma changed from C@sub 4@F@sub 8@ to C@sub 2@F@sub 4@, and finally changed into C@sub 2@F@sub 6@ as residence time gets longer. C@sub 2@F@sub 4@, whose residence time dependency had a bowed profile, was the species to deposit a-C:F films and to prevent SiO@sub 2@ etching. O@sub 2@ addition to this plasma chemistry accelerate the decomposition of C@sub 4@F@sub 8@ and suppresses the C@sub 2@F@sub 4@ concentration. The residence time dependency of etching profiles were examined and discussed. Moreover, to investigate the surface reaction of SiO@sub 2@ etching, test structure was employed to make detail analysis through feature scale study. The gas phase analysis made by AMS method and the measurement of residence time dependency of each species concentration combined with feature scale analysis were sensitive tool to understand the major reaction path.

5:00pm **PS-TuA10 Selective Silicon Nitride Etching by ECR Plasmas Using SF6 and NF3 Based Gas Mixtures***, C. Reyes-Betanzo,* INAOE- Instituto Nacional de Astrofisica, Mexico*; S.A. Moshkalyov, A.C.S. Ramos, **J.W. Swart**,* UNICAMP, Brazil

Removal of silicon nitride films is critical step in CMOS and other semiconductor technologies as possible overetch during the nitride layer processing may result in damages of a thin oxide or a silicon substrate. Hence high nitride etching selectivity over oxide and Si is required. In recent chemical dry etching experiments, mixtures rich in oxygen and nitrogen with small additions of fluorine containing gases were shown to etch the nitride selectively. The role of NO molecules in the surface chemistry was shown to be important for improvement of the etching selectivity. This is attributed to an exothermic reaction of NO molecules with surface nitrogen atoms which promotes the enhanced removal of nitrogen (in a molecular form) from the nitride surface and thus accelerates the overall reaction rate. Here, the results of a study of silicon nitride, oxide and Si etching in SF6 and NF3 based mixtures using a high-density ECR plasma are presented. For the two fluorine containing gases used, the main mechanisms responsible for selective nitride etching are distinctly different. In the SF6 case, best results are achieved in O2/N2 rich plasmas where the nitride etching by fluorine can be enhanced by NO molecules produced in gas phase reactions. Formation of NO molecules was observed in spectra emitted from the plasma. In NF3 based mixtures, the nitride etching is more likely to be dominated by NFx reaction intermediates rather than by NO radicals. Higher selectivities over oxide (up to 100) were obtained with NF3 , while higher selectivities over Si (up to 10) were obtained with SF6 based mixtures.

Semiconductors
Room 321/322 - Session SC-TuA

Compound Semiconductor Growth and Processing

Moderator: P.I. Cohen, University of Minnesota

2:00pm **SC-TuA1 Complex Formation between Magnesocene (MgCp@sub 2@) and NH@sub 3@: Origin of the "Memory Effect"***, **G.T. Wang**, J.R. Creighton,* Sandia National Laboratories

Magnesocene (MgCp@sub 2@) is a common Mg precursor for the p-type doping of Group III nitride semiconductor materials. Unfortunately, difficulties remain with controlling the incorporation of Mg during MOCVD film growth, which often exhibits poorly understood memory effects. While the formation of a reaction product between magnesocene and ammonia has been previously speculated, one has never been experimentally isolated or identified. We have spectroscopically observed and identified, for the first time, the adducts formed between magnesocene and ammonia. Density functional theory (DFT) quantum chemistry calculations have also been performed on the system to determine the structures and energetics of the reaction products. It was found that ammonia can form complexes with magnesocene in both 1:1 and 2:1 ratios, i.e. NH@sub 3@:MgCp@sub 2@ and 2NH@sub 3@:MgCp@sub 2@, via NH@sub 3@ attack of the positively charged Mg center of MgCp@sub 2@. Adduct formation is reversible and the 1:1 and 2:1 products can be converted to one another by varying the NH@sub 3@ partial pressure. Both adducts are condensable at room temperature and their formation is the probable origin of the magnesium memory effects that have been observed during MOCVD of III-Nitride materials. Improved understanding of the equilibrium between condensed phase adducts, gas phase adducts, and precursors should allow for reactor and processing adjustments that reduce or eliminate the memory effects. 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.

2:20pm **SC-TuA2 Real-time Optical Monitoring of Gas Phase Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures***, **N. Dietz**, V. Woods,* Georgia State University

Understanding the kinetics of nucleation and coalescence of heteroepitaxial thin films is a crucial step in controlling a chemical vapor deposition process, since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. The initial nucleation process also defines the film quality during the later stages of film growth. The growth of emerging materials heterostructures such as InN or indium-rich GaxIn1-xN requires deposition methods operating at high vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition experiments. The extension of chemical vapor deposition (CVD) to elevated pressure is also necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. The here presented research focuses on the base material InN and addresses the real-time optical monitoring of gas phase- and surface chemistry processes during high pressure (100 bar) CVD of InN. The high pressure CVD reactor has integrated optical diagnostics to monitor in real-time gas flow dynamics, gas-phase decomposition kinetics, and the film growth process itself. These experimental data are of crucial importance to provide (a) input parameter for process models and simulation codes, and (b) establish growth parameter sets needed for analysis and control of chemical vapor deposition at elevated pressure. Data are presented for the optical methods of real-time process monitoring to analyze the initial stages of heteroepitaxy and steady-state growth in the different pressure ranges.

2:40pm **SC-TuA3 Chemical Complexities of AlGaInN MOCVD***, **J.R. Creighton**, G.T. Wang, M.E. Coltrin, W.G. Breiland,* Sandia National Laboratories **INVITED**

We have used a variety of experimental techniques to investigate possible sources of the parasitic chemical reactions that occur during AlGaInN MOCVD. Growth rates for GaN, AlGaN, and InGaN were measured over a wide range of reactor conditions and compared to reactive flow simulations in order to test possible parasitic chemical reaction mechanisms. All of our results indicate that the parasitic chemical reactions require high temperatures and occur in the boundary layer near the growing surface. These reactions ultimately lead to the formation of nanoparticles, which we have recently observed using in situ laser light scattering. Thermophoresis keeps the nanoparticles from reaching the surface, so the material tied-up in nanoparticles cannot participate in the thin film deposition process. In the case of AlN, the particle size was determined to be 48 nm, and the particle density was in the range of 10@super 8-9@ cm@super-3@. At these densities a significant fraction (20% or more) of the input Al is converted into nanoparticles. We have also directly examined precursor chemistry in the 30-300°C range using in situ FTIR. All three commonly used group-III precursors form adducts with ammonia, but this reaction is entirely reversible for trimethylgallium and trimethylindium. In this temperature range only trimethylaluminum reacts irreversibly with ammonia, evolving methane and forming the expected (CH@sub 3@)@sub 2@Al-NH@sub 2@ product. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.).

3:20pm **SC-TuA5 Ab initio Prediction of the Gas-Phase Precursors for AlN Sublimation Growth@footnote 1@***, **Y. Li**, D.W. Brenner,* North Carolina State University

A free energy model using input from ab initio calculations is used to predict the concentration and saturation state (with respect to the growing crystal) of 16 Al@sub n@N@sub m@ species under conditions typical of AlN sublimation growth. The calculations predict that Al and N@sub 2@ are the dominant species, in agreement with available experimental measurements. However, our calculations predict that the N@sub 2@ molecule is undersaturated and therefore is not likely a growth precursor. Instead, our model predicts that Al@sub 2@N, Al@sub 3@N, and Al@sub 4@N, while in much smaller concentrations than N@sub 4@, are supersaturated and therefore are the source of nitrogen to the growing crystal. This prediction is in stark contrast to assumptions made in prior growth models, and may help explain why very small sticking coefficients had to be assumed for N@sub 2@ in prior modeling studies to match experimental growth rates. @FootnoteText@ @footnote 1@ Funded by the Office of Naval Research through MURI contract N00014-01-1-0302.

3:40pm **SC-TuA6 Reflectance Interferometry During III-V Nitride Growth, Much More than a Growth Rate Monitor***, **C.R. Eddy, Jr.**, R.T. Holm, R.L. Henry, J.C. Culbertson,* Naval Research Laboratory

The application of laser interferometry to the monitoring of wide bandgap semiconductor nitride growth has expanded considerably in recent years. At present, a rapidly growing number of III-V nitride growth systems, MBE and MOCVD alike, employ some version of the technique to monitor growth rates. But growth rate monitoring makes use of a small subset of the useful information the technique affords. In this paper, we discuss the application and interpretation of laser interferometry in the MOCVD growth of gallium nitride and aluminum gallium nitride thin films that employ AlN nucleation layers. We employ a 543.5 nm HeNe laser, lock-in amplifier, and ratiometer (to normalize out laser fluctuations) to monitor growth in a simple vertical tube reactor that is rf heated. In this application, the technique has proven useful as a monitor of not only the thickness, but also the quality of the material grown. Further, the technique can help identify drifts in the process from run to run and within a given run. We will comment on the usefulness of the technique in monitoring surface and interface roughness, film stoichiometry (for ternaries) and thickness uniformity. Finally, we will highlight specific examples where the technique has proven useful in troubleshooting growth irregularities.

4:00pm **SC-TuA7 Real-time Diagnostics of OMCVD Epitaxy with an Integrated Rotating-compensator/Rotating-sample Polarimeter***, K.F. Flock, S.J. Kim, **M. Asar**, D.E. Aspnes,* North Carolina State University

We obtain new insights on III-V epitaxy and heteroepitaxy with a rotating-compensator/rotating-sample ellipsometer/polarimeter for diagnostics and control of organometallic chemical vapor deposition (OMCVD). The system obtains up to 5 1024-pixel spectra per second from 230 to 840 nm, allowing the p- and s-polarized reflectances and the complex reflectance ratio to be determined from the dc, 2@omega@t, and 4@omega@t components of the transmitted intensity. In addition the optical anisotropy follows from the 10@omega@t component, and alignment parameters from the @omega@t and 3@omega@t components, providing the maximum amount of sample information obtainable from optical data over the available spectral range. Rotating-compensator operation eliminates the serious shortcoming of older, rotating-analyzer and -polarizere designs associated with the loss of phase information when the phases of the complex reflectance ratios are near 0 or 180 degrees. The anisotropy data returns surface-chemical information through their spectral dependences. We relate these non-normal-incidence anisotropy spectra to RDS data obtained at normal incidence by numerical analysis of the system transfer function. This combination of capabilities allows OMCVD growth processes to be studied in greater detail, especially when combined with a recently developed algorithm for simultaneously determining the thickness and dielectric function of films in the Å thickness range. For example we follow the growth of nm thick layers of Ga on (001)GaAs substrates, and track the connection between surface reconstruction and film growth. The relatively short data-acquisition time also allows us to follow growth under highly nonequilibrium "burst" conditions, which appear to be necessary to establish uniform layers of some III-V materials on chemically different substrates.

4:20pm **SC-TuA8 GaN Nucleation Layer Evolution on Sapphire***, **D.D. Koleske**, J.J. Figiel, M.E. Coltrin, A.A. Allerman, K.C. Cross, C.C. Mitchell, M.J. Russell,* Sandia National Laboratories

For UV, blue, green and eventually white light LEDs, GaN is most often grown on low-cost sapphire substrates. To improve the GaN epitaxial quality and reduce dislocations, a low temperature GaN nucleation layer (NL) is first deposited prior to high temperature (T) GaN growth. Despite the progress in the MOCVD growth of GaN, details of the NL and high temperature growth evolution are not well understood. In this presentation the GaN NL evolution as it is annealed from low to high T will be investigated using optical reflectance and AFM measurements of stopped growth runs. During the anneal, the NL morphology changes from a continuous 30 nm thick layer composed of 20 nm sized grains to a discontinuous layer that contains large grains approaching 500 nm in width to 180 nm in height. Further annealing of the NL causes a decrease in the size of these large grains. Since only NH@sub 3@ and H@sub 2@ are flowing during the NL annealing, the growth of the large GaN grains is explained by partial decomposition of the NL@footnote 1@ and redeposition of the Ga atoms on the growing grains through a gas phase desorption and readsorption mechanism rather than a surface diffusion mechanism. Evidence for this mechanism is obtained from the height-height correlation functions@footnote 2@ measured from the AFM images of the annealed nucleation layers as well as direct measurements of the GaN NL decomposition kinetics using optical reflectance@footnote 1@. Based on details of the decomposition kinetics and NL roughening, fits to the optical reflectance waveform will be presented. Contributions of the surface diffusion, bulk diffusion, and desorption/readsorption mechanisms to the overall GaN NL morphology will also be discussed along with guidance as to when the NL achieves optimal morphology for further GaN growth at high T. @FootnoteText@ @footnote 1@D. D. Koleske, et al., Appl. Phys. Lett 82, 1170 (2003). @footnote 2@Tong and Williams, Annu. Rev. Phys. Chem. 45, 401 (1994).

4:40pm **SC-TuA9 Investigations of Plasma Etching and Contact Processing on AlGaN Alloys Containing 0 to 50% Al***, **K.H.A. Bogart**, A.J. Fischer, M.H. Crawford, D.D. Koleske, A.A. Allerman, R.J. Shul, D.E. Peebles,* Sandia National Laboratories*; I. Adesida,* University of Illinois at Urbana Champaign*; S. Jones,* Sandia National Laboratories*; D. Selvanathan,* University of Illinois at Urbana Champaign*; K.W. Fullmer, F. Jalali,* Sandia National Laboratories

AlGaN alloys are suitable for a variety of light emitting devices including LEDs and laser diodes as well as electronic devices such as high electron mobility transistors. Deep UV (<300 nm) LEDs have important applications as UV light sources for chemical-biological sensors, non-line-of-sight optical communications, and UV curing. Optical performance near 300 nm requires Al stoichiometry of 0.25 to 0.5, or more. The difficulty of forming high-quality ohmic contacts to n-type AlGaN materials increases with increasing percent Al due to the difficulty in effectively doping high %Al AlGaN. We performed a series of experiments to study the effects of several contact processing steps on the resultant material and device characteristics for AlGaN alloys with the percent Al ranging from 0 to 50%. For example, during LED device processing, plasma etching of the p-type material and the active material is done in order to access the underlyingn-type material for contact formation. We determined the effect of percent Al in AlGaN alloys on the surface roughness, etching rates, and resist selectivity, as a function of plasma etch method (ICP vs. RIE) and etching parameters such as substrate bias voltage. We also varied the pre-metallization surface treatments using dry plasma etching and wet chemical (BOE and HCl) etching. We evaporated metal contacts of either TiAlNiAu or TiAlMoAu and determined metal adhesion and specific contact resistance as a function of percent Al (0 to 50%). Annealing studies were also performed on materials after the contact deposition. Surface analysis by XPS, performed before and after plasma etching showed striking stoichiometric differences between the as-grown alloy and the etched surface. The composition of the metal-AlGaN interface was also investigated by XPS. The results from all of these studies will be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

5:00pm **SC-TuA10 Morphological Evolution of GaAs Surface during Damage-free Etching***, **S.H. Lee**, H.P. Gillis,* UCLA

GaAs was etched in Cl@sub 2@/H@sub 2@/Ar plasmas both with ion and electron enhancement. Since bombardment with higher energy ions induces structural damage, electron bombardment and low-energy ion bombardment were used to prevent etch-induced damage. Damage was checked with XRD which shows peak broadening after etching when structural damage is induced on a surface or in a sub-surface layer. XRD peak broadening was seen in high-energy ion bombardment, but not in electron or low-energy ion bombardment. In order to study the competition between the thermal reaction and the electron enhanced reaction, temperature and bias for samples were varied as etching parameters. SEM images and AFM images were obtained and compared for the samples etched at different conditions. Under the damage-free etchig conditions morphology development was followed by measuring etch rate, surface roughness, skewness, and autocorrelation function (ACF) for surface roughness. The evolution of ACF was interpreted by scaling theory. Chemical and bombardment effects were explained based on the scaling theory. Morophological evolution steps and a key effect that determines surface morphology during etching were revealed from this study, and a way to control surface smoothness during dry etching was found.

Advanced Surface Engineering
Room 323 - Session SE-TuA

High Temperature Protective Coatings

Moderator: A. Matthews, University of Hull, UK

2:00pm **SE-TuA1 Synthesis and High Temperature Performance of SiAlON Thin Film Coatings***, J.I. Krassikoff, G.P. Bernhardt, M. Call, **R.J. Lad**,* University of Maine

SiAlON ceramics made by alloying Al@sub 2@O@sub 3@ and Si@sub 3@N@sub 4@ possess oxidation resistance, high strength, and thermal shock resistance, which make them extremely attractive for high temperature coating applications. However, most work to date has emphasized bulk sintered SiAlONs rather than thin coatings. We have synthesized well-defined SiAlON thin films using rf magnetron sputtering of Al and Si targets in Ar / O@sub 2@ / N@sub 2@ mixtures on sapphire substrates. By manipulating the relative amounts of the deposition fluxes, homogenous versus multilayer or gradient SiAlON structures with a range of stoichiometries were produced. The films remain amorphous even with post-deposition annealing in vacuum or air up to 1000°C. Moreover, the film stoichiometries remain stable at high temperature in vacuum but lose nitrogen during air annealing. A thin film Ni-Cr corrosion sensor was embedded at the SiAlON / substrate interface, and the rate of oxygen penetration through the SiAlON film structures was measured in situ during accelerated thermal cycling tests in 1000°C oxidative environments. The time to failure ranges from hours to weeks depending on the exact SiAlON composition. Multilayer films with an Al@sub 2@O@sub 3@ overlayer exhibit the best oxidation resistance. Pin-on-disk wear tests indicate that the wear rate is also a function of the SiAlON stoichiometry. Our results yield important information that can be used to design and fabricate multifunctional SiAlON environmental barrier and thermal barrier coatings.@footnote 1@ @FootnoteText@@footnote 1@ Supported by AFOSR Grant #F49620-02-1-0323.

2:20pm **SE-TuA2 Synthesis and Characterization of Nanolayered TiO@sub x@/Al@sub 2@O@sub 3@ Coatings for Possible Elevated Temperature Applications***, **K.W. Lee**, M. Sturino, Y.W. Chung, L.M. Keer,* Northwestern University

It was demonstrated from previous studies that nanolayered coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such nanolayered coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800-1000@super o@C regime or higher. For this reason, TiO@sub 2@ and a-Al@sub 2@O@sub 3@ were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode reactive magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates include M2 steel and Si(001). These coatings were exposed to air at 1000@super o@C. Coatings deposited on silicon were characterized before and after the heat treatment in terms of surface roughness, residual stress, and nanoindentation hardness. Actual dry machining will be performed to evaluate the performance of these coatings. These results will be presented and discussed in terms of the coating potential in dry machining and high-temperature tribological applications.

2:40pm **SE-TuA3 Advances in Surface Engineering for High Temperature and Wear Resistant Applications***, **A. Inspektor**,* Kennametal Inc. **INVITED**

Many components, when exposed to aggressive environments like high temperatures and cyclic stresses, fail when their surfaces have degraded beyond a predetermined limit. Thus, the demand for improved performance requires early integration of coatings into product design in order to assemble a functional surface tailored to resist the particular environment in which the component is working. This functional surface, with a unique combination of bulk and surface properties, is vital to the successful performance of the component. The corresponding surface engineering technique is an integral part of the manufacturing process. This paper will review present and future trends in surface engineering with an emphasis on the design and on the preparation of functional surfaces for high temperature and for wear resistant applications. Topics to be covered are nanostructured coatings architecture and substrate-surface integration for improved hardness, thermal stability, oxidation resistance and tribological properties of cutting tools and of wear parts. An effort will be made to identify performance needs in these applications and the corresponding surface engineering solutions. A discussion will be held how to meet the challenge of surface engineering and of substrate-coating integration in materials design.

3:20pm **SE-TuA5 Processing and Properties of NiAl-Hf Coatings via DC Magnetron Sputtering***, **B. Ning**, M.L. Weaver,* The University of Alabama

Crystalline NiAl-0.1Hf coatings (20 µm thick) were deposited onto CMSX-4 substrates at temperatures ranging from room temperature up to 300 °C using direct current (DC) magnetron sputtering. The microstructures of the coatings were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The as deposited coatings were single phase, and exhibit dense columnar Zone T microstructures. Column sizes were observed to increase from approximately 250 nm at room temperature to more than 2 µm in diameter at 250 °C. Annealing in argon at 1000ÂºC for 1h resulted in densification of the coatings and in increased adhesion between the coatings and the substrate. Microstructural and compositional changes of the coating system after isothermal oxidation were studied using SEM and energy dispersive spectroscopy (EDS) techniques. The mechanical properties of the coatings were studied via nanoindentation in the as deposited condition, after annealing, and following various oxidation heat treatments. The hardness and modulus of the coatings were observed to correlate with oxidation time. Extended oxidation resulted in decreased hardness due to grain growth and diffusion induced precipitation and phase transformations. The results are discussed relative to conventional CVD aluminide coatings.

4:20pm **SE-TuA8 Surface Alloying of Aluminum Films by Electron Beam Evaporation on Zirc-4 Substrates and Hydrothermal Crystal Growth in Sub-critical Condition***, **S.T. Park**, R.H. Baney,* University of Florida

Waterside corrosion of the Zircaloy cladding encasing the uranium oxide pellets is one of the primary factors limiting high "burn up" of nuclear fuel in pressurized water reactor (PWR) nuclear reactors. High "burn up" can significantly impact plant safety and economics. This research has been performed to develop ceramic coating corrosion protection system. Aluminum films were deposited on Zircaloy substrates by electron-beam evaporation and surface-alloyed by controlled oxidation at near the melting temperature of aluminum. Two different oxidation procedures were employed to make compositional gradient compound layers. These gradient compound layers can increase the corrosion resistance and minimize the interface defects like grain boundaries that can occur in multilayer coatings. The substrate surface roughness, aluminum film thickness, and air oxidation time and temperature were varied. The durability of films was tested through the use of an autoclave test in sub-critical condition that is the same condition as in actual PWR. The samples were then evaluated to determine the film condition. Deposited films were characterized for morphology and elemental composition using field emission scanning electron microscopy (FE SEM), energy dispersive x-ray analysis (EDX), and auger electron spectroscopy (AES). AES analysis of the oxidized coatings showed that gradient compositions were obtained as expected, with Al, Zr, and O content varying through the coating thickness. Glancing angle x-ray diffraction (GAXRD) analysis also showed that variety of intermetallic and oxide phases (such as Al@sub 3@Zr, Al@sub 2@Zr@sub 3@, Al@sub 2@O@sub 3@, ZrO@sub 2@ and Zr@sub 3@O) were formed in the coatings during processing. Hydrothermal growth of well-faceted particulates was observed after autoclave test. They were identified to be hydrothermal synthesized aluminum hydroxide, Boehmite by GAXRD and transmission electron microscopy (TEM).

4:40pm **SE-TuA9 Surface Studies of the High Temperature Corrosion of Stainless Steel by Oxygen Contolled Lead-Bismuth Eutectic***, **A.L. Johnson**, D. Parsons, J. Manzerova, D. Koury, B. Hosterman,* University of Nevada, Las Vegas*; D.L. Perry,* Lawrence Berkeley National Laboratory*; J.W. Farley,* University of Nevada, Las Vegas

There has been a resurgence of interest in the use of oxygen controlled Lead/Bismuth Eutectic (LBE) and similar high Z liquid metals as neutron spallation targets and coolants in advanced technology reactors. LBE was used in the Russian Alpha class nuclear submarines, with encouraging results. We have been investigating the corrosion of some western steels by oxygen controlled LBE in a Russian test loop using a number of techniques including SEM, EDAX, XPS and sputter depth profiling. We found for some mixtures of composition and surface preparation an order of magnitude lower oxidation and dissolution, associated with a change in morphology of the protective oxide layer. We shall discuss the effects of surface and near surface preparation and composition on this interesting oxidation/dissolution corrosion system.

Surface Science
Room 326 - Session SS1-TuA
Water at Interfaces II: Adsorbed Layers

Moderator: C.J. Hirschmugl, University of Wisconsin-Milwaukee

2:00pm **SS1-TuA1 Why Water Wets Precious Metals@footnote 1@***, **P.J. Feibelman**,* Sandia National Laboratories **INVITED**

To categorize surfaces as hydrophobic or hydrophilic by measuring contact-angles is a step toward understanding water-solid interactions, but a small one. To predict wetting, control aqueous surface chemistry or design nanofluidic systems, atomic-scale understanding of water-adlayer structure and dynamics is wanted. The research involved is risky -- systematic error is an ever-present concern in dealing with weakly interacting species, like water, which are commonplace in the natural world. To explore the limits of current ab initio methods for water on solids, I have been applying first principles Density Functional Calculations to the simplest examples: periodic water adlayers on close-packed, precious metal surfaces. On Ru(0001), the calculations invite the inference that wetting involves forming a half-dissociated monolayer with water molecules and hydroxyl fragments hydrogen-bonded in a hexagonal structure and hydrogen atoms bound directly to the metal. Refinements of this idea are needed, however, to make contact with measured vibration spectra. New understanding is also necessary to explain the occurrence of periodic adlayers on surfaces like Rh(111) and Pt(111), too unreactive to make dissociation energetically favorable, and to give meaning to beautiful STM images of water clusters obtained at LBNL on Pd(111). @FootnoteText@ @footnote 1@Work supported in part by the DOE Office of Basic Energy Sciences, Division of Material Sciences and Engineering. 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-TuA3 Absence of Surface Water Crystallization***, E. Backus, M. Grecea, **A.W. Kleyn**, M. Bonn,* Leiden University, The Netherlands

For the transition from amorphous solid water to crystalline ice, it has been proposed that the required hydrogen bond rearrangement may occur more readily for the less coordinated water molecules at the surface so that the amorphous-crystalline transition would be expected to nucleate at the solid-air interface. By simultaneously monitoring the phase state of the bulk and the surface passing through this transition, we demonstrate conclusively that crystallization commences in the bulk. In our experiments, water is deposited on a low-temperature Pt substrate by means of a molecular beam in Ultra High Vacuum (UHV), on which it forms a layer of amorphous solid water. By slowly heating the substrate, the water crystallizes. Using RAIRS (reflectance absorption infrared spectroscopy), we can follow the crystallization kinetics real-time, since the RAIRS spectra for crystalline and amorphous ice are very different. Hence by measuring RAIRS spectra while we are heating the crystal, we can deduce the spatially averaged, i.e. bulk fraction of crystalline ice in the water layer throughout the crystallization process. We can also determine surface fraction of crystalline ice in the water layer by monitoring chloroform desorption from the (partially crystallized) ice layer: the desorption of chloroform occurs at temperatures well below the water phase transition, and the desorption temperature from amorphous solid water and crystalline ice differ by 15 K. Therefore chloroform is a good probe for study the crystallinity of the surface of the water layer. In this manner we can correlate surface to bulk crystallinity. We find that the surface crystallinity is always lagging compared to the bulk. We can therefore unequivocally conclude that the crystallization of water nucleates in the bulk and not on the substrate-water interface or on the water-vacuum interface. We further find that initiation of the crystallization process (the nucleation grain) involves ~100 water molecules.

3:00pm **SS1-TuA4 Surface Science - A New Tool for Laboratory Astrophysics***, M.P. Collings, J.W. Dever,* University of Nottingham, UK*; H.J. Fraser,* University of Leiden, The Netherlands*; **M.R.S. McCoustra**,* University of Nottingham, UK

The evolution of our galaxy, and that of others in the Universe, is subtley controlled by a combination of physics and chemistry. Molecules prevade the galaxy and are found to play a key role in controlling the very processes that give birth to new stars, their planetary systems, and potentially the precursors of life itself. Astronomical observations can give us much detail as to the nature of these molecules but laboratory measurements are necessary to understand the physics and chemistry that lead to their formation. Gas phase chemistry is important in this respect, but in recent years the molecular astrophysics community has come to realise that the interaction of the interstellar gas with solid grains plays a crucial role. Our laboratory effort has sought to apply surface science techniques and methodologies to understanding aspects of the gas-grain interaction. In particular, we will report on combined temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) measurements of the interaction of carbon monoxide (CO), carbon dioxide (CO@sub 2@) and molecular hydrogen (H@sub 2@) with vapour deposited ultrathin films of water (H@sub 2@O) ice under conditions that a closely mimic those in the denser regions of the interstellar medium where stars are known to form. Results will be presented that demonstrate a complex interplay of surface diffusion, substrate morphological change, pore trapping of gases and desorption that modifies the simple model of the behaviour of these systems currently utilised by the molecular astrophysics community.

3:20pm **SS1-TuA5 Formation and Dynamics of Water Clusters on Ru(001)**, ***M. Asscher,*** Hebrew University, Israel

The adsorption kinetics of water on Ru(001) was simulated using molecular dynamics (MD) and equilibrium-model approach. The results nicely reproduce observations from STM imaging, work function change and IR measurements. The agreement with experimental results is based on the formation of stable clusters already at very low surface coverage and temperature. Tetramers are predicted to be relatively stable compared to smaller and larger clusters. The dipole moment per water molecule continuously decreases from 2.2D for the monomer down to 1.1D for pentamer and larger clusters. Dimers diffuse faster than monomers or larger clusters, in agreement with STM measurements. A unique mechanism for dimers diffusion is proposed. Photo-dissociation of H2O/Ru(001) with 193nm photons support recent DFT calculations that claim thermal decomposition.

3:40pm **SS1-TuA6 Comprehensive Structural Analysis of H@sub 2@O/MgO(111) using DLD-LEED and IR Spectroscopy**, ***D.A. Human,*** *C.J. Hirschmugl,* University of Wisconsin-Milwaukee

The polar MgO(111) surface is predicted to be charged, and may dissociate water molecules or reconstruct to minimize its energy. Structural analysis using a powerful combination of Low Energy Electron Diffraction (LEED) and UHV infrared spectroscopy provides new insights into this water/oxide interface. A pico-ampere LEED study reveals a @sr@3x@sr@3 R30° structure, and IR transmission spectroscopy suggests the presence of OH and H@sub 2@O species. To perform the LEED study, a new instrument incorporating a delay line detector has been constructed to rapidly collect high-quality digital LEED images with low total electron exposures, thus reducing incident beam effects. The characteristics of the new LEED instrument and the structure and species identification of monolayer and bilayer water coverages will be discussed.

4:00pm **SS1-TuA7 The Growth of Water Monolayers on Pd(111)**, *T. Mitsui, E. Fomin, M.K. Rose, D.F. Ogletree,* ***M. Salmeron,*** Lawrence Berkeley National Lab, University of California at Berkeley **INVITED**

Using STM at low temperature we have followed the structures formed by water growing on a clean Pd(111) substrate. Starting with the monomers the process of cluster formation proceeds via formation of dimers, trimers and so forth. We found a surprising increase in diffusivity for the small clusters (2 to 4 molecules), which we attribute to mismatch between the cluster's structure and the substrate. Cluster mobility decreases substantially when the sizes is 5 and above. Continued adsorption of water results in the formation of honeycomb-like structures reminiscent of ice-like hexagonal bilayers. These structures are limited in size below 90K approximately, indicating kinetic limitations to the growth. Above 100K more extensive honeycomb structures are formed. Above 130K new structures with larger periodicity are formed. The observations will be discussed in light of recent wetting models involving the possible partial dissociation of the first water layer.

4:40pm **SS1-TuA9 The Surface Chelate Effect**, ***R. Major,*** *X.-Y. Zhu,* University of Minnesota

The adsorption of metal ions from a liquid phase to a molecularly functionalized solid surface is important in many disciplines, such as chemical sensing, environmental cleanup, protein purification, and "molecular beaker epitaxy". Few studies have investigated the kinetics and thermodynamics in adsorption at a such a liquid-solid interface. One distinguishing factor related to the coordination of metal ions to surfaces is that the surface functional groups can be arranged in a two-dimensional array. We set out to explore how this two-dimensional arrangement may lead to an inherent chelate effect, using the model system of Cu2+ ions adsorption on self-assembled monolayers of 16-mercaptohexadecanoic acid (MHA) on Au. The formation constant of Cu2+ with the MHA surface was found to be two orders of magnitude greater than Cu2+ with succinic acid or glutaric acid in aqueous solutions. Both of these molecules are known to chelate to metal ions forming 7 and 8-membered rings. The greater surface chelate effect is attributed to the presence of the two-dimensional array of ligands on the surface. We believe the surface chelate effect demonstrated here is of general significance to adsorption on functional surfaces and should depend strongly on chemical functionality and monolayer structure.

Surface Science
Room 327 - Session SS2-TuA
Surfaces and Interfaces of Semiconductors and Compound Materials

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2-TuA1 The Plasmons of ErAs (100)**, ***H.K. Jeong***[1], *T. Komesu, P.A. Dowben,* University of Nebraska, Lincoln; *B.D. Schultz, C.J. Palmstrom,* University of Minnesota

Momentum resolved inelastic electron energy loss has been exploited to measure the surface and bulk plasmons of ErAs(100). The effects of the electronic band structure is seen in the weak plasmon dispersion. This is consistent with heavy mass of the states near the Fermi energy in the experimentally determined band structure. The ratio of bulk and surface plasmon energy is roughly . In both Hg@footnote 1@ and ErAs,@footnote 2,3@ there are indications that the surface is significantly less metallic in character than the bulk. The behavior of the surface plasmon is related to the metallicity of the surface,@footnote 1@ so as with mercury thin films,@footnote 4@ the band structure of ErAs@footnote 2@ should strongly influence the surface and bulk plasmons. While there are a number of studies of the plasmons of simple metals, there are only a few studies of plamons in 4f-5d systems, such as those undertaken from Hg thin films.@footnote 4@ @FootnoteText@ @footnote 1@P.A. Dowben, Surface Science Reports 40, 151 (2000) @footnote 2@H.K. Jeong, Takashi Komesu, P.A. Dowben, B.D. Schultz and C.J. Palmstrom, Physics Letters A 302, 217 (2002) @footnote 3@Takashi Komesu, Hae-Kyung Jeong, Jaewu Choi, C.N. Borca, P.A. Dowben, A.G. Petukhov, B.D. Schultz, and C.J. Palmstrom, Physical Review B 67, art. no. 035104 (2003) @footnote 4@B.-O. Kim, G. Lee. E.W. Plummer, P.A. Dowben and A. Liebsch, Phys. Rev. B 52, 6057 (1995) .

2:20pm **SS2-TuA2 Growth Characteristics of ErAs Interlayers in Metal/Ga@sub 1-x@Al@sub x@As Heterostructures**, ***B.D. Schultz,*** *J.L. Hilton,* University of Minnesota; *K. Lüdge,* Technische Universität Berlin, Germany; *C.J. Palmstrom,* University of Minnesota

Properties of thin-film metal contacts grown on GaAs substrates have long been explored for electronic device applications. For modern spintronic applications, control of the interfacial properties and the reactions between ferromagnetic metals and semiconductors is important for optimizing spin dependent transport across these interfaces. ErAs interlayers, as thin as 5ML, have been used as diffusion barriers to drastically reduce interfacial reactions between Fe@sub 1-x@Co@sub x@ and GaAs for growth temperatures up to 225°C. However, surface segregation of both Ga and As are observed during the Fe@sub 1-x@Co@sub x@ growth and are related to the growth characteristics of the ErAs interlayer. In-situ scanning tunneling microscopy (STM) studies of ErAs films grown by molecular beam epitaxy (MBE) at 535°C show that ErAs initially nucleates as 3-4 monolayer high islands embedded within, rather than on top of, the GaAs(100) surface. These islands grow laterally in size until a complete uniform film is formed, whereby additional growth occurs in a layer-by-layer mode. X-ray photoemission spectroscopy (XPS) reveals both the presence of Ga and As atoms on the ErAs surface following the formation of a continuous layer and the continued segregation of these atoms to the surface during growth. The excess As atoms dissociate from the ErAs surface upon post-growth anneals above 450°C, and STM images show additional ordering of the ErAs surface following these anneals.

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

Growth of ErAs on AlAs(200Å)/GaAs(100) heterostructures eliminates the segregation of Ga to the ErAs surface and results in no surface segregation of Al atoms. This paper reports on the control of the growth modes and the surface composition of ErAs interlayers grown by MBE on Ga@sub 1-x@Al@sub x@As(100) surfaces as characterized in-situ by reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), STM, and XPS. Supported by ONR, DARPA, and NSF.

2:40pm **SS2-TuA3 Some Tricks in Photoelectron Diffraction Experiments for Structural Investigations at Surfaces***, **J. Osterwalder,*** University of Zuerich, Switzerland **INVITED**

A certain class of structural problems at surfaces is readily accessible to investigation by x-ray photoelectron diffraction (XPD). This is usually the case for surface and interface geometries where core levels of specific atoms can be singled out from the XPD spectrum that are located below the topmost atomic layer. Other atoms are thus placed in a forward scattering geometry, and their relative positions are exposed by the associated forward focussing peaks. Prominent examples for such geometries are multilayer epitaxial film growth or intermixing phenomena at interfaces. Yet, there are important structural problems where such forward scattering geometries are often absent, like the internal structure of a single monolayer film, the registry of the film with respect to the substrate, or the adsorption geometries of atomic adsorbates. Over the last several years, various tricks have been devised that expand the scope of XPD to this kind of problems: -(i) For O/Rh(111) it has been demonstrated that the weak backscattering off the substrate atoms can reveal the exact bonding site of the atomic adsorbate. Prerequisites are a high atomic number of the substrate material and low temperature. -(ii) For well ordered monolayer films, the internal film structure can be determined by measuring first and higher order diffraction fringes. This is exemplified by the system of hexagonal boron nitride (h-BN) on Ni(111) as well as several alkali monolayer systems on Al surfaces. -(iii) When a monolayer film is strictly commensurate with the substrate and well ordered, the film structure and registry can be extracted from XPD data of a substrate signal, measured with and without the monolayer present on the surface. The resulting difference data sets need to be compared to simulated data resulting from multiple scattering model calculations. Again, the case in point is h-BN on Ni(111).

3:20pm **SS2-TuA5 Synthesis and Characterization of an Ordered Ge Overlayer and Pt@sub 2@Ge Compound on Pt(100)***, **T. Matsumoto**, M. Batzill, C. Ho, B.E. Koel,* University of Southern California

A c(2 x 2)-Ge overlayer and Pt@sub 2@Ge compound were formed by Ge deposition and annealing to 600 K on Pt(100) and characterized by Na@super +@-ALISS, XPD, LEED and STM. STM topographs and LEED patterns indicate a c(2 x 2) structure after 0.5-ML Ge deposition or 1.5-ML Ge deposition with annealing to 600 K. ALISS was used to unambigously distinguish between the c(2 x 2) overlayer and surface alloy phases. This technique showed Ge-scattering angular peaks assigned to a large separation of Ge atoms along the [011] azimuth corresponding to a c(2 x 2)-Ge overlayer after 0.5-ML Ge deposition. Following 1.5-ML Ge deposition and annealing to 600 K, a new Ge-scattering angular peak appeared that was assigned to scattering from third-layer Ge atoms, however, no second-layer Ge scattering peak was observed. This structure is consistent with a body-centered tetragonal Pt@sub 2@Ge layer surface alloy which has alternating c(2 x 2) Ge-Pt and (1 x 1)-Pt(100) layers. XPD results also support this structural model. Annealing these surfaces to 900 and 1200 K resulted in partial dissolution of Ge atoms deeply into the bulk. XPS was also used to characterize the chemical nature of Ge and Pt at these surfaces.

3:40pm **SS2-TuA6 New Structural Model for Au/Si(111)5x2 from First Principles***, **S.C. Erwin,*** Naval Research Laboratory

Gold induces quasi-1D reconstructions on several faces of silicon, including (111), (557), and (995). These systems have been widely studied for their unusual electronic properties, but the lack of any accepted structural model has hampered theoretical understanding and modeling of those properties. Here, a new structural model for Au/Si(111)5x2 is presented, based on first-principles density-functional calculations, which explains a number of experimentally observed features. The model is a variant of the "honeycomb-chain channel" now accepted as the structure of alkali-induced Si(111)3x1, but with Au atoms occupying top-layer Si positions to form a double chain structure. Energetically, the model is far more favorable than all previously published models. Moreover, the model explains the bright "protrusions" commonly observed in STM as single Si adatoms, which serve to stabilize the 5x2 reconstruction with respect to its 5x1 parent structure. The model also reproduces the "Y"-shaped features observed in STM far from the bright protrusions. Electronically, the predicted band structure is a combination of p-like cosine bands, consistent with angle-resolved photoemission measurements on the closely related Au/Si(557) surface.

4:00pm **SS2-TuA7 First Principles Study of the Stability of Ag Ultra-thin Films on III-V Substrates: An Interfacial Study***, **D.L. Irving**, S.B. Sinnott,* University of Florida*; R.F. Wood,* Oak Ridge National Laboratory

Under normal deposition conditions, most metals grow on semiconducting and insulating substrates in either a Volmer-Weber or a Stranski-Krastinow fashion. However, recent experiments on Ag/GaAs(110) show that atomically flat Ag overlayers can be grown by use of a two-step deposition process. The final morphology of these films is not only dependent on the deposition temperature, but also on the amount of metal initially deposited. Quantum size effects have been proposed as the reason for the preferential stability of the metallic overlayer and a simple theory has been used to predict whether a material system will exhibit it. This study compares the adhesion energy trends predicted by this theory with those calculated by first principles density functional theory calculations. The first principles calculations are performed on both the Ag(111)/GaAs(110) and the Ag(111)/GaSb(110) interfacial systems. The results show how the stability and electronic structure of the Ag films changes as a function of film thickness.

4:20pm **SS2-TuA8 A Self-Assembled Two Dimensional Electron Gas: @sr@7x@sr@3 In on Si(111)***, **E. Rotenberg**, H. Koh,* Lawrence Berkeley National Laboratory*; H.W. Yeom,* Yonsei University, Korea*; J. Schaefer,* University of Augsberg, Germany*; B. Krenzer, M. Rocha, S.D. Kevan,* University of Oregon

We present low-temperature, high-resolution photoemission measurements of the Fermi surface and bandstructure of single-domain @sr@7x@sr@3 Indium on Si(111). Electrons from both indium valence electrons and the silicon dangling bonds form a nearly free, two-dimensional electron gas (2DEG) on a pseudosquare lattice, which is almost completely decoupled from the underlying hexagonal silicon lattice at the Fermi level. Structural analysis with LEED and photoelectron diffraction is consistent with the pseudo-four-fold structure, and rule out both pseudo-six-fold as well as triple (120°-rotated) domains which were reported in previous studies. About half of the Si dangling bond electrons are donated directly to the 2DEG, while the remainder form three bands -- confined to relatively small regions of k-space -- which we associate with In/Si covalent bond formation. The mean free path of carriers in the 2DEG is found to be at least 500 Å along the interface.

4:40pm **SS2-TuA9 Buckling of Si and Ge(111)2x1 Surfaces***, **S. Nie**, R.M. Feenstra,* Carnegie Mellon University*; J.Y. Lee, M.H. Kang,* Pohang University of Science and Technology, Korea

The structure of cleaved Si or Ge (111)2x1 surfaces is well established as consisting of @pi@-bonded chains.@footnote 1@ However, the buckling (i.e. tilt) of these chains has been the subject of recent interest, primarily because a determination of buckling will enable a better comparison between optical absorption data and recent quasi-particle calculations of the surface bandgap and optical response.@footnote 2@ Based on such a comparison it has been suggested that the sign of the buckling may be opposite on Si and Ge surfaces.@footnote 2@ Recent voltage-dependent scanning tunneling microscopy results support that interpretation,@footnote 3@ although that data were restricted to a narrow range of voltages and were performed only on Ge (not Si). In the present work we have performed detailed voltage-dependent STM imaging of both Si and Ge (111)2x1 surfaces, over a wide range of sample-tip voltages. The results are compared with first-principles theoretical predictions, for both positive and negative values of the buckling angle. We find that the wide range of voltages used in the study enables a definitive determination of buckling. Our results demonstrate that the sign of the buckling is indeed opposite on Si and Ge surface, in agreement with the prior work.@footnote 2@ We furthermore deduce from a comparison of the experimental and theoretical STM images a comprehensive view of the image contrast mechanism, incorporating energy-dependent contributions from each atoms in the unit cell. In particular, for empty states, the contrast shifts as the sample-tip voltage is increased from the lower atoms to the upper ones. @FootnoteText@@footnote 1@ K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981); 49, 223 (1982).@footnote 2@ M. Rohlfing, M. Palummo, G. Onida, and R. Del Sole, Phys. Rev. Lett. 85, 5440 (2000).@footnote 3@ R. M. Feenstra, G. Meyer, F. Moresco, and K. H. Rieder, Phys. Rev. B 64, 081306 (2001).

5:00pm **SS2-TuA10 Dimer Structure of the Si(001)2x1 Surface Observed below 10K by Scanning Tunneling Microscope***, **M. Ono**, A. Kamoshida, E. Ishikawa, T. Eguchi, Y. Hasegawa,* The University of Tokyo, Japan

The dimer structure of the Si(001) surface has been discussed after recent low-temperature STM observations, which reported symmetric dimers at 5K. Various models to explain the observation contradictory to the previous reports, such as anomalous flip-flop dimer motion and new ground state induced by spin configuration, were proposed. To solve this issue, we studied it using an STM which can be operated under multiple extreme conditions of ultrahigh vacuum (>6x10@super -9@ Pa), low temperature (>2.8K), and high magnetic field (

Surface Science
Room 328 - Session SS3-TuA
Organic Functionalization of Semiconductor Surfaces

Moderator: J.J. Boland, Trinity College Dublin, Ireland

2:00pm **SS3-TuA1 Adsorption of Substituted Butadienes on Si(100)***, **L.C. Teague**,* University of North Carolina at Chapel Hill, Ireland*; J.J. Boland,* Trinity College Dublin, Ireland

Current interest in the addition of small organics to the Si(100) surface is driven by their potential applications in "bottom-up" fabrication methods. The ability to strategically place and/or manipulate individual molecules into functional structures on surfaces has potentially important implications for molecular electronics.@footnote 1,2@ Although several studies have focused on these types of reactions, it is evident from our previous work with 1,3-cyclohexadiene (1,3-CHD)@footnote 3@ that these reactions are more complicated than originally assumed. STM studies of other organics such as 2,3-dimethyl-1,3-butadiene (DMBD) and 2,3-dimethoxy-1,3-butadiene (DMeOBD) on Si(100) can provide additional information about cycloaddition reactions. Both systems are similar to 1,3-CHD in that they are systems of 4@pi@ electrons, therefore possessing the same reaction possibilities as 1,3-CHD, however they are chain-like rather than ringed structures. Reaction products for DMBD and DMeOBD can be characterized in the same manner as those of 1,3-CHD, i.e., via the location of the remaining C=C bond in the adsorbed molecule. We present a study of the reactions of DMBD and DMeOBD on Si(100), and contrast both the appearance and attachment geometry for reaction products of DMBD and DMeOBD with those of cyclic molecules like 1,3-CHD. Several initial differences between 1,3-CHD products and those of DMBD and DMeOBD are reported, including the presence of dimer buckling induced on the surface after exposure to DMBD and DMeOBD. Different attachment geometries available to chain-like molecules such as DMBD and DMeOBD are shown to account for the dimer buckling observed on the surface. @FootnoteText@@footnote 1@Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. Nature, 2000, 406, 48; Bent, S. F. Surf. Sci. 2002, 500, 879, and references therein.@footnote 2@Whitesides, G. M.; Love, C. J. Sci. Am. 2001, 285, 39.@footnote 3@Teague, L. C.; Boland, J. J. J. Phys. Chem. B 2003, 107, 3820.

2:20pm **SS3-TuA2 Surface Chemistry of Conjugated Heteroatomic Compounds on Diamond and Silicon (100)***, **J.N. Russell**,* Naval Research Laboratory*; M.P. Schwartz,* University of Wisconsin*; D.E. Barlow, J.E. Butler,* Naval Research Laboratory*; M.P. @ag D@Evelyn,* GE Global Systems*; R.J. Hamers,* University of Wisconsin

Diamond and silicon (100)-2x1 surfaces are comprised of dimers linked by a @sigma@ bond and a highly-strained @pi@ bond, but there are notable differences in their structure and chemical reactivity. Using multiple internal reflection infrared spectroscopy, the surface chemistry of conjugated heteroatomic compounds was examined on diamond and silicon (100). Acrylonitrile chemisorbed on diamond via a [2+2] cycloaddition reaction, resulting in a product spectrum similar to that of chemisorbed CD@sub 3@CH=CH@sub 2@. In contrast, acrylonitrile reacts through the nitrile group on Si(100). Cyclohexanedione, which easily tautomerizes into a keto-enol in the gas phase, maintains the enol structure when adsorbed on diamond, but chemisorbs on silicon as the diether, i.e. the [4+2] reaction product. We will examine the role of ring strain, electron donating and withdrawing groups, and dimer tilt on the adsorption probability and structure of the chemisorbed species.

2:40pm **SS3-TuA3 Reaction of Acetyl Chloride on Ge(100)-2x1: Formation of a Surface-bound Carbonyl***, **M.A. Filler**, S.F. Bent,* Stanford University

Since the introduction of vacuum-based organic functionalization of group-IV semiconductor surfaces, there has been considerable interest in attaching molecules beyond the initial monolayer. However, functional groups that are expected to be reactive in second layer reactions, such as amines and ketones, also react directly with the bare semiconductor surface. It is therefore necessary to protect these groups during the deposition of the initial layer or use a molecule where other pathways can kinetically compete and leave the reactive moiety intact. To this end, we have studied the reaction of acetyl chloride on Ge(100)-2x1 at 300K with infrared spectroscopy, temperature programmed desorption, and density functional theory. Infrared spectra show a strong @nu@(C=O) stretching peak near 1680 cm@super -1@ and no vibration modes in the @nu@(Ge-H) region indicating that Cl dissociation to produce a surface-bound carbonyl is the dominant reaction pathway. TPD results provide additional evidence of this surface product; ketene evolves near 525K while at higher temperatures H@sub 2@, HCl, and GeCl@sub 2@ desorb. DFT calculations predict that the barrier to Cl dissociation is only 1 kcal/mol above a chlorine dative-bonded state and is considerably smaller than that of any other reaction pathway. All of this data is strong evidence for a Cl dissociation reaction leaving a surface-bound carbonyl, which is expected to be more reactive toward second layer attachment chemistries and possibly enable layer-by-layer deposition of ultrathin organic films.

3:00pm **SS3-TuA4 Diethyl Ether Reactions with the Si(100) Surface***, **S.M. Casey**,* University of Nevada, Reno

The interactions of diethyl ether with the Si(100) surface have been examined computationally, using ab initio and density functional theoretical techniques, as well as experimentally, using Auger electron spectroscopy and thermal desorption spectroscopy. This surface appears to be relatively inert with respect to reaction with the ether functional group. The reaction paths available to diethyl ether on Si(100) can be contrasted to the interactions of this surface with alcohols and amines, both of which can undergo facile addition reactions upon interacting with this surface. The interactions of ether molecules containing additional, more reactive functional groups, such as a C=C bond, with the silicon surface will also be discussed. .

3:20pm **SS3-TuA5 Modification of Silicon Surfaces: Toward Functional Organic and Bioorganic Interfaces***, B. Fabre,* National Research Council of Canada*; **G.P. Lopinski**,* National Research Council of Canada, Canada*; D.D.M. Wayner,* National Research Council of Canada **INVITED**

Over the last decade there has been increasing awareness of the opportunities presented by the convergence of surface science and organic chemistry. This work is underpinning the development of revolutionary concepts for the design of molecular scale devices and for the integration of solid state, inorganic structures with biologically active interfaces. Although the reactions of organic molecules with silicon surfaces are not new, this area which traditionally has been dominated by physical scientists has increasingly been influenced by organic and bioorganic chemists. This organic perspective has brought new levels of complexity of structure and function and greater understanding of the molecular basis of reactivity. Much of the work so far has focused on exploring the scope of the chemistry and on understanding the structure and quality of the organic-silicon interfaces. An example is the reaction of hydrogen-terminated silicon with styrene that proceeds as a chain reaction on the silicon surface. We have developed simple chemical approaches to introduce essentially any chemical function at the ends of Si-alkyl monolayers. Most recently, we are developing strategies to pattern silicon surfaces with biologically active molecules such as proteins and DNA as well as with conducting polymers (polythiophene). A few simple devices have been prepared using electrochemically grafted polythiophene as a top contact. I will describe the preparation as well as the electrochemical and electrical characterization of these simple metal-insulator-semiconductor structures

4:00pm **SS3-TuA7 Investigation of the Adsorption of Acetic Acid on Ge(100)-2x1***, **J.A. Van Deventer**, M.A. Filler, S.F. Bent,* Stanford University

The modification of group-IV semiconductor surfaces has been an active area of research over the past several years because a greater understanding of semiconductor surface reactivity may lead to applications in nanopatterning, biological recognition, and molecular electronics. In the present work, we investigate the reaction of acetic acid and related isotopes on Ge(100)-2x1 at 300K using infrared spectroscopy and density functional theory. This reactive system is noteworthy because it combines the carbonyl and alcohol functional groups studied in previous investigations into one bifunctional molecule, allowing competition and selectivity to be studied in detail. IR spectroscopy following chemisorption of acetic acid shows a strong absorption at 1664 cm@super -1@ in the @nu@(C=O) region and two large peaks at 1962 and 1925 cm@super -1@

in the @nu@(Ge-H) region. We attribute these features to intradimer and interdimer O-H dissociation products. DFT calculations suggest that these O-H dissociation products are likely to occur through one of two oxygen dative-bonded states. Interestingly, the more stable dative-bonded precursor state is the result of a stabilized ring formed by electron donation from the nucleophilic dimer atom to the nearby hydroxyl hydrogen atom of the adsorbed molecule. The kinetic barrier to reaction of this pathway is calculated to be 3.09 kcal/mol above the dative-bonded state, leading to a final product that lies 39.52 kcal/mol below the vacuum level. The O-H dissociation product is both kinetically and thermodynamically favorable compared to the other pathways, such as @alpha@-CH dissociation and [2+2] C=O, available to the molecule.

4:20pm **SS3-TuA8 Electron Beam Effect of Diethylsilane on Si (100) Surfaces Investigated by TPD and LISD**, ***P. Wang***, *J. Lozano, K. Kimberlin, J. Craig,* Bradley University

Various coverages, from 0.03 to 5.0 L, of diethylsilane (DES) on Si (100) surfaces at 100 K were bombarded by 600 eV electrons and the effect of electron on DES/Si(110) system was investigated by using Temperature Programmed Desorption (TPD) and Laser Induced Stimulated Desorption techniques. Laser photons from Nd:YAG were used in LISD technique. TPD and LISD spectra were immediately taken after each dosing and compared to the spectra after the system was irradiated by 600 eV electrons. Desorption of physisorbed species of mass 2, 28 and 59 species was seen at 130 K after coverages of DES larger than 0.07 L. However, mass 2 and 28 species were also thermally desorbed at 810 and 770 K, respectively. Desorption peak areas of mass 2, 28, and 59 with and without electron/photon bombardment were investigated as functions of coverage and electron/photon fluences. It was found that the carbon hydrides were removed from surface after both electcron and laser photon radiation. The concentration changes in desorption species in TPD and LISD beam dissociation effects as well as beam induced state will be discussed.

4:40pm **SS3-TuA9 Adsorption of Naphthalene on a Si(100)-2x1 Surface Investigated by Infrared Absorption Spectroscopy**, *K. Okamura, H. Ishii, Y. Kimura,* ***M. Niwano***, Tohoku University, Japan

Recently, adsorption of organic molecules on a Si surface has attracted a lot of interest in relation to possible application to organic-inorganic hybrid devices. Understanding of the adsorption process is required for the control of the structural and electrical properties of the interface between organic and inorganic materials. In this study, the adsorption of the naphthalene molecule, with two benzene-like rings fused together, onto the Si(100)-2x1 surface was investigated using infrared adsorption spectroscopy in the multiple internal reflection geometry. To determine the most preferred adsorption structure of naphthalene on Si(100)(2x1) at room temperature, we have carried out cluster calculations based on the hybrid density-functional theory (DFT), and compared the calculated C-H vibration frequencies with the experimental ones. The central result is that naphthalene adsorbs in different manners depending on the surface coverage of naphthalene, which is the same trend as observed for the adsorption of benzene on Si(100)(2x1). At low coverage the molecule adsorb in the bridging manner between two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface so as to reduce the repulsive interaction between two adjacent naphthalene molecules adsorbed on the same dimer row. We discuss the reason why the adsorption structure depends on surface coverage, in comparison with the results of cluster calculations.

5:00pm **SS3-TuA10 Vapor-phase Adsorption Kinetics of 1-Decene on H-terminated Si(100)**, *M.R. Kosuri, H. Gerung, Q. Li,* ***S.M. Han,*** University of New Mexico*; B.C. Bunker, T.M. Mayer,* Sandia National Laboratories

We have investigated in situ and in real time the vapor-phase self-assembly of 1-decene on Si, using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The adsorption of 1-decene on hydrogenated Si(100) results in an alkane terminated hydrophobic surface. The sessile drop water contact angle after the self-assembly of 1-decene is 107 ± 2°. The absolute saturation coverage of decane is approximately 3.2x10@super 14@ cm@super -2@ based on the IR absorbance of C-H stretching vibrational modes near 2900 cm@super -1@. We also report the adsorption rate constant of 1-decene on hydrogenated Si(100) at 160 °C under 30 mTorr of vapor-phase 1-decene. The adsorption rate constant based on a Langmuir isotherm is 1 ± 0.1 Torr@super -1@min@super -1@. The estimated thickness of the decane monolayer, determined by X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry, is approximately 16 Å. Monitoring the decane monolayer over a period of 2 months using XPS has shown that the silicon surface underneath the decane monolayer gets oxidized with time, leading to the degradation of the decane layer.

Thin Films
Room 329 - Session TF-TuA
Transparent Conducting Oxides

Moderator: G. Ockenfuss, OCLI - JDS Uniphase

2:00pm **TF-TuA1 Enhanced Conductivity in Post Deposition Annealed Spinel Oxide Films**, *G.J. Exarhos,* Pacific Northwest National Laboratory*;* ***R.R. Owings***, University of Florida*; C.F. Windisch,* Pacific Northwest National Laboratory*; P.H. Holloway,* University of Florida

Infrared transparent nickel cobalt spinel oxides exhibit p-type polaron conductivity that is highly dependent on the content of nickel in the structure. In this system, the relatively high covalency of nickel and the distribution of cation oxidation states among the available tetrahedral and octahedral lattice sites act to promote polaron formation. The nature of the polaron formed and its mobility are very much dependent upon composition and lattice parameter which, in turn, can be altered by choice of deposition parameters and post deposition treatment. Film conductivity is affected directly by post deposition annealing and can be enhanced or degraded reversibly upon rapid quenching or slow cooling to produce a set of recoverable conductivity values. The addition of lithium into the nickel cobalt system promotes enhanced conductivity as well, if included in small enough amounts. As the nickel concentration in the film increases, less lithium is required to produce a conductivity increase. Lithium containing films also exhibit the same recoverable conductivity behavior when subjected to heat treatment. Electrical property measurements are correlated with vibrational and electron spectroscopy results. Structural nuances are characterized by means of HRTEM. Perturbations to the conductivity are thought to arise from the presence of chemisorbed species such as carbonate and cation partitioning among available sites in the lattice.

2:20pm **TF-TuA2 Reactive-Environment, Hollow Cathode Sputtering: Basic Characteristics and Application to Al@sub 2@O@sub 3@ and Doped ZnO**, ***A.E. Delahoy***, *S.Y. Guo,* Energy Photovoltaics, Inc.

A novel method for thin film deposition by reactive sputtering has been studied. The method is based on metal sputtering in a hollow cathode configuration with supply of a reactive gas to the vicinity of the substrate. The working gas and entrained sputtered atoms exited the cathode through a slot having an aspect ratio of 8:1. The reactive gas is thereby largely prevented from reaching the target. The basic operation of the cathode was studied using a Cu target. These studies included lateral and longitudinal film thickness profiles, the dependence of deposition rate on power, pressure, and flow rate, and film resistivity as a function of substrate temperature and low energy ion bombardment. Al and Zn targets were used to prepare Al@sub 2@O@sub 3@ and ZnO films in a reactive environment of oxygen. Using quartz crystal rate monitoring it was demonstrated that only a very small amount of oxygen passing through the cathode will oxidize (poison) the target, whereas large quantities of oxygen supplied externally to the cathode need not affect the target at all. A very stable plasma discharge and ease of Al@sub 2@O@sub 3@ formation was realized in this latter mode. Using a Zn target, the method was then applied to the preparation of transparent, conductive films of ZnO doped with Al and B. The Al was introduced by co-sputtering, and the B from B@sub 2@H@sub 6@. The dopant concentrations were measured by ICP. The film resistivity was found to depend strongly on oxygen flow rate. Low film resistivities (0.49 x 10@super -3@ ohm-cm) and high deposition rates (a dynamic rate of 17 nm m/min) were achieved.

2:40pm **TF-TuA3 Transparent Electronics: An Overview of Materials, Devices, and Applications**, ***J.F. Wager***, *H.Q. Chiang, D. Hong, B.J. Norris, J.P. Bender, M.M. Valencia, C.-H. Park, J. Anderson, J.Y. Jeong,* Oregon State University*; D.A. Keszler,* Oregon State University, U.S.A*; H. Yanagi, M. Price, J. Tate,* Oregon State University*; R.L. Hoffman,* Hewlett-Packard Company **INVITED**

The objective of transparent electronics is to fabricate invisible electronic circuits. Part of the motivation for the development of transparent electronics is the recent availability of p-type transparent conductive oxides (TCOs). With the emergence of p-type TCOs, in addition to conventional n-type TCOs such as indium-tin oxide, tin oxide, and zinc oxide, fabrication of transparent bipolar electronic devices becomes feasible. This presentation will emphasize four topics. First, a brief overview of conventional n-type

TCOs will establish the context for the pursuit of transparent electronics. Second, recent work on the development of p-type TCOs, as well as other non-oxide transparent conductors, will be reviewed. Third, the fabrication and performance of a novel ZnO-based transparent thin-film transistor will be described. Fourth, transparent electronic applications such as transparent select transistors for active-matrix liquid-crystal displays and transparent back-plane electronic drivers for transparent displays will be discussed.

3:20pm **TF-TuA5 Expanding Thermal Plasma Deposition of Textured ZnO: Plasma Processes and Film Growth***, **R. Groenen**, I.M. Volintiru, M. Creatore, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Zinc oxide (ZnO) is a transparent conducting oxide (TCO) of considerable technological interest. Recently, the utilization of an expanding thermal plasma (ETP) created with a cascaded arc is demonstrated for low temperature textured ZnO deposition.@footnote 1@ The remote configuration of the ETP technique allows for separate control of plasma production, gas phase chemistry and substrate surface treatment and is suitable for large area deposition. Films are deposited on glass substrates from oxygen, diethylzinc and for doped material additionally trimethylaluminum. A controllable, rough surface texture which is essential for application as a front electrode in thin film solar cells, is inherently obtained during deposition. Here, a fundamental study of the plasma processes and film growth is presented. Complementary in-situ diagnostics (e.g. Langmuir probe, quadrupole mass spectrometry, optical emission spectroscopy and spectroscopic ellipsometry) are used to correlate plasma composition, film growth and material properties. Film growth appears to be dominated by molecular (i.e. background) instead of atomic oxygen. The relation between detected species and the observed texture development allows for further improvement of the material light trapping properties. @FootnoteText@@footnote 1@R. Groenen, et al., Appl. Surf. Sci. 173 (2001) 40.

3:40pm **TF-TuA6 Transparent Conducting Amorphous Zn-Sn-O Films Deposited by Simultaneous DC Sputtering***, **T. Moriga**, Y. Hayashi, K. Kondo, K. Matsuo, H. Fukumoto, K. Murai, K. Tominaga, I. Nakabayashi,* The University of Tokushima, Japan

The films of ZnO-SnO@sub 2@ system were deposited on glass substrates by simultaneous DC magnetron sputtering apparatus, where ZnO and SnO@sub 2@:Sb (Sb@sub 2@O@sub 5@ 3wt% doped) targets were faced each other. The substrate temparature were maintained at 150 and 250°C. As an experimental parameter, current ratio @delta@, ZnO target current divided by the sum of ZnO and SnO@sub 2@:Sb target currents, was adopted. Monophasic amorphous transparent films appeared for Zn/(Sn+Zn)=0.50-0.73. At Zn/(Sn+Zn)=1/2 (@delta@=0.62), 2/3 (@delta@=0.73) and any other ratio in as-deposited films, neither crystalline ZnSnO@sub 3@ nor Zn@sub 2@SnO@sub 4@ was obtained. Minimum resistivity was found at @delta@=0.50, whose composition was approximately SnO@sub 2@ZnSnO@sub 3@. Amorphous tin oxide coexisting with amorphous zinc stannate ZnSnO@sub 3@ would have an important role to reduce the resistivity. Resistivity increased linearly with an increase of the current ratio, until the composition reached the zinc stannate Zn@sub 2@SnO@sub 4@.

4:20pm **TF-TuA8 Highly Transparent and Conductive ZnO:Al Thin Films Prepared by Vacuum Arc Plasma Evaporation***, **T. Miyata**, S. Ida, Y. Minamino, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, we reported preparation of undoped and impurity-doped ZnO thin films on large area substrates by a newly developed vacuum arc plasma evaporation (VAPE) method using oxide fragments as a low-cost source material. Resistivities on the order of 10@super -4@@ohm@cm were obtained in Ga- or F-doped ZnO thin films. However, doping Al into ZnO films was very difficult because of the large difference in decomposition energy (vapor pressure) between Al@sub 2@O@sub 3@ and ZnO. In this paper, we describe the preparation of Al-doped ZnO (AZO) thin films by a newly developed VAPE method using ZnO fragments and a gas source Al dopant. The film depositions were carried out under the following conditions: substrate, large area glass; substrate temperature, RT to 450@super o@C; oxide fragments, sintered ZnO; pressure, 0.08 to 1 Pa; Al dopant gas pressure (flow rate), 0.01 to 0.5 Pa; Ar and O2 gas flow rates, 20 and 0 to 20 sccm; and cathode plasma power, 4.5 to 10 kW. A low resistivity on the order of 10@super -4@@ohm@cm and an average transmittance above 85% in the visible range were obtained in AZO thin films. In addition, a deposition rate of 150 nm/min as well as a uniform distribution of resistivity and thickness on the substrate surface was obtained. It was found that the Al content in AZO films was altered by varying the partial pressure (or flow rate) of the Al dopant gas. It is concluded that the newly developed VAPE method, using both oxide fragments and gas sources as source materials, is very effective for the preparation of multicomponent oxide thin films.

Biomaterial Interfaces
Room Hall A-C - Session BI-TuP
Poster Session

BI-TuP2 Plasma Processing pf Polymers to Reduce Bio-Fouling for Cardiac Applications*, M. Neumann*, *P. Fackler, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Polymers are playing an increasing role in cardiac medicine as components of implants and diagnostic devices, such as tubes, diaphragms, filters, pacemaker components, blood bags, sutures, vascular grafts and shunts. Polymers exhibit high strength to weight ratio, wide range of flexibility, ease of formability, and economics of production, but processes designed to achieve desired surface properties can compromise the overall bulk material. The ability to alter the surface of the polymer while leaving the underlying bulk material unchanged has a large potential for development in the area of biomaterials. Modifying the surface of a polymeric material so as to impede water adhesion and the ability of proteins, bacteria, and cells to grow on the surface can be minimized on those surfaces that are incorporated into biological systems. This can minimize infection, thrombosis, and other undesirable interactions. Polymer surface modification was accomplished via plasma etching and deposition in a commercial size plasma-etching device, which achieves plasma densities and electron temperatures up to 10@super 11@ cm@super -3@ and 4 eV. The degree of change is controlled by macroscopic external controls, rather than invasive internal modifications. This process lends itself well for use in existing systems. Water contact measurements taken before and after treatment of HDPE that show a change from a pretreatment angle of 85° to post treatment angles of 5°, which corresponds to a dramatic change in surface energy of the polymer and biological interaction potential. This modification is both physical and chemical, but limited to a few microns of the surface of the material. Plasma analysis is done through use of Langmuir probes, microwave interferometery, and optical spectroscopy. Surface analysis is done through XPS. Blood-material interactions are studied through two-dimensional electrophoresis in order to determine the extent and nature of protein coverage.

BI-TuP3 Non-Fouling Surfaces for Biosensors and Biomaterials*, L. Li*, *S. Chen, J. Zheng, S. Jiang,* University of Washington

Non-fouling surfaces are critical to the performance of biosensors and biomaterials. Despite of their importance and enormous effort, non-fouling mechanism is still not quite clear at present. It was shown in our previous work that the behavior of protein adsorption depended on nano-scale structures of a surface with which proteins interact. Therefore, molecular details of a surface are of great importance to protein adsorption. However, there is still a considerable lack of the fundamental understanding of how nano-scale structures affect protein adsorption at the molecular level. The objective of this work is to demonstrate that nano-scale structures of a surface are responsible for protein resistance. Polyethylene glycol (PEG) self-assembled monolayers (SAMs) are used as model systems and the nano-scale structures of the surfaces are altered by adjusting factors such as the assembly substrates, the assembly conditions, and the composition of mixed SAMs. These SAMs are characterized by atomic force microscopy (AFM)/scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Protein adsorption on these surfaces was investigated by surface plasmon resonance (SPR) biosensors and tapping-mode AFM. Furthermore, experimental results are directly compared with those from molecular simulations, which can also provide additional information not easily accessible to current laboratory experiments, such as adsorbed water structures at protein/SAM interfaces. Results from combined experimental and simulation studies provide insight on how nano-scale structures affect protein adsorption and shed light on non-fouling mechanisms.

BI-TuP4 Patterned Immobilization of Proteins on High-density PEG Coated Si Surfaces*, Y. Jun*, *X.-Y. Zhu,* University of Minnesota

Spatially localized patterns of chemical and biological functions on solid surfaces are of great interest to a number of research fields, such as biochips and cell biology. We have developed a novel chemical strategy for the formation of micro-scale patterns of chemical and biological functions on silicon surfaces using soft lithography techniques. This is based on an efficient reaction between alcohol functional groups and chlorine terminated silicon surfaces. The features formed by soft lithography show exceptionally high resolution and fidelity, with edge resolution as high as 10 nm. We demonstrate the immobilization of protein molecules to spatially localized surface functional groups on high-density PEG brush coated silicon. The spatially localized activation of the PEG brush is achieved via either partial oxidation to form aldehyde groups or via attachment of efficient leaving groups. Protein molecules are covalently immobilized to these activated regions on the PEG/Si surface.

BI-TuP5 The Topography and Viscoelastic Properties of Salivary Pellicle and Their Interaction with Tannins*, M.E. Dickinson*, *A.B. Mann,* Rutgers University

The acquired pellicle is an organic film formed by the adsorption of proteins and carbohydrates on dental enamel exposed to the oral environment. The pellicle is now understood to have several roles including lubrication and reduction of friction between teeth during mastication, as well as protection against acidic solutions. Using in vitro AFM, growth, structure and topology of pellicle grown in vivo on a clean enamel surface has been studied. Complete coverage of the enamel surface was found to occur within the first few minutes of exposure, with the layer increasing in thickness until a maximum is reached at around 2 hours. The thickness of the pellicle varies with position, but fully developed pellicle can range in thickness from 200-500nm. Tannins found in food can interact with pellicle to change its viscoelastic properties and alter the color which is a cause of extrinsic staining in teeth. Tannins are phenolic compounds capable of precipitating alkaloids, gelatin and other proteins, they are naturally found in many food stuffs especially leafy products such as tea. The topology of the pellicle surface, as studied using AFM and SEM, consists of a dense arrangement of adsorbed globular shaped proteins with no break in the structure, even when tannins are added. The viscoelastic properties of the pellicle have been studied using nanoscale dynamic mechanical analysis, this shows that substantial variations in the storage and loss modulus occur with increasing exposure to tannin containing solutions. These changes in viscoelasticity will impinge directly on the pellicle's performance as a lubricant and also its ability to act as a chemical barrier to acid attack.

BI-TuP7 Attachment of Blood Proteins to Chitosan Surfaces*, D.W. Thompsons*, *W.H. Nosal, S. Sarkar, A. Subramanian, J.A. Woollam,* University of Nebraska, Lincoln

Chitosan is a biomaterial of interest because of the potential to modify its amine groups to control its interactions with surfaces. Though chitosan itself is thrombogenic, such modifications may lead to a surface with enhanced biocompatibility. In this work we use spectroscopic ellipsometry to monitor the attachment of three blood proteins (albumin, IgG, and fibrinogen) to a spin-cast chitosan surface in phosphate-buffered saline solution. The moisture-induced swelling of the chitosan film is characterized, and optical constants for chitosan and the proteins are determined independently for use in modelling the time-dependent data. Ex-situ infrared ellipsometry is used to characterize the chemical nature of the protein attachment and compare chitosan films with varying degrees of deacetylation. Material anisotropy due to preferred molecule orientation is apparent from ellipsometry.

BI-TuP8 Operation of the QCM-D Technique at Elevated Oscillation Amplitudes*, M.E.M. Edvardsson*, *F. Höök,* Chalmers University of Technology, Sweden

An often raised question with respect to applications of the quartz crystal microbalance technique is whether the shear oscillation of the sensor surface influences the measured binding events. This is indeed a relevant question, especially since solid proofs for bond rupture at elevated amplitudes was recently presented.@footnote 1,2@ In part inspired by these observations, our QCM-D device has been further developed to operate at variable driving amplitudes (from 1 V to 10 V corresponding to maximum oscillation amplitude between 4nm and 40nm), while still maintaining the possibility to perform combined f and D measurements - a combination that was not implemented in previous work. In order to test the device, we choose the well established process by which intact vesicles adsorb and decompose into a planar supported lipid bilayer on SiO@sub 2@, known to be very sensitive to external perturbations. Up to driving amplitudes of 2V, the adsorption behavior is essentially unaffected, whereas it becomes significantly affected at driving amplitudes above 2V. These results thus nicely demonstrate the possibility to implement variable driving amplitudes, and proves that an entirely new dimension will be possible to explore in detail, especially when combined with f and D data at multiple harmonics and proper theoretical modeling is implemented: The amplitude variation can be used to either affect the system being studied, or to extract new information about it by going from the harmonic to the anharmonic regime, which will be discussed in this paper. @FootnoteText@ @footnote 1@Cooper MA, et al.; Direct and sensitive detection of a human virus by rupture event scanning. Nature

Biotechnology 2001, 19:833-837@footnote 2@Dultsev FN, et al.; "Hearing" bond breakage. Measurement of bond rupture forces using a quartz crystal microbalance. Langmuir 2000, 16:5036-5040.

BI-TuP9 Protein Immobilization for Multi-Channel Sensor Detection*, J. Ladd*, *Q. Yu, S. Chen,* University of Washington*; J. Homola,* Institute of Radio Engineering and Electronics, Czech Republic*; S. Jiang,* University of Washington

The simultaneous detection of multiple analytes is an important consideration for the advancement of current biosensor technology. Currently, few sensor systems possess the capability to accurately and precisely detect multiple antigens. The work presented demonstrates a novel approach for the functionalization of sensor surfaces for multi-channel detection. This approach combines inkjet-printing technology with self-assembled monolayer (SAM) chemistry to create a protein array. A modified commercial Epson C40UX inkjet printer is used in this work. The sensor platform is based on a layer of streptavidin immobilized on a mixed SAM of biotinylated alkanethiol (BAT) and poly(ethylene oxide) (PEO). Non-specific binding, and thus false positives, are minimized with the non-fouling background of the sensor surface. The described platform is used in a home-built surface plasmon resonance (SPR) biosensor. Results show excellent specificity in protein immobilization to the proper locations in the array, eliminating the possibility of a false detection within a channel. Analysis of multiple proteins in solution shows a similar behavior and response to pure protein solutions. The detection capabilities of a sensor using this protein array have been characterized using human choriogonadotropin (hCG).

BI-TuP10 Chemisorption of Aromatic Amino Acid Derivatives on Gold Surface*, R.M. Petoral, Jr.,* *K. Uvdal,* Linköping University, Sweden

The interfacial property of adsorbate and thin layers of biomolecules on solid surfaces is of great significance in biomaterials and biosensor application. Understanding the binding and molecular orientation of the adsorbates is then of great importance. Amino acids with aromatic side chains such as Tyrosine and 3,4-dihydroxyphenylalanine (DOPA) is linked to a short thiol through a peptide bond and is adsorbed and self-assembled to polycrystalline gold surfaces. The molecular adsorption, chemical binding and orientation of the amino acid analogue to the surface are studied by X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection-Absorption Spectroscopy (IRAS) and Near-edge X-ray Absorption Fine Structures (NEXAFS). Strong molecular binding of the amino acid derivatives on gold surface through the sulfur atom was attained. Angle dependent XPS results showed that the aromatic ring is oriented away from the gold surface. Parallel orientation of the C=O bond of the amide moiety relative to the gold surface is deduced from the IRAS and NEXAFS results. The average orientation of the aromatic ring and main molecular axis of the molecules relative to the gold surface are also determined. The aromatic amino acid derivatives are able to self-assemble and form an ordered monolayer with minimal degree of orientational disorder. Results from this experiment are valuable in our development of sensor surfaces to be used for interaction studies with other biomolecules and metal ions.

BI-TuP11 Multi-Technique Characterization of Self-Assembled Peptide Monolayers*, N.T. Samuel,* University of Washington*; K. McCrea,* Polymer Technology Group*; L.J. Gamble,* University of Washington*; D.A. Fischer,* National Institute of Standards and Technology*; P.S. Stayton,* University of Washington*; G.A. Somorjai,* University of California, Berkeley*; D.G. Castner,* University of Washington

There is considerable interest in the immobilization of bioactive peptides for applications such as affinity separations, diagnostics, cell culture and biomedical implants. We have synthesized a series of lysine and leucine containing peptides, which are designed to attach to surfaces with different secondary structures (alpha helix, beta sheet, etc.). These peptides were attached to carboxy-terminated self-assembled monolayers and characterized with ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry), SFG (Sum Frequency Generation) and NEXAFS (Near Edge X-ray Absorption Fine Structure Spectroscopy). The ToF-SIMS spectra from these peptides were analyzed by principal component analysis. Principal component 1 (PC 1), which captures 89% of the variance in the spectrum, represents the variation in the bulk amino acid composition of the different monolayers. PC 2, which captures 10% of the variance, separates the peptides with different secondary structures, suggesting ToF-SIMS is sensitive to different secondary structures of the peptides. SFG spectra were acquired for the alpha helical peptide adsorbed onto both hydrophobic and negatively charged substrates. The hydrophobic surface spectrum showed strong peaks in the CH stretch regions while the negatively charged surface spectrum showed strong peaks in the NH stretch region. The SFG results indicate the alpha helical peptide binds differently to these two surfaces. These observations were also confirmed by ToF-SIMS experiments, which reveal a strong dependence of the amount of peptide adsorbed onto negatively charged substrates when the solution pH is varied. We have recently developed a simple protocol to attach a short thiol linker onto these peptides at their amine terminus. This provides an additional handle to immobilize these peptides onto surfaces and control their orientation. Polarization-dependent NEXAFS experiments on these monolayers are in progress.

BI-TuP12 Molecular Simulation of Cytochrome C Adsorbed on Self-Assembled Monolayers*, J. Zhou*, *J. Zheng, S. Jiang,* University of Washington

Cytochrome c, a membrane electron transfer protein, plays an important role not only in a wide range of basic life processes, but also in biomaterial and biosensor applications. To enable the electron transfer fast, cytochrome c should sit on the surfaces with an orientation that the heme ring close and perpendicular to surfaces. Moreover, the adsorbed cytochrome c should keep its native conformation. Self-assembled monolayers are ideal platforms for the study of protein adsorption. In this work, the orientation and conformation of cytochrome c on charged self-assembled monolayers are investigated by a combined Monte Carlo and molecular dynamics simulation approach. The effects of positively and negatively charged SAMs, degree of dissociation of COOH-terminated SAM, ionic strength are examined. CHARMM force field was used to model the protein and SAM. Both implicit and explicit solvent model were used. The root mean square deviation, gyration radius, eccentricity, Ramachandran angles, heme orientation and superimposed structures of cytochrome c were calculated during the simulation. Simulation results show that desired orientation could be obtained on a negatively charged surface. The dissociation degree of the terminal group affects the conformation of adsorbed protein. This work sheds light on the mechanism of the orientation and conformation of adsorbed proteins at the molecular level, and would be useful for the design and development of biosensors and biomaterials.

BI-TuP13 SPARC Binding with ECM Proteins and its Influence on Cell Adhesion*, H. Wang*, *S. Chen,* University of Washington*; T. Barker, H. Sage,* Hope Heart Institute*; B.D. Ratner, S. Jiang,* University of Washington

The secreted protein acidic and rich in cystein (SPARC/osteonectin/BM-40) is associated with events characterized by changes in cell shape and mobility. Although the molecular mechanism remains unclear, it is generally believed that the counter-adhesive properties of SPARC are related to its interactions with ECM proteins. In this study, the interactions of SPARC with ECM proteins, such as collagen I and fibronectin, are characterized and quantified using atomic force microscope (AFM) and surface plasma resonance (SPR), and their influence on cell adhesion are examined. AFM can characterize the binding of SPARC with both collagen I and fibronectin at the molecular level. SPARC has been shown to interact with collagen I, but direct topographic image has not been reported. Whether SPARC interacts with fibronectin still remains inconclusive. In this work, AFM is used to determine the number and location of binding sites on individual collagen I and fibronectin. Monoclonal antibodies of SPARC are used to assist for better visualization. These studies provide direct information about how and where binding occurs. SPR is used to quantify these interactions. It was shown that these interactions have ionic nature. Furthermore, the C-terminal region of SPARC, which contains a high-affinity Ca2+-binding site, may play an important role in its binding with ECM proteins. Thus, the influence of ionic strength and concentration of Ca2+ on binding are studied in SPR experiments. Cell culture and adhesion assays are used to study SPARC as a modulator of the adhesive process of cells seeded on ECM proteins. The influence of SPARC-collagen I interaction is studied using smooth muscle cells while the influence of SPARC-fibronectin interaction is studied using endothelial cells. The number and spreading area of cells, as well as the focal adhesion plagues are obtained as a function of the relative amount of SPARC added.

BI-TuP14 Molecular Dynamics Study of Protein Adsorption on Controlled Surfaces*, J. Zheng*, *S. Jiang,* University of Washington

Surface resistance to protein adsorption is currently a subject of great interest with potential applications in many areas, including biomaterials and biosensors. Despite its importance, there has been a lack of molecular-level understanding of protein interactions with surfaces and the mechanism of resistance to protein adsorption remains a problem to be solved. It is well known that SAMs presenting oligo (ethylene glycol) (OEG) groups, such as S(CH2)m-(EG)nOH or -(EG)nOCH3 resist the adsorption of proteins. The molecular-level understanding of protein resistance to surfaces is needed in order to provide insights of non-fouling mechanism. In the work, we investigate interactions of protein (e.g., lysozyme) with OEG SAM (inner) surfaces using a combined Monte Carlo and molecular dynamics simulation approach in the presence of explicit water molecules. The CHARMM (version 27), an all-atom potential force field, was used to model the protein and methyl terminated SAMs. The TIP3P potential was used to describe water interactions. For the OEG terminated SAMs, we used a SJY model that reproduces very well the helix structure of OEG tails. Results from inert surfaces will be compared with those from methyl terminated SAM surfaces. The behavior of water at protein/SAM interfaces is characterized by self-diffusion coefficient, order parameter, hydrogen bonding, and radial distribution. In these simulations the effects of surface (charge, hydrophobicity, and defect), solvent, pH, and ion strength will be taken into account. Results from this work will shed a light on non-fouling mechanism at the atomic-scale level and guide the design of better biocompatible materials and biosensors.

BI-TuP15 Creation of Surface Macromolecular Docking Sites for the Reversible Immobilization of Proteins in Active Conformation and Controlled Orientation*, **G. Zhen**, E. Zobeley, V. Eggli, R. Glockshuber, M. Textor,* Swiss Federal Institute of Technology, Switzerland

Our contribution describes the comparative performance of two docking site concepts for the immobilization of biomolecules in active conformation and controlled immobilization. They are based on biotin-(Strep)avidin and NTA-Ni@super 2+@-histag linkage techniques, in combination with polycationic, PEG-grafted, NTA(nitrilotriacetic acid) functionalized and biotinylated copolymers. Enzyme @beta@-lactamase served as the model protein for the verification of the linkage concept and for the investigation of the activity of the surface-immobilized protein and its dependence on the molecular orientation. Five different variants of @beta@-lactamase with single cysteine site-directed mutagenesis on the surface were engineered. Two platforms were tested in order to determine how the mechanical and dynamic properties of the interface influence the enzyme-orientation-dependent catalytic activity: polymeric interface (flexible chains, soft) and functionalized alkanethiol monolayers on gold (comparatively immobile, stiff). The @beta@-lactamase variants were biotinylated at free thiol-group with a cleavable biotinylation reagent allowing for controlled release of the surface-bound enzyme. The immobilization was achieved on niobium oxide surface coated with biotinylated Poly(L-lysine)-g-poly(ethylene glycol) and on gold coated with mixture of alkanethiol-biotin and alkanethiol-OH self-assembled monolayer. The biotinylated @beta@-lactamase was subsequently bound to the surface via NeutrAvidin. The long-term stability of the immobilized proteins was evaluated. The amount of immobilized @beta@-lactamase on the chips was measured by three different techniques: OWLS, SPR and specific enzymatic activity via photospectroscopic detection of the turnover of the chromogenic substrate nitrocefin. Specific immobilization could be discriminated from non-specific adsorption. Furthermore the effect of the immobilization scheme on the biological activity was quantitatively examined.

BI-TuP16 X-ray Surface Scattering for the Structural Analysis of Adsorbed Proteins at Hydrated Interfaces*, **C.A. Pavloski,** S.S. Lateef, M.L. Schlossman, L. Hanley,* University of Illinois at Chicago

Protein adsorption onto solid surfaces is a significant process in a wide variety of applications including biomaterials, tissue engineering, biosensors, immunoassays and protein arrays. Surface properties are altered by synthetic and naturally occurring molecular adsorbates when a biomaterial is brought into contact with a biological fluid. We are interested in determining the structural conformation of adsorbed proteins at this aqueous-solid interface. We examine the surface adsorption of bovine serum albumin (BSA), the most abundant protein in blood. We bromine label BSA to allow probes of its adsorbed conformation on an amine-functionalized monolayer on a silicon wafer. We use x-ray photoelectron spectroscopy and atomic force microscopy to study the chemistry and structure of the dry surface. We then apply x-ray reflectivity and x-ray standing wave fluorescence to probe the conformation of adsorbed BSA at the hydrated interface.

BI-TuP17 Assembly and Disassembly of Hydrogels to Entrap, Grow, and Release Cells*, **G.F. Payne**, T. Chen, L.-Q. Wu, D.A. Small, H. Yi,* University of Maryland Biotechnology Institute*; R. Ghodssi, G.W. Rubloff,* University of Maryland*; W.E. Bentley,* University of Maryland Biotechnology Institute

Hydrogels provide a bio-friendly environment for cultivating cells. Standard methods for entrapping cells within hydrogel matrices exploit the photopolymerization of synthetic monomers (or macromonomers). The strength of photopolymerization is that standard lithographic approaches can be exploited to exert considerable spatial and temporal control of hydrogel formation. The weaknesses of photopolymerization are that these methods are not always benign to cells, and the hydrogel matrices are generally permanent. We are examining an alternative method for in situ hydrogel formation based on biopolymers and enzymes. Specifically, we mix cells with the protein gelatin, and add the protein-crosslinking enzyme transglutaminase. Gel formation occurs over the course of 1-2 hours. In situ-entrapped bacterial cells (E. coli) were observed to grow to high densities within the crosslinked gelatin matrices, and these cultured cells could sense and respond to appropriate inducers (we examined the inducible expression of green fluorescent protein). After growing the cells, they could be released from the hydrogel using the protein-degrading enzyme, proteinase K. Cells were released over the course of 1 hour and they remained viable and inducible. This study demonstrates that; one enzyme (transglutaminase) can entrap cells within a hydrogel, the cells can proliferate to high densities within the matrix, and a second enzyme (proteinase K) can "dissolve" the hydrogel to release the cells. This capability should provide unique opportunities for microfluidic biosensors.

BI-TuP18 Customized Tissue Engineering Using Photopolymerizable Hydrogels and Stereolithography Techniques*, **B. Dhariwala**, E. Hunt, T. Boland,* Clemson University

The power of tissue engineering can be enhanced using customizable scaffolds to repair defects caused by birth or accidents. For customized tissue engineering, one of the variables accessible and tunable by the engineer is the form and aspects of the scaffold onto which cells are seeded. Here we are studying hydrogels as materials that can be used for custom designed scaffolds. For this study, we employed photopolymerizable hydrogels fabricated by crosslinking polyethylene oxide (PEO) with polyethylene dimethacrylate (PEGDM) monomer using 2-methyl-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (IRGACURE) as the photoinitiator. Several hydrogels have been prepared including custom shaped hydrogels made using polypropylene molds. Initial characterization of these gels will be presented. Use of stereolithography technique has been carried out to make customized scaffolds. This is a computerized technique where a high intensity UV laser beam is used to form the hydrogel according to a 3D image of the defect. The laser scans in the X-Y plane and there is a movable platform which serves as the Z plane. Different scaffold shapes were made using this technique. Some mechanical tests were carried out on the polymer will also be overviewed and their results will be shown. Toxicity studies of the photoinitiator were carried out to determine adequate amount of initiator to be used. Initial cell studies were carried out to ensure cell viability in the polymer. Cells were mixed with the polymer, which was then photopolymerized, and their viability was studied and results will be discussed. We would further investigate cell viability & cell growth over extended periods of time. Stereolithography is a very efficient method of preparing 3D scaffolds and holds a promising future for tissue engineering.

BI-TuP19 Cell-Based Biosensors - A Tool for High Throughput Toxin Detection*, **K. Varghese**, A. Jamshidi, K. Sieverdes, P. Molnar, M. Das, C.A. Gregory, J.J. Hickman,* Clemson University

Cell-based biosensors incorporate a cellular sensing element that detects a change in the cells immediate environment and converts the cellular signal with an electrical impulse that is conducive for integration to a silicon environment. Cell-based electrophysiology can be broadly divided into two categories - those based on intracellular potentials (eg. using glass microelectrodes as in patch clamping) and those based on extracellular potentials. Our research focuses on the latter, wherein extracellular microelectrode arrays are used as a noninvasive and long-term approach for the measurement of biopotentials. The objective of this study is to culture cardiac myocytes on Metal Microelectrode Arrays (MEAs) and Field Effect Transistors (FETs) and test them upon exposure to various toxins. The culture conditions (serum vs serum free), were also investigated to compare and contrast the results obtained therein. In the first and present part of this study, cardiac myocytes from Day 6 chicken embryos were cultured on MEAs and tested for their response to different concentrations of Cadmium Chloride and Cesium Chloride, which are known environmental toxins. Studies also were carried out to study the effect of various adhesive surfaces on the health and response of these cardiac myocytes. DETA, fibronectin and Entactin-Collagen-Laminin (ECL) matrix were the surfaces studied. Preliminary results have shown a healthier monolayer and higher beat frequency with serum free conditions. In the comparative study between different surfaces, best results have been obtained on DETA for beat frequency.

**BI-TuP20 In-vitro Electrophysiological Comparison of Embryonic Hippocampal Neurons Grown in 2D and 3D Environments*, T. Xu*, *P. Molnar, C.A. Gregory, M. Das, J.J. Hickman, T. Boland,* Clemson University

To compare electrophysiological differences between neurons cultured in 2D and 3D environments, neurons dissociated form embryonic rat brain were seeded onto type-I collage thin coating, collagen gel surface, and were entrapped randomly into collagen gel, which were set up for imitating a 2D culture environment, a defined 3D environment and a random 3D environment for neuron culture respectively. Double-immunostaining for MAP-2, a neuronal cell body and dendritic marker, and anti-neurofilament antibody, an axonal marker, was used to identify neuron morphology. Hippocampal neuron polarities and outgrowth of neurites were evaluated by confocal microscope images. The gels were optimized for neuronal 3D cultures by varying concentrations, porosities, and glial cell densities. Surface properties of the gels will be characterized by AFM. Whole-cell patch clamp experiments were carried out to investigate electrophysiology of hippocampal neurons cultured in different conditions. Improvements of patch clamp technique for neuronal 3D culture over traditional 2D culture were applied. Membrane and synaptic properties of neurons in response to their different culture conditions were recorded and compared. Our preliminary results show that hippocampal neurons cultured in 2D and 3D environments exhibited similar passive membrane properties and sodium and potassium currents. Repetitive firings of action potential were found in neurons cultured in 3D environment over 14 days. Results will be presented on functional synapse formation for neurons cultured in 3D environment as measured by the combination of the patch clamp technique and the sharp microelectrode technique. The results of this study indicate that embryonic hippocampal neurons retain a clearly neuronal electrophysiological phenotype in a engineered in-vitro 3D culture condition, which is holding potential in applications ranging from neural tissue engineering to providing active neuronal networks for neuro-computing.

**BI-TuP21 Detection of E. Coli O157:H7 with Surface Plasmon Resonance Biosensor in Complex Matrices*, A. Taylor*, *Q. Yu, S. Jiang,* University of Washington

There is an urgent need for fast, sensitive, and reliable methods for detecting biological warfare agents and food contaminants. Large analytes (i.e. Escherichia coli, Salmonella enteritidis, or Listeria monocytogenes) are difficult to detect and quantify at low concentrations without time-consuming amplifications (i.e. culturing and PCR). E. coli O157:H7, an important food contaminant, was detected with a surface plasmon resonance (SPR) biosensor. However, with amplification, the detection limit was 5x10@super 7@ cfu/ml. In this work, we detect E. coli in both buffer and complex matrices using a home-built SPR. Antibody specific to the O antigen protein expressed on the membrane of the E. coli cell was immobilized on sensing surface via self-assembled monolayers. Atomic force microscopy (AFM) is combined with SPR to optimize surface chemistries and antibody immobilization at the molecular level. Transport of large charged bacteria to the antibody functionalized surface is one important factor limiting the ability to detect low concentrations. Thus, we study the effects of flow rate and pattern on detection. The biosensor was proven to differentiate between E. coli strains O157:H7 and K12 based on the antibody chosen. Furthermore, immunomagnetic separation methods using antibody functionalized magnetic particles were used to separate analytes from complex matrices (i.e. ground beef). The objectives of this work are to improve low detection limit and to minimize non-specific binding for SPR detection of larger-sized analytes in complex matrices.

**BI-TuP22 A Comparative Study of Bone Cell Attachment and Spreading on Various Metal Surfaces by Cryo-SEM and QCM-D*, M. Foss*, *J. Justesen, M. Duch, A.-L. Stranne, J. Chevallier, C. Modin, F.S. Pedersen, F. Besenbacher,* University of Aarhus, Denmark

The detailed understanding of the attachment of bone-forming cells on surfaces is crucial for the development of new generations of orthopaedic implant materials. The goal of these studies is to establish methods for a more quantitative measurement of biocompatibility. Here, traditional methods of cell counting and cell area measurements are correlated with data obtained by the Quartz Crystal Microbalance technique (QCM-D, Q-Sense AB) of cell attachment and spreading. The spreading and attachment of the murine preosteoblastic MC3T3-E1 cells were quantified by cryo-SEM. Cells were seeded and allowed to attach for various periods of time, fixed and snap-frozen in liquid nitrogen. The number of attached cells and the mean area were determined using a standard image analysis program. After attachment the shape of the cells changes from round to an initial maximum spread at the surface. The time-scale for maximum spread at serum-free conditions has been determined to 40 - 50 min, which is in good agreement with QCM-D data where the maximum shifts in both frequency and dissipation are reached at similar time points. The examinations have been applied to several relevant metal surfaces including tantalum and chromium. At cell concentrations ranging from 50,000 cells/ml to 300,000 cells/ml, a variation in the degree of cell spreading is observed between these two metals implying differences in the cell attachment at the chemically different surfaces. However, the viscoelastic properties of the cells are independent of the substrate material. The results point to the establishment of a fast and accurate general method for screening biomaterials with QCM-D. The methods will furthermore be applied to surfaces functionalized by prototype proteins including BSA and fibronectin.

**BI-TuP23 Control of Osteopontin Behavior on Surfaces for Cell Adhesion*, L. Liu*, *S. Chen, B.D. Ratner, S. Jiang,* University of Washington

Osteopontin (OPN) is an important extracellular matrix protein shown to function in wound healing, inflammation and foreign body reaction and has been identified as a potential target for engineered biomaterials. It contains RGD moiety that has been shown to mediate cell adhesion through interaction with integrins. In preferred orientation and conformation, the RGD tripeptide of OPN will be presented to the cells to the greatest extent. However, control of OPN orientation/conformation is seldom investigated so far. In this work, we investigate OPN adsorption and cell adhesion on self-assembled monolayers (SAMs) of alkanethiols terminated with different functional groups to tailor surface properties. Four different alkanethiols terminated with -CH3, -OH, -NH2 and -COOH were used to form surfaces representing hydrophobic, hydrophilic, positive and negative surfaces. Atomic force microscopy (AFM) is used to characterize the adsorption of OPN on various SAM surfaces. Our AFM results show that the amount of adsorbed OPN on -COOH surface is slightly less than that on -NH2 surface. In vitro cell adhesion assay of bovine aortic endothelial cells (BAEC) was performed to test OPN function on various SAMs. Our results show that on -NH2 surface BAEC adhesion is the most and cell appears most spread. Both cell counts and average cell spreading area on -COOH and -CH3 surfaces are much less than those on -NH2 surface. The -OH surface is resistant to both OPN adsorption and cell adhesion. By comparing results from AFM and cell adhesion experiments, it is suggested that the orientation/conformation of OPN on -NH2 positively charged surface is more favorable for cell interaction than on -COOH negatively charged surface. This is consistent with our molecular simulation prediction. Our studies clearly show that surface properties will alter OPN behavior on surfaces, thus cell interactions with OPN. In addition, we use atomic force microscopy (AFM) to image the binding of OPN onto type I collagen monomer. Interactions among extracellular matrix (ECM) proteins are important in many aspects such as orientating ligand proteins and correctly delivering signals into a cell. Recent experiments show that osteopontin (OPN)-incubated collagen I chemically immobilized on poly(HEMA) promotes cell adhesion in vitro. It is speculated that bound OPN on a collagen matrix may have better orientation/ conformation and thus influence its cell-binding ability. Although it has been reported that OPN is able to bind with type I collagen, direct visualization of OPN-collagen binding complexes has not been reported and OPN binding sites on collagen I are still unknown. In our work, AFM is used to image the binding of OPN onto individual triple-helical collagen I monomer on freshly cleaved mica for the first time. Analysis of AFM results clearly shows binding patterns of OPN to collagen I. This work provides a direct means to identify binding among ECM proteins and a better understanding of ECM proteins on cell adhesion.

**BI-TuP24 Tissue Formation of Endothelial Cells on a Microporous Film of Biodegradable Polymer*, T. Nishikawa*, *T.A. Ohzono, J. Hayashi, M. Hara, M.A. Shimomura,* The Institute of Physical and Chemical Research, Japan

Micropatterned surface is considered to be a promising biointerface that can control both surface chemistry and surface morphology of cell culture substrates. The biointerface to be issued in this report is a microporous film of biodegradable polymers. Honeycomb films are microporous films of polymers which are formed by applying moist air to a spread polymer solution. We report the tissue formation of endothelial cells (ECs) on self-supporting honeycomb films. The tissue formation was studied in regard to cell-matrix adhesion, proliferation, and movement. Honeycomb films were prepared from mixtures of biodegradable polymers (poly(L-lactic acid) (PLLA) and poly(@epsilon@-caprolactone) (PCL)) and amphiphilic polymers). Adhesion behavior of ECs was characterized by formation of stress fiber of actin and localization of focal adhesion proteins at the interface between cells and culture substrate. ECs did not form focal adhesions on self-supporting microporous films. The modulated cell adhesion on the microporous films influenced cell-division cycle of ECs. Doubling time represents an average period of cell-division cycle. The doubling time of ECs estimated from the proliferation curves was 20 hrs on flat cast film of PCL and 27 hrs on microporous films of PCL. Micropores can be considered to be pathways connecting two sides of a self-supporting honeycomb film of PLLA. ECs were seeded onto a top side of a honeycomb film having an average poresize of 5 µm and an average thickness of 3 µm. At the day 11 of culturing, the cell culture was observed by confocal microscopy after staining filamentous actin of ECs and a honeycomb film with fluorescent probes. Monolayer of ECs was confirmed at each side of the honeycomb film. This suggests that ECs attached onto the top side pass through the micropores, appear on the bottom side of a honeycomb film, grow, proliferate, and finally cover the both sides of the honeycomb film.

High-k Gate Dielectrics and Devices Topical Conference Room Hall A-C - Session DI-TuP

Poster Session

DI-TuP1 Investigation of Initial Growth Stage of HfO@sub 2@ Films on Si (100) Grown by Atomic-layer Deposition using In-situ Medium Energy Ion Scattering, ***H.S. Chang***, *H. Hwang,* Kwangju Institute of Science and Technology (KJIST), South Korea; *M.-H. Cho, Y.J. Cho, K.J. Kim, D.W. Moon,* Korean Research Institute of Standards and Science (KRISS), South Korea

The initial growth stage of HfO@sub 2@ films on p-type Si(100) grown by atomic-layer deposition (ALD) was investigated using in-situ medium energy ion scattering (MEIS). The interaction between adsorbed HfCl@sub 4@ molecules and Si substrate was examined in relation to the film thickness, substrate temperatures, and surface states of the Si substrates. Interfacial reaction between Hf and Si at the initial growth stage was occurred and significantly depended on the surface state of the Si. The hafnium silicate with an amorphous structure was grown on the oxidized Si substrate at an initial growth stage. In particular, the interfacial layer thickness and the stoichiometry of the layer were depended on the surface state of Si substrate. As thickness of the film increased, the silicate formation was gradually changed into HfO@sub 2@ state. The physical analysis of the films with XPS and TEM also supported the interfacial reactions. Based on the interfacial interaction at the initial growth stage, we suggested the model for the interaction between Hf and Si at the initial growth stage in relation to the atomic size, bonding characteristics, and formation energy. This study will be helpful to understand the interfacial reactions at the initial growth stage and to control the reactions for the application of high-k dielectrics.

DI-TuP2 Effects of Annealing Temperature on the Characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ High-k Gate Oxides, ***H.-D. Kim***, *Y. Roh, D. Jung, N.-E. Lee,* Sungkyunkwan University, Korea

Several candidates for the future high-k gate oxides have been extensively studied by many research groups to overcome the problems such as large leakage current caused by the direct tunneling through extremely thin SiO@sub 2@. Recently, we reported that simple oxidation of sputtered Hf films on Si produces HfO@sub 2@/HfSi@sub x@O@sub y@ high-k oxides with excellent properties. We argued that the effective k of HfO@sub 2@/HfSi@sub x@O@sub y@ film may be controlled by changing the thickness ratio between HfO@sub 2@ and HfSi@sub x@O@sub y@. In this work, we further investigated the characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ high-k gate oxides to clarify the roles of annealing process. The 1.5 nm Hf film was directly deposited on Si substrate by sputtering at plasma power of 50 W for 4 min. Oxidation was performed at 500 °C for 60 min, followed by annealing at 500-900 °C in furnace under N@sub 2@ ambient. Pd gate metal was thermally evaporated on the HfO@sub 2@ film. Using the physical and electrical measurement techniques, we confirmed that the oxidation of the thin Hf films on Si results in the HfO@sub 2@/HfSi@sub x@O@sub y@ stack layer with the excellent electrical properties; negligible hysteresis, excellent EOT value (1.2 nm) and low leakage current (~2 X 10@super -3@ A/cm@super 2@ at 1.5 V after compensating V@sub fb@). Furthermore, we found that the level of leakage current decreases as annealing temperature increases. However, over 500 °C, annealing deteriorates the EOT value; e.g., 1.2 and 1.7 nm EOT values were obtained from 500 and 900 °C samples, respectively. We speculate that both thickness increase of HfO@sub 2@/HfSi@sub x@O@sub y@ films and the formation of additional SiO@sub 2@ layer between HfSi@sub x@O@sub y@ and Si cause these phenomena. We therefore suggest that annealing temperature must be carefully controlled to maintain the excellent characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ high-k gate oxides.

DI-TuP3 Thermal Stability of Al- and Zr- doped HfO@sub 2@ Thin Films by DC Magnetron Sputtering, ***Y.E. Hong***, *Y.S. Kim, D.H. Ko, D.W. Lee,* Yonsei University, South Korea; *J.-H. Ku,* Samsung Electronics, South Korea

Currently, high-k materials are under consideration as replacements for SiO@sub 2@ because physically thick film with high dielectric constant is possible solution for reducing leakage current. Among some metal oxides such as Al@sub 2@O@sub 3@, ZrO@sub 2@, and HfO@sub 2@, particularly HfO@sub 2@ exhibits excellent material properties such as high permittivity of up to 30, energy gap of 5.6eV and thermal stability in contact with silicon. However, after post-deposition annealing above 400°C, as-deposited amorphous HfO@sub 2@ crystallizes which may induce grain boundary leakage current. In addition, annealing in an oxygen rich ambient leads to fast diffusion of oxygen through the HfO@sub 2@, resulting in the growth of uncontrollable interfacial layer between HfO@sub 2@ and silicon substrate. In this study, we investigated comparatively the thermal stability properties of HfO@sub 2@ based films with Al- and Zr-doping. HfO@sub 2@ was prepared by sputtering Hf target in a mixture of oxygen and argon at room temperature. Al- and Zr-doping is achieved by co-sputtering using Al and Zr target. And the compositions of the doped films were controlled by target power. After the formation of the films, annealing at 500~900°C for 5min by furnace in N@sub 2@ ambient was followed. The compositions and the chemical states of the oxide films were confirmed by RBS and XPS. The crystallization temperature of the HfO@sub 2@ film which has 10% Al was 900°C. However, most of the Zr-doped HfO@sub 2@ films were crystallized from as deposited condition. As an annealing temperature increases, HRTEM analyses of the all doped films show the increased interfacial layer thickness, and the interfacial layer of the Zr-doped HfO@sub 2@ films is thicker than the Al-doped. The increased CET and leakage current values through CV/IV measurements and dielectric constant difference between Al- and Hf-doped HfO@sub 2@ films will be presented and discussed.

DI-TuP5 NH@sub 3@ Nitridation Effect on HfO@sub 2@-Al@sub 2@O@sub 3@ Films in the MOS Capacitor, ***C. Lee***, *J. Choi, M. Cho, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

High-k gate dielectrics, such as HfO@sub 2@ and Al@sub 2@O@sub 3@, have been investigated as an alternative to SiO@sub 2@ for low power device due to high dielectric constant, thermodynamic compatibility of the interface with Si substrate, and a relatively large band gap. We investigated the nitrogen diffusion behavior and electrical characteristics, especially flat band voltage (V@sub fb@) shift and V@sub fb@ hysteresis by NH@sub 3@ nitridation of the MOS capacitors. The nitrided MOS capacitors include the various high-k gate dielectric stacks such as Pt gate/HfO@sub 2@/p-type Si, Pt gate/HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si, and Pt gate/capping Al@sub 2@O@sub 3@-HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si. HfO@sub 2@ and Al@sub 2@O@sub 3@ films were deposited on p-type epitaxial Si (100) wafers with a resistivity of 1 @ohm@cm by atomic layer deposition (ALD) technique using HfCl@sub 4@, Al(CH@sub 3@)@sub 3@ and H@sub 2@O at 300°C after RCA SC1 and HF cleaning. Post deposition annealing (PDA) of the samples was performed with rapid thermal annealing (RTA) at 700°C, 800°C, and 900°C in NH@sub 3@ for 30 seconds. Post-metallization annealing (PMA) of Pt-top electrodes was performed at 400°C for 30 min. under a 5% H@sub 2@ + 95% N@sub 2@ atmosphere. V@sub fb@ shifted negatively with increasing nitridation temperature, but it moved positively with increasing Al@sub 2@O@sub 3@ thickness. HfO@sub 2@-Al@sub 2@O@sub 3@ film showed excellent V@sub fb@ shift and hysteresis characteristics when it was post-metallization annealed in NH@sub 3@ at 800°C for 30 seconds. NH@sub 3@ nitridation effect on Pt gate/HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si MOS capacitors with increasing PDA temperature was analyzed by electrical evaluation, Auger Electron Spectroscopy (AES), atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM).

DI-TuP6 Structural and Electrical Characterization of Aluminum Oxynitride Thin Films Obtained by RF-Sputtering*, **J.J. Araiza,*** UAZ, Mexico*; M.A. Aguilar,* CICATA-IPN, Mexico, Spain*; C. Falcony, M. Jergel,* CINVESTAV-IPN, Mexico

The structural and electrical characteristics of aluminum oxynitride thin films deposited on silicon substrates by rf-sputtering are reported. The properties of the films were studied as a function of the deposition parameters, such as substrate temperature, RF sputtering power and the relative amount of argon and nitrogen gases introduced to the chamber. The films were characterized by atomic force microscopy, transmission and scanning electron microscopy, X ray diffraction, Infrared and Uv-vis spectroscopy and ellipsometry. Metal-Oxide-Semiconductors structures were also fabricated with the films deposited. Films with characteristics close to aluminum oxide and aluminum nitride were obtained, depending on the deposition parameters. It was found that the films can withstand electric fields up to 4.5 MV/cm, without observing destructive breakdown, with dielectric constants up to 8.7. In addition, the as deposited films present a surface roughness lower than 1.6 nm, refractive indexes from 1.5 to 2.0 and deposition rates up to 7.0 nm/min.

DI-TuP7 Plasma and Thermal Etching of High-k Materials for ALD Chamber Cleaning*, B. Ji, **D. Wu**, R.M. Pearlstein, S.A. Motika, E.J. Karwacki, M.J. Plishka,* Air Products and Chemicals, Inc.

High dielectric constant (high-k) materials such as Al@sub 2@O@sub 3@, HfO@sub 2@, and ZrO@sub 2@ are deposited onto semiconductor wafer surfaces by atomic layer deposition (ALD) in integrated circuits manufacturing. High-k ALD reactors must undergo periodic chamber cleaning to remove deposition residues from the internal surfaces of the reactor in order to maintain production yield. Due to their high chemical inertness and extremely low volatility, etching and cleaning high-k deposition residues has been technically challenging. By combining thermochemical calculations and experimental screening, we have identified BCl@sub 3@ as the most effective reagent for removing high-k materials from ALD chambers. We will report both plasma and thermal etching of Al@sub 2@O@sub 3@, HfO@sub 2@, and ZrO@sub 2@ using BCl@sub 3@. We will discuss the chemical mechanism of BCl@sub 3@-metal oxide reaction, and the influence of various process parameters on high-k materials etch rate.

Electronic Materials and Devices
Room Hall A-C - Session EM+SC-TuP
Poster Session

EM+SC-TuP2 A New Method to Produce Silicon-on-Insulator Wafer-Ar@super +@ Implantation with H@super +@-plasma Processing*, **B. Chen,*** New Jersey Institute of Technology*; A. Usenko,* New Jersey Silicon Wafer Tech*; W. Carr,* New Jersey Institute of Technology

In this paper, we describe a new method to fabricate SOI wafer. Ar+ ions were implanted into Si(100) at energy ranging from 30 KeV to 200 KeV and dose from 1*10@super 15@ to 1*10@super 16@ cm@super -2@. To avoid amorphization, the samples were thermally insulated and the beam current was maintained high enough (about 3mA/cm2). After implantation, pieces of these samples were subjected to thermal annealing at temperature ranging from 200°C to 800°C. The evolution of microstructure of these samples were investigated by TEM. In the annealed samples, Argon clusters are found in either 2-D cavities (Nano-cracks) or 3D cavities (bubbles). Then, these samples were processed by H+ plasma. Nano-cracks and bubbles will help trapping H diffused from the surface. Then this hydrogenated wafer was bonded with the other oxidized wafer. After annealed at 600 °C, a thin layer will be transferred from the hydrogenated wafer to the oxidized one. In this way, we can get the thin layer SOI wafer.

EM+SC-TuP3 Effects of Remasking Materials and Dimensions on Sidewall Roughness of Deep Etched Waveguide*, **J.W. Bae**, W. Zhao, J.H. Jang, I. Adesida,* University of Illinois at Urbana Champaign*; A. Lepore, M. Kwakernaak, J.H. Abeles,* Sarnoff Corporation

Photonic devices and circuits based on InP/InGaAsP materials require optical waveguides with highly anisotropic and smooth sidewall profile to achieve good optical mode quality and low loss performance. In the fabrication of optical waveguides, critical factors include lithography, masking, and etching. Each factor introduces various degrees of sidewall roughness (SWR). The rough sidewall of waveguides causes scattering loss, which is one of the major sources of optical loss in deep etched waveguides. Therefore, the characterization of sidewall roughness for the various processes is required. In this study, the SWR of InP/InGaAsP heterostructures fabricated using inductively-coupled-plasma etching (ICP) was investigated as a function of the remasking materials and the dimensions of masks. Among the factors introducing SWR, lithography and etching conditions were fixed at optimum condition that was previously determined. Remasking materials including silicon dioxide and silicon nitride were deposited on NiCr (40 nm)/SiO@sub 2@ (600 nm) mask using plasma enhanced chemical vapor deposition. Also, the effects of thicknesses of NiCr mask layer and remasking materials on the SWR were investigated in the range from 40 to 100 nm and 25 to 100 nm, respectively. Atomic force microscopy (AFM) was utilized to directly measure the SWR of waveguides. Electron beam lithography was used to delineate specially designed line patterns that permitted AFM tips to be directly utilized to measure SWR. Results on SWR from various sources will be presented and discussed with relation to optical losses.

EM+SC-TuP4 Sub 100 nm Radius of Curvature Wide-Bandgap III-Nitride Vacuum Microelectronic Field Emitter Structures Sharpened by ICP Etching*, **P.B. Shah**, M.D. Derenge, B.M. Nichols, T.S. Zheleva, K.A. Jones,* US Army Research Laboratory

Nanometer scale tips make possible cold cathodes that when used in vacuum microelectronic (VME) devices bring together the advantages of high power that vacuum tubes provide with the advantages of instantaneous turn-on (no need for tedious warm up), miniaturization and long device lifetime. The advantage of gallium nitride (GaN) in these applications is it’s very small electron affinity (energy necessary to remove the electron from the material surface into vacuum.) Aluminum nitride (AlN) is even better because it may exhibit a negative electron affinity. For vacuum microelectronic devices we are developing field emitters using inductively coupled plasma (ICP) etching. This technique involves two steps, first, a fast deep etch to define columns of a given aspect ratio followed by etches to sharpen the columns. We investigate and optimized gas flow rates, etch times, gas pressures, ICP coil RF power, chuck RF power, and masking material. Advantages of this technique over other demonstrated techniques for producing GaN based field emitters such as selective area deposition are that it can be easily transferred to existing fabrication lines and that it allows for easy definition of complex VME device structures. Using an ICP etch high aspect ratio field emitters were fabricated from MOCVD grown GaN exhibiting a tip radius of 80 nm and height of 900 nm. Currently we are optimizing the technique to achieve a smaller GaN tip radius. In parallel an etch process is being optimized to produce field emitter tips from AlN. Our presentation will discuss optimized etch chemistries and preliminary electrical performance along with surface passivation and cleanup techniques.

EM+SC-TuP5 A Study of Silicon Carbide (SiC) Etching Characteristics using Magnetized Inductively Coupled Plasmas (MICP)*, **H.Y. Lee**, D.W. Kim,* Sungkyunkwan University, South Korea*; Y.J. Sung,* Samsung Advanced Institute of Technology, South Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

SiC is an attractive material for electronic devices operating at high power levels and high temperatures. In addition, the large Si-C bonding energy makes the components made of SiC resistant to chemical attack and radiation, and thus attractive for the applications in harsh environments. SiC is also used as a substrate for microelectromechanical system(MEMS) and GaN epitaxial devices due to its excellent electrical, thermal, and mechanical properties. However, due to its stability and inertness of SiC in conventional acid or base solutions at normal temperatures, plasma-based etching plays a important role in patterning SiC for the fabrication of electronic devices. Optimum etch strategies for the fabrication of these devices demand excellent profile control, low ion-induced etch damage, smooth etch surfaces, and high etch rates. In this article we report on the SiC etching in SF6 based discharges and the etch selectivity of SiC over various mask materials to obtain high etch rates and low surface damages. The etch characteristics such as etch rates, etch selectivities, and etch profiles in addition to the plasma characteristics were investigated as functions of source power, and dc bias voltage to the substrate, gas mixtures and applied external magnetic field strength.

EM+SC-TuP6 Electroless Copper Deposition as a Seed Layer on TiSiN Barrier*, **Y.C. EE**, Z. Chen, S. Xu,* Nanyang Technological University, Singapore*; L. Chan, K.H. See, S.B. Law,* Chartered Semiconductor Manufacturing Ltd., Singapore

Electroless deposition of copper as a seeding technology has received considerable attention in back-end-of-line device fabrication. This work explores the effects of plasmas processing parameters such as argon gas flow rate and nitrogen plasmas treatment time on the properties of electrolessly plated Cu on TiSiN barrier layers formed by a low-frequency inductively coupled plasma process. TiSiN films have emerged as a promising candidate for the future generation barrier material because of its good adhesion to Cu. The properties of deposited electroless copper were characterized by X-ray diffraction (XRD), four-point resistivity probe, atomic force microscopy (AFM) and field emission secondary electron microscope (FESEM). Comparison is made with the Cu seed layer on TiN. It is found that the required palladium activation time is greatly reduced on TiSiN. The results also show that there is a preferred crystal orientation of Cu in (111) plane. Cu grain size is within the range of 24-33 nm. The sheet resistance of the Cu seed layer is less than 1.2 @ohm@ per square area. The roughness of plated Cu layer largely follows the one of the underlying TiSiN. Good surface coverage of electroless Cu seed layer on TiSiN is obtained in our experiments.

EM+SC-TuP8 Thermal Conductivity Analysis of Highly-Oriented Diamond Films for Silicon on Diamond Electronic Applications*, **N. Govindaraju,*** North Carolina State University*; A. Aleksov,* North Carolina State Univeristy*; F. Okuzumi, G.N. Yushin,* North Carolina State University*; S.D. Wolter, J.T. Prater,* Army Research Office / AMSRL- RO-PM*; Z. Sitar,* North Carolina State University

The extremely high thermal conductivity of diamond (~ 22 W/cmK) along with its wide bandgap (5.3 eV) and high specific resistance (~10@super 12@ @ohm@cm) make it an alluring material for incorporation as a dielectric in Silicon On Diamond (SOD) technology. SOD offers enhanced thermal transport properties in addition to the speed and power enhancing properties offered by the traditional Silicon On Insulator (SOI) technology. As the single crystal growth of diamond on silicon proves elusive, the pragmatic approach would entail the use of Highly Oriented Diamond (HOD) films. It is imperative, for the proposed SOD technology, that the thermal properties be well characterized. The current study seeks to fulfill this requirement by measuring all aspects of thermal conductivity of HOD films. Commercially available thin wire thermocouples (Type K) were used in conjunction with a thin film heater to carry out steady state measurements using the traditional heated bar technique. Preliminary results indicated an average value of ~ 8 W/cmK for measurements done on free standing HOD films. To further refine the accuracy of the measured thermal conductivity, measurements using a thin film heater and thin film thermocouples were implemented. Studies by Graebner@footnote 1@ have shown that grain size has a great impact on the thermal conductivity of randomly oriented polycrystalline diamond. Since it is known that the size of the columnar grains varies as a function of diamond film thickness, we studied thermal conductivity as a function of thickness. This was achieved by etching away the diamond using an argon-oxygen plasma and implementing the thermal measurements recursively. All thermal conductivity data has been measured as a function of temperature. @FootnoteText@@footnote 1@J.E. Graebner, et. al., Diamond and Related Materials, 2 (1993), 1059-1063.

EM+SC-TuP9 Deposition and Field-Emission Characterization of Electrically Conductive Diamond-Like Amorphous Carbon Films*, **H. Kinoshita**, R. Ikuta, K. Sakurai, S. Murakami,* Shizuoka University, Japan

Diamond-like amorphous carbon films doped with nitrogen (DAC:N) were formed using intermittent supermagnetron plasma chemical vapor deposition (CVD) technique,@footnote 1@ for the fabrication of high performance field emitters. DAC:N films were deposited on Si and glass wafers using i-C@sub 4@H@sub 10@/N@sub 2@ plasma to investigate the influence of discharge-off time, at lower-electrode temperature of 100°C, upper- and lower-electrode rf powers (UPRF/LORF) of 800W/100W, and electrode spacing of 40mm. Discharge-on time was 1min, and off time (cooling time) was controlled to 15sec-10min. With decrease of cooling time, resistivity was decreased. At cooling time of 15sec, however, DAC:N film was peeled off from a wafer by its plasma heating. By reducing the electrode spacing from 40mm to 20mm, resistivity and optical band gap of DAC:N film deposited at 800W/800W rf powers and 5min cooling time decreased to 0.11@ohm@cm and 0eV, respectively. A DAC:N film of 500Å thickness was deposited on a n-Si wafer at 850W/100W, and was patterned in many island shapes of 1µm x 1µm sizes. Using it, a threshold emission current density of 0.01mA/cm@super 2@ was observed at the electric field of 12V/µm. At the electric field of 21V/µm, maximum field-emission current density (IMAX) of 3mA/cm@super 2@ was observed at the electric field of 21V/µm. A flat DAC:N film of 700Å thickness was deposited on a n-Si wafer at 800W/800W. Using the flat DAC:N film, a threshold electric field of 18V/µm, and IMAX of 2.2mA/cm@super 2@ was observed at the electric field of 32V/µm. @FootnoteText@ @footnote 1@H.Kinoshita and T.Murakami, J.Vac.Sci.Tecnol.A 20, (2002) 403.

EM+SC-TuP10 Avalanche Ballistic Electron Emission Microscopy (BEEM) Studies of Subthreshold BEEM Current and STM Induced Photocurrent*, **C. Tivarus**, E.R. Heller, J.P. Pelz,* The Ohio State University

We present Ballistic Electron Emission Microscopy (BEEM) studies where the metal is deposited directly over an avalanche pn diode. Because the avalanche diode provides a hot electron gain of up to many millions, intrinsic BEEM current noise levels as low as 20 aA are possible. Hence, this technique can be very useful in nm-resolution studies of electronic transport in structures that otherwise show very low ballistic current for traditional BEEM measurements. Using this technique we were able to accurately study the shape of the subthreshold regions of the BEEM current-voltage curves where all the BEEM current is due to thermally excited electrons above the Fermi level in the STM tip. One of the problems encountered when interpreting the measurements for this avalanche BEEM technique is the presence of the Scanning Tunneling Microscopy induced photo current (STM-PC). Since this STM-PC resembles a normal BEEM current, [E.R. Heller and J.P. Pelz, Appl. Phys. Lett. to be published] it can interfere with BEEM measurements of structures with low signal and/or intrinsic BEEM threshold voltage larger than the substrate bandgap. We have characterized this low signal STM-PC effect using the high photon sensitivity and large collector solid angle of the underlying avalanche diode and will discuss methods to distinguish true BEEM current from STM-PC.

EM+SC-TuP11 Submicron MTJ Cell Selectivity and Switching Field Analysis using Scanning Probe Microcopy Technique*, **D.S. Kim**, J. Heo, I.S. Chung,* SungKyunKwan University, Korea

It has been reported that in a Synthetic Anti Ferromagnet (SyAF) deposited MTJ bit, the demagnetizing magneto static domain will be diminished regardless of its size with a very low aspect ratio. Thus, the anisotropy ratio and the size of the MTJ (Magnetoresistance Tunneling Junction) cell can be reduced more. Scanning Probe Microscopy (SPM) analysis has great advantage in submicron MTJ bit characterization, since it does not need to make a MTJ contact. We have successfully attained the H-R curve using SPM under controlling external magnetic field for submicron scaled MTJ bits. Therefore, We made to investigate the issues in selectivity characteristics and switching field characteristics in terms of various anisotropy ratio and sizes. We can attain the asteroid curve by applying both hard axis and easy axis magnetic field simultaneously either by rotating sample in diagonal or by applying current through write line. We found the newly introduced SPM diagonal field appliance method would be more efficient than conventional ones, in investigating a MTJ bit switching field characterization.

EM+SC-TuP12 The Analysis on the Origin of High Resistivity in Polycrystalline CdZnTe Thick Films*, **K.H. Kim**, S.Y. Ahn, M.H. Kim, Y.J. Park, K.N. Oh,* Korea University*; S.U. Kim,* Korea University, Korea

The CdZnTe have an inherently high stoping power, an excellent carrier transport property, and relatively wide band gap energy. Therefore detectors using this materials have the potential for sufficient X-ray sensitivity and DQE at a sufficiently low leakage current.@footnote 1@ Although research results have been presented on single crystal CdTe and CdZnTe detectors with small sized silicon readout devices, it would be difficult to apply these results to large area flat-panel detectors. Alternatives of single crystal, we have grown large area (10 x 10 cm @super 2@) polycrystalline CdZnTe films by thermal evaporation method. The thickness, average grain size and Zn composition was 150 µm , 3 µm and 4%. Resisitivity of CdZnTe films is in the order of 2 x 10@super 9@ @Omega@cm which is comparable that of CdZnTe single crystal samples. In X-ray detectors, high leakage current limits the maximum integration time of the a-Si array for X-ray imaging applications so that high resistivity receptor material is required. Recent reports have identified deep level defects which are likely to be associated with semi-insulating property.@footnote 2@ Based on multiple trapping model, the localized state distributions of high resistivity polycrystalline CdZnTe from TOF (time of flight) transient current are examined using Laplace transform and Tikhonov reularization methods.@footnote 3@ We found 3 different deep localized states above valence band related to the resistivity. In TOF measurements, indium was used as top electrode to form Schottky type cotact to prevent carrier injection. @FootnoteText@@footnote 1@ S. Tokuda, H. Kishihara, S. Adachi, T. Sato, Y. Izumi, O. Teranuma, Y. Yamane, and S. Yamada, Proceedings of SPIE Vol. 4682 , 30 (2002)@footnote 2@ A. Zumbiehl, S. Mergui, M. Ayoub, M. Hage-Ali, A. Zerrai, K. Cherkaoui, G.

Marrakchi, Y. Daricim, Material Science and Engineering B 71, 297 (2000)@footnote 3@ J. Weese , Comput. Phys. Commun. 69, 99 (1992).

EM+SC-TuP13 Electrical, Thermal, and Elastic Properties of MAX Phase Materials*, S.E. Lofland, P. Finkel,* ***J.D. Hettinger****,* Rowan University*; M.W. Barsoum, A. Ganguly, S. Gupta,* Drexel University*; K. Harrell, J. Palma, B. Seaman,* Rowan University

We have characterized physical properties of several materials in the MAX phase family.@footnote 1@ These materials derive their name from the basic chemical formula M@sub n@AX@sub n-1@, where M is an early transition metal, A is an A-group element, and X is either N or C. These highly conductive ceramics are readily machinable and possess very desirable structural properties.@footnote 1@ From a systematic study of the transport properties, we find most of these materials require two conduction bands, one consisting of holes and the other of electrons, to explain the electrical conductivity, Hall coefficient, and magnetoresistance. A Wiedemann-Franz analysis of the thermal conductivity suggests that, in most of the materials investigated, the mean-free-path of the entropy carriers is the same as that for the charge carriers. The Lorenz number at room temperature indicates that the thermal conductivity is mostly electronic in nature. We have also performed heat capacity and speed of sound measurements on many of the MAX phase materials allowing the extraction of the elastic moduli and Debye temperatures. We find very good agreement between the Debye temperature as determined from specific heat and that determined from elastic measurements. We find that the electronic term in the specific heat depends strongly on the transition metal element and very weakly on the A-group element. In general we find that the transition metal element impacts the electrical properties more dramatically than the A-group element. In contrast, the A-group element seems to more strongly impact the elastic properties of the materials. The justification for these statements will be presented. This work was supported by the New Jersey Commission on Higher Education, the NSF under grants DMR-0072067 and DMR-0114073 and Rowan University. @FootnoteText@@footnote 1@M. W. Barsoum, Prog. Solid State Chem. 28, 201(2000).

EM+SC-TuP14 Photo-electronic Properties of n-ZnO:Al/p-Si Heterojunctions*,* ***F. Mohammed****, A. Pontarelli, S. Bokhari, J.R. Doyle,* Macalester College

We present a study of the photo-electronic properties of n-ZnO:Al/p-Si heterojunctions. Transparent conducting ZnO:Al layers having resistivities < 1 x 10@super -3@ ohm-cm and transparencies of about 80% are deposited on p-Si using reactive dc magnetron sputtering. In some devices a higher resistance ZnO:Al buffer layer was inserted between the highly conducting ZnO:Al and silicon. The junctions are characterized by dark current-voltage measurements as a function of temperature (IVT), capacitance-voltage measurements (CV), spectral response measurements, and conversion efficiency. Excellent rectification is obtained, with soft breakdown voltages typically in the range of 3-5 V reverse bias. Analysis of the IVT characteristics imply that the carrier transport is mainly tunneling limited, and the CV measurements imply a barrier height of about 1 eV. The presence of the buffer layer has no systematic effect on the dark junction characteristics. However, the buffer layer devices exhibited a significantly enhanced spectral response and efficiency, with the best devices resulting in a 3 % conversion effeciency under 100 mW/cm@super 2@ white light illumination. Possible roles of the buffer layer in enhancing the photoresponse will be discussed, as well as the potential application of these devices as photodetectors and solar cells.

EM+SC-TuP15 Effects of Threading Dislocations and In Composition on Structural and Optical Properties in InGaN/GaN Triangular-shaped Quantum Wells*,* ***R.J. Choi****, Y.B. Hahn, H.J. Lee,* Chonbuk National University, Korea

Structural and optical properties of InGaN/GaN multiple triangular quantum well (QW) structures have been studied with different threading dislocation (TD) densities and wavelengths (or In compositions). As the In composition increased, the extent of variation of the linewidth of photoluminescence (PL) measurements increased over a temperature range of 13 - 300 K. The structural quality of the quantum wells is not consistent with the PL intensity. More fluctuation of the local In composition and severer degradation of PL intensity at a higher TD density were observed, which were attributed to the stress field created by the dislocations. Observations by X-ray diffraction, transmission electron microscopy, and monochromated scanning cathodoluminescence imaging revealed that the optical property of the InGaN/GaN triangular-shaped MQWs is greatly affected by structural imperfections.

EM+SC-TuP16 Electroluminescence in the Infrared Region from Thin Film Zinc Sulfide Doped with Rare Earth Fluorides*,* ***D. DeVito****, N. Shepherd, A.S. Kale, W. Glass, M.R. Davidson, P.H. Holloway,* University of Florida

While electroluminescent phosphors are routinely studied for flat panel display technology, infrared emission is often ignored. A variety of applications exist for infrared emitters, including chemical analysis, infrared displays, communications and therapeutic medical treatment. Thin film electroluminescent devices could serve as highly efficient, reliable, rugged infrared emitters. Electroluminescence in high-field devices is generated by impact excitation and subsequent radiative relaxation by electronic transitions located on the luminescent centers. Rare earth elements, including erbium, terbium and holmium, are good choices for luminescent centers as they exhibit many transitions ranging from visible (550 nm) to the mid-infrared wavelengths (5 micron), as will be documented with experimental data from ZnS films deposited by RF planar magnetron sputtering. Among these, holmium is particularly interesting because of transitions at 1210 nm, 1400 nm, 2.9 micron, 4.8 micron and 5 micron. Suppression of emission at visible wavelengths and enhanced infrared emission by selective processing of sputter deposited films is achieved through proper selection of annealing temperature. Optimum luminance at characteristic wavelengths was developed by the appropriate choice of luminescent center and activator concentration, deposition temperature and annealing conditions. Low temperature device measurements are presented to evaluate the effects of room temperature on the number of energy transitions and energy transfer mechanisms in thin film devices.

EM+SC-TuP17 Visible and Near-infrared Electroluminescence from Er-doped GaN Thin Films Prepared by RF Planar Magnetron Sputter Deposition*, J.H. Kim,* ***M.R. Davidson****, N. Shepherd, P.H. Holloway,* University of Florida

Erbium (Er)-doped GaN thin films were prepared by radio frequency (RF) planar magnetron co-sputtering of a commercial GaN target and a metallic Er target in a pure nitrogen atmosphere. The alternating-current thin-film electroluminescent (ACTFEL) devices were fabricated using a standard half-stack configuration with an Al metal electrode, GaN:Er electroluminescent layer, ATO (Al@sub2@O@sub3@-TiO@sub2@) dielectric, and ITO (indium-tin-oxide) transparent conducting electrode. Visible and near-infrared (NIR) EL emission peaks were observed from the fabricated devices at 530, 550, 660, 1000, and 1550 nm. These emissions were attributed to the Er@super3+@ 4f - 4f intrashell transitions from the @super2@H@sub11/2@, @super4@S@sub3/2@, @super4@F@sub9/2@, @super4@I@sub11/2@, and @super4@I@sub13/2@ excited-state levels to the @super4@I@sub15/2@ ground-state, respectively. GaN host films had a wurtzite polycrystalline structure with a preferred orientation in the [0001] direction perpendicular to the film surface. Full width at half maximum (FWHM) of the (0002) wurtzite-GaN diffraction peak and the lattice constant, c both increased from 0.38° to 0.45° and from 5.18 Å to 5.205 Å, respectively, as the Er concentration in GaN host was varied from 0 to around 5 at.%, indicating that incorporation of larger Er atoms into GaN host expands the host lattice. The optimum concentration of Er was determined to be around 1 at.% for both of the green 530 nm and NIR 1550 nm emissions.

Microelectromechanical Systems (MEMS)

Room Hall A-C - Session MM-TuP

Poster Session

MM-TuP1 Electrostatic Actuation in BioMEMS*,* ***T.L. Sounart****, T.A. Michalske,* Sandia National Laboratories

Electrostatic MEMS actuators exhibit fast response times and are easily integrated into microsystems because they can be fabricated with standard silicon IC micromachining processes. Although electrostatic actuators have been used extensively in "dry" MEMS, they have received little attention in microfluidic bioMEMS, despite the added advantage of 80 times the energy density in water relative to that in air. This is probably because electrostatic actuation in most liquid media presents new challenges such as electrolytic gas generation, anodic oxidation, and electrode polarization. Electrolysis is avoided completely at O(1) V electrode potentials, and although such potentials are also too low for actuation in air, they are sufficient to actuate many devices in water. Unfortunately, at equilibrium ionic solutes in conducting fluids screen the electrode potential (electrode polarization) and disable the actuator. We are currently investigating electrostatically-driven biological sensors and other bioMEMS devices by employing ac drive signals to prevent charge screening, which enables electrostatic actuation in many liquids, at potentials low enough to avoid electrochemistry. Here we measure the frequency response of an interdigitated silicon comb drive actuator in liquids spanning a decade of dielectric permittivities and four decades of conductivity, and present a simple theory that predicts the characteristic actuation frequency. The analysis demonstrates the importance of the native oxide on silicon actuator response, and suggests that the actuation frequency can be shifted by controlling the thickness of the oxide. For native silicon devices, actuation is initiated at frequencies less than 10 MHz, in electrolytes of ionic strength up to 100 mmol/L, and thus electrostatic actuation is feasible in many bioMEMS and other microfluidic applications.

MM-TuP2 Capillary Electrophoresis On-chip: Glass and Polymeric Materials for Cell Fabrication*, **Y. Mourzina**, A. Offenhaeusser,* Research Centre Juelich, Germany

The advances of bioanalytical chemistry and biotechnology stimulated interest in on-chip integrated microfluidic systems and analytical techniques for accurate, precise and high-effective analysis of proteins. Capillary electrophoresis on chip is rapidly developing field by learning on fabrication technologies in the field of MEMS. In the present work, two approaches to realize 3-D microstructures in glass wafers or polymeric materials for on-chip capillary electrophoretic separation of proteins are presented. The microchannel configurations in Pyrex glass wafers have been realized by means of photolithography, thin film deposition and etching steps. The dimensions of the channels are 6 to 16 µm depth and 40 to 120 µm width. Different processing sequences are compared. The structures have been visualized by means of REM to observe the profile and the edge roughness. Special attention has been paid to the optimization of the deposition of the metal thin films as sacrificial layer for glass etching, and to the influence of the composition of the etch solution on glass etch velocity, undercut phenomenon and the quality of the structures. Soft lithography is presented as an alternative approach to realize microfluidic channels in polymeric material. The master has been fabricated of the high aspect ratio SU 8 photoresist on Si wafers. Depending on the type of photoresist and the parameters of processing, the masters with different height of the structures (10 to 25 µm) have been obtained. The master has been used for microreplication in polymer PDMS. The dimensions of the separation channels of the polymeric devices are 10 to 25 µm depth and 20 to 80 µm width. Fluorescent microscopy was used to visualize the microchannels. To validate the performance of on-chip electrophoresis, the results of the separation of phosphoproteins in the prepared devices will be compared with the resolution of the conventional gel electrophoresis.

MM-TuP3 Stiction Measurements Made with an Atomic Force Microscope on Test Structures Mounted with Various Die-Attach Materials*, **E.J. Thoreson,*** Worcester Polytechnic Institute*; J. Martin,* Analog Devices*; N.A. Burnham,* Worcester Polytechnic Institute

An atomic force microscope (AFM) was used to determine the stiction between silicon oxide tips and silicon oxide substrates coated with a few angstroms of phenylsiloxane. The substrates were mounted in their usual packaging with three different types of die-attach materials, which were silicone, polyimide silicone, and silver glass. There was also a control group in which the substrates were not attached. The packages were opened and an AFM determined the adhesive force between the AFM tip and the substrate in force spectroscopy mode. A preliminary data set showed that the adhesive force normalized to the tip radius was respectively twice and four times as big for the polyimide silicone and silver glass as for the control group and silicone, the latter two being close in value. The percent variations in the measurements were 70% to 80% percent for the control group and silicone, 150% for polyimide silicone, and 25% for silver glass. Further work will verify these initial results and also study the dependence of adhesive force upon the tip radius.

MM-TuP4 Vacuum Encapsulation of Micron-Sized Vacuum Field Emission Triodes*, **S.J. Randolph,*** University of Tennessee, Knoxville*; M.A. Guillorn,* University of Tennessee, Knoxville and Oak Ridge National Lab*; M.D. Hale, P.D. Rack,* University of Tennessee, Knoxville

In recent years, carbon nanotubes have shown promise for use as stable field emitting elements in gated cathode devices. Vacuum conditions are ideal for the operation of field emission triodes, however, issues of practicality require that they be able to function outside the confines of a vacuum chamber. For this reason, a microfabrication technique has been developed for encapsulating a field emission triode in a micron-sized, vacuum-sealed environment. Patterned photoresist is thermally treated in order to form a temporary structural mold covering the device. The effects of photoresist thickness and geometry are being studied in order to minimize the duration and temperature requirements of this treatment process. The photoresist mold is then metallized and a reactive ion etch (RIE) process is used to create vias for photoresist removal. Also under investigation are the relationships between the film stresses and structural stability of the devices. Upon removal of the photoresist, a final metallization by an evaporation process is used to seal the structure under vacuum conditions. In this presentation the process flow for the vacuum micro-encapsulation package will be described and the materials requirements will be enumerated.

MM-TuP5 Investigation on Metal-coated Nano-aperture Array*, **D.W. Kim**, J.T. Ok, S.S. Choi,* Sun Moon University, Korea*; J.W. Kim, J.H. Boo,* Sungkyunkwan University, Korea*; C.K. Chun,* Sun Moon University, Korea*; J.S. Yang,* Myongji University, Korea

There have been considerable interests in the nano-aperture due to its potential application for promising near-field optical recording. Near-field optical recording can increase the data storage density drastically as it circumvents the diffraction limit. For the development of the practical optical storage device, a parallel processing technique based on nano-aperture array has been being investigated. In this work, the controllable method for the fabrication of metal-coated nano-aperture array and its optical characteristics in the far-field regime will be presented. At first, the arrays of inverted pyramidal structures were generated by anisotropic etching using 5 µm size pattern. Next, the stress-dependent oxide growth on the concave Si surface of the hollow pyramids was performed at 1000 °C. Backside Si etching by alkaline solution was followed and released the hollow oxide pyramids array with intentionally designed convex lens-like facets. Nano-apertures have been opened at the apices of pyramids by 50:1 diluted HF solution and the relation between the aperture diameter and the etch time showed good linearity with the aperture opening rate of ~25 nm/min. Finally, Al thin layer was deposited on the outer surface of oxide pyramid by PVD for the purpose of further reducing the aperture diameter, which will play the role of a wave-guide as well. The diameter of the completed aperture was observed to be inversely proportional to the thickness of Al layer. The details of the fabrication procedure and the far-field optical characteristics will be reported.

Manufacturing Science and Technology
Room Hall A-C - Session MS-TuP
Poster Session

MS-TuP1 Perfluoroelastomer Sealing Performance in Plasma Environments*, **S. Wang**, J.M. Legare,* DuPont Dow Elastomers, L.L.C.

Perfluoroelastomers (FFKM, e.g. Kalrez, etc.) are widely used as seals on semiconductor wafer processing equipment where plasma technology is applied. These processes include etching, ashing and plasma enhanced chemical vapor deposition. The seals need to exhibit good plasma resistance in order to withstand chemical attack and maintain sealing functionality. The seals must contribute minimal contamination to the process, hence particle generation and metallic contamination are of major concerns when selecting sealing materials. This paper discusses the interactions of plasma with sealing materials, and the test methods used in the evaluation, and then compares the performance of various FFKM's with varying compositions. The results indicate that conventional FFKM products, which contain carbon black or mineral fillers, are not suitable for plasma applications where both etch rate/weight loss and particle generation are critical. Unfilled FFKM's, or FFKM's with fillers that react with plasma to form volatiles, are better suited for sealing applications on semiconductor wafer processing equipment where reactive plasmas are used.

MS-TuP2 A Novel Power Supply with Arc Handling for High Peak Power Magnetron Sputtering*, **D.J. Christie**, F. Tomasel, W.D. Sproul, D.C. Carter,* Advanced Energy Industries, Inc.

The potential of high peak power magnetron sputtering has created growing interest, because it can generate a dense plasma with high target material ion content. At the required power densities, process arcs are not avoidable. Unless properly handled, arcs generate macro-particles and target damage, limiting the usefulness of the technique. However, coatings quite suitable for industrial applications may be applied if the pulsed supply incorporates arc handling. We have created such a power supply, capable of peak powers up to 3 mega-Watts and peak currents to 3000 A, at discharge voltages reaching 2 kV. It has voltage ring-up capability for pulse by pulse plasma ignition. This new power supply technology enables the practical application of a whole new range of sputtering processes, based on pulsing magnetrons to high peak powers.

MS-TuP3 GaAs Recycling using Supercritical Fluid SCFCO@sub2@ with O@sub2@ and H@sub2@O*, T. Momose, O. Otomo,* Miyagi National College of Technology, Japan

Contamination with valuable and poisnous metals such as GaAs dust produced in semicondutor technology must be controlled not to contaminate our life cycles. Most of the metals are embeded underground sealed by concrete, but not complete. Therefore, supercritical fluid (SCF) carbon dioxide (CO@sub2@) with high solubility for organic compounds was employed for simpler recycling for metals.@footnote 1@ Samples were GaAs(1:99) grains obtained from the wall of the sputtering apparatus. They(0.5 g) were kept in SCFCO@sub2@ with H@sub2@O of 4 c.c. for 30 min at a constant temperature and pressure. The treated water was analyzed using ICP (Vop-MarkII, Kyoto-Koken or Z-5700, Hitachi). However, the solubility of GaAs using SCFCO@sub2@ with H@sub2@O was low about 30 mg/L for As @footnote 2@. Therefore, to increase solubility, oxygen gas (O@sub2@) was introduced into the treatment chamber and SCFCO@sub2@ was filled and treated. The solubility at 50 °C for 30 minute was 3 g/L at 10-30 mega-Pascal (MPa) in SCFCO@sub2@ with O@sub2@ of 0.05 MPa and 6 g/L at 25 MPa in SCFCO@sub2@ with O@sub2@ of 0.15 MPa. The addition of O@sub2@ into SCFCO@sub2@ is effective to increase the solubility of Ga about two orders.@footnote 1@ T.Momose et.al, JVST, A17(4), Jul/Aug, 1999, 1391.@footnote 2@ T.Momose et.al, Proc. 55th Appl. Phys. Tohoku Local Conf., 8pB7, Tohoku Univ., Dec. 2000, 198.

MS-TuP4 Progress toward Spatially Programmable CVD*, J. Choo, L. Henn-Lecordier, Y. Liu, R.A. Adomaitis, G.W. Rubloff,* University of Maryland

A preliminary sequence of experimental tests performed to obtain engineering performance data for the Programmable CVD reactor system, together with simulation-based analysis of these data, will be described in this paper. The Programmable Reactor system was developed to improve across wafer sensing and control of reactant gas composition; to demonstrate this concept, a 3-segment prototype reactor was constructed by modifying a commercial tungsten CVD cluster tool. The key design features of the prototype system include a segmented showerhead assembly which allows control of precursor gas composition to each segment, a reversed flow of residual gas up through the showerhead to reduce inter-segment gas transport, and in-situ residual gas sampling tubes within each segment. These modifications constitute a major evolution in actuator and sampling capabilities relative to conventional CVD designs. To assess the ability of the prototype system to control gas composition across the wafer surface, a sequence of experiments was performed in which the spacing between the showerhead assembly and wafer surface was varied; pure Ar, WF6, and H2 was fed to each of the 3 segments in each test. Visual observations of the deposition patterns demonstrate sharp hexagonal deposition patterns corresponding to the shape of the showerhead segments for the close-spaced experiments; the pattern becomes more diffused as spacing is increased due to increased across-wafer diffusion. Surface resistance measurements reveal the thickest deposition directly under the WF6-fed segment and measurable deposition under Ar and H2 fed segments; simulation analysis of transport within the 1D segments will show that there is significant back-diffusion down each segment from a common exhaust volume, accounting for the observed deposition patterns.

MS-TuP6 Effects of Oxidant on Polishing Selectivity in the Chemical Mechanical Planarization of W/Ti/TiN Layer*, K.J. Lee, Y.-J. Seo,* DAEBUL University, Korea*; S.Y. Kim,* ANAM Semicondctor Co., Inc., Korea*; W.S. Lee,* Chosun University, Korea

Tungsten is widely used as a plug for the multi-level interconnection structures. However, due to the poor adhesive properties of tungsten on SiO2 layer, the Ti/TiN barrier layer is usually deposited onto SiO@sub 2@ for increasing adhesion ability with tungsten film. Generally, for the tungsten-chemical mechanical polishing (W-CMP) process, the passivation layer on the tungsten surface during CMP plays an important role. In this paper, the effects of oxidants controlling the polishing selectivity of W/Ti/TiN layer were investigated. The alumina(Al@sub 2@O@sub3@) abrasive containing slurry with 5 % H@SUB2@O@SUB2@ as the oxidizer was studied. As our preliminary experimental results, very low removal rates were observed for the case of no-oxidant slurry. This low removal rate is only due to the mechanical abrasive force. However, for Ti and TiN with 5 % H@SUB2@O@SUB2@ oxidizer, different removal rate was observed. The removal mechanism of Ti during CMP is mainly due to mechanical abrasive, whereas for TiN, it is due to the formation of metastable soluble peroxide complex. This work was supported by Korea Research Foundation Grant(KRF-2002-005-D00011).

MS-TuP7 Slurry Characteristics by Surfactant Condition at Copper CMP Process*, I.P. Kim, N.H. Kim,* Chung-Ang University, Korea*; J.H. Lim,* Growell Telecom*; S.Y. Kim,* Dongbu-Anam Semiconductor, Korea*; E.G. Chang,* Chung-Ang University, Korea

Copper is rapidly replacing aluminum interconnections due to its higher conductivity and lower electrical resistance in the semiconductor industry. Therefore, CMP (chemical mechanical polishing) is essential technology in microelectronic fabrication for the planarization of globally complex device topography. In this study, we evaluated the characteristics by the addition of 3 different kinds of nonionic surfactant to improve the dispersion stability of slurries. Slurry stability is an issue in any industry in which settling of particles can result in poor performance. So we observed the variation of particle size and settling rate when the concentration and addition time of surfactant are changed. When the surfactant is added after milling process, the particle size and pH became low. It is supposed that the particle agglomeration was disturbed by adsorption of surfactant on alumina abrasive. The settling rate was relatively stable when nonionic surfactant is added about 0.1-1.0 wt%. When molecular weight (MW) is too small like Brij 35, it was appeared low effect on dispersion stability. It is assumed that it can't prevent coagulation and subsequent settling with too small MW. The proper quality of MW for slurry stability was presented about 500,000. Consequently, the addition of nonionic surfactant to alumina slurry has been shown to have very good effect on slurry stabilization. If we apply these results to copper CMP process, it is thought that we will be able to obtain better yield.

MS-TuP8 A Study on Recycle of Abrasive Particles in One-used Chemical Mechanical Polishing (CMP) Slurry*, S.W. Park, Y.-J. Seo,* DAEBUL University, Korea*; S.Y. Kim,* ANAM Semiconductor Co., Inc., Korea

Recently, the recycle of CMP (chemical mechanical polishing) slurries have been positively considered in order to reduce the high COO (cost of ownership) and COC (cost of consumables) in CMP process. Among the composition of slurries (buffer solution, bulk solution, abrasive particle, oxidizer, inhibitor, suspension, antifoaming agent, dispersion agent), the abrasive particles are one of the most important components. Especially, the abrasive particles of slurry are needed in order to achieve a good removal rate. However, the cost of abrasives is still very high. In this paper, we have collected the silica abrasive powders by filtering after subsequent CMP process for the purpose of abrasive particle recycling. And then, we have studied the possibility of recycle of reused silica abrasive through the analysis of particle size and hardness. Also, we annealed the collected abrasive powders to promote the mechanical strength of reduced abrasion force. Finally, we compared the CMP characteristics between self-developed KOH-based silica abrasive slurry and original slurry. As our experimental results, we obtained the comparable removal rate and good planarity with commercial products. Consequently, we can expect the saving of high cost slurry. This work was supported by Korea Research Foundation Grant(KRF-2002-041-D00235).

MS-TuP9 Corrosion Characteristics of Diffusion Barrier Ta in Copper CMP*, D.W. Lee, N.H. Kim,* Chung-Ang University, Korea*; J.H. Lim,* Growell Telecom*; S.Y. Kim,* Dongbu-Anam Semiconductor*; E.G. Chang,* Chung-Ang University, Korea

The diffusion barriers are require for Cu metallization because of the higher diffusivity of Cu in Si and dielectrics. Several barrier materials such as TiN, W, and Ta(TaN) have been studied for diffusion barrier. Among them, Ta-based diffusion barrier has been put emphasis on presently. Ta-base diffusion barrier has no reaction with Cu, better adhesion to both Cu and dielectric, desirable microstucture against Cu diffusion, and heteroepitaxial relationship with Cu. On this study, The corrosion characteristics of the diffusion barrier Ta in Copper Chemical Mechanical Polishing has been investigated. Key experimental variables that has been investigated are the corrosion rate by different agents containing slurry of Cu CMP. Whenever Cu and Ta films were corroded adding each oxidizer, the corrosion rate of Ta was much lower than that of Cu. That is, the difference in the corrosion rates of Ta by oxidizer was not larger as compared with Cu. As corroded by complexing agents, the corrosion rate of Ta was close to 0. The corrosion rate of Ta increased as added HNO@footnote 1@ and CH@footnote 2@COOH compared with the reference slurry; on the other hand, it decreased with addition of HF. In addition, resulting corrosion rate went up with lower pH of agent. However, the corrosion rates by agents were significant small. Hence, it doesn't affect on the removal rate of Cu CMP practically. Consequently, this can be explained by assuming that the mechanical effect dominates than the chemical effect on the polishing rate of Ta(TaN). @FootnoteText@ @sub 3@ @sub 3@.

MS-TuP10 Measurement of Energy Flux at the Substrate in a Magnetron Sputter System Using an Integrated Sensor, ***S.D. Ekpe***, *S.K. Dew,* University of Alberta, Canada

Knowledge of the energy flux in a sputter deposition system is essential in predicting the properties of the growing film. The use of discrete sensors such as thermocouples for heat measurement has a potential contact problem due to the temperature jump between the surface of the wall and the surrounding gas especially at very low pressures. Embedded sensors such as a microfabricated polysilicon thin film thermistor eliminates the problem associated with the discrete sensors. In this study, the fabricated sensor is calibrated using ohmic self-heating before the deposition plasma is switched on, and also after the plasma is switched off (passive mode). At low pressures (up to 20 mTorr), pressure has an insignificant effect on the thermal resistance of the sensor. For substrate temperatures of up to 250°C, the sensor response is linear with input power. Values of steady state energy flux measured with the sensor range from 5 to 46 mW/cm@super2@ for aluminum and 14 to 114 mW/cm@super2@ for copper depending on the process conditions, and compare well with those determined theoretically. Magnetron power was varied between 75 and 300 W, gas pressure 5 - 10 mTorr and substrate-target distance 10.8 - 21 cm.

MS-TuP11 Temperature Sensor for Multi-layered Substrate using Optical Fiber type Low-coherence Interferometry, ***K. Takeda***, *T. Shiina, M. Ito, Y. Okamura,* Wakayama University, Japan; *N. Ishii,* Tokyo Electron Ltd., Japan

Multi-layered substrates, such as silicon on insulator (SOI) are very useful for MEMS and so on. In the fabrication processes of multi-layered substrates, plasma etching is frequently employed. In such process, the temperature control of each layer, especially top layer, will be required to realize much finer pattern because the interlayer of SOI etc. is dielectric with low thermal conductivity. We have developed novel temperature sensor for measuring each layer of multi-layered substrates using low-coherence interferometry. The sensor is based on Michelson interferometer, which consists of a super luminescent diode (SLD: wavelength = 1550 nm), a laser diode (LD: wavelength = 850 nm), a scanning reference mirror, optical fibers and so on. In this sensor, the optical pass length of each layer is derived from the length between peaks of SLD interference signals. The shift of each optical pass length is precisely measured by Michelson interferometer using LD, which uses the same optical path as that using SLD. The sensor is, therefore, robust to mechanical and temperature disturbances. We have evaluated the shift of each layer of the three-layered substrate. The top and bottom layers of the substrate are silicon, 360 µm in thickness. The interlayer is made of quartz, 1 mm in thickness. As a result, it has been verified that the shift of optical length of each layer is proportional to each temperature measured by thermo-couple sensors, which corresponds to theoretical values. From these results, we have confirmed that the developed sensor can measure the temperature of each layer without continuous monitoring the shift of optical pass length if the initial temperature is known.

MS-TuP13 Calibration Standards for X-ray Metrology Systems using a Traceable High-resolution Diffractometer, ***D. Windover***, *J. Cline,* National Institute of Standards and Technology

The wealth of information that can be obtained from the characterization of thin film structures by means of X-rays techniques has lead to a dramatic increase in their use in recent years. However, currently their are no traceable standards available to calibrate the behavior of these new specialized characterization systems. High resolution X-ray instruments require an entirely new type of artifact to characterize both the the parallel beam optics and the performance of the goniometers. Likewise, X-Ray reflectivity requires accuracy in the incident and reflection angles orders of magnitude higher than needed for previous conventional powder diffraction calibration. This work details current efforts for providing NIST Standard Reference Materials for high resolution X-ray diffraction and reflectivity that are traceable to the SI. We focus primarily on the construction and calibration of an advanced X-ray diffractometer designed from the onset to offer flexibility in its configuration and traceable measurements. Features include: high intensity, well characterized, parallel beam X-rays produced using a rotating anode and finely controlled goniometer rotations with both accuracy and precision monitored by optical encoders. We discuss the calibration of the accuracy for the @theta@ and 2@theta@ axes through the method of circle closure. We demonstrate both vibration and temperature effects on goniometer positioning and discuss current improvements to the system designed to account for these effects. Proposed structures for high resolution and reflectivity standards will be presented.

Nanometer Structures

Room Hall A-C - Session NS-TuP

Poster Session

NS-TuP1 Electrical Characteristics of Semiconductor-Atomic Superlattice for Silicon-on-Insulator Application, ***Y.-J. Seo,*** DAEBUL University, Korea; *R. Tsu,* University of North Carolina at Charlotte

Silicon on insulator (SOI) structure is a critical material for future ultra-large scale integration (ULSI). Recently, we had been reported that the Si-O superlattice can be serve as an epitaxially grown insulating layer as possible replacement of SOI. Up to a bias of 30 V, the field inside the multi-layer structure reaches ~ 3x10@super 7@ V/cm. There is no sign of breakdown. However, the low voltage isolation is not quite sufficient for implement as a substitute for silicon on insulator. In this paper, the monolayers of oxygen atoms sandwitched between the adjacent silicon layers formed by ultra high vacuum-chemical vapor deposition (UHV-CVD). This multi-layer Si-O superlattice forms a new type of superlattice, semiconductor-atomic superattice (SAS). According to the preliminary results, high-resolution cross-sectional transmission electron microscopy (HRTEM) shows epitaxial system. Also, the current-voltage (I-V) measurement results show the stable and good insulating behavior with high breakdown voltage. It is apparent that the system may form an epitaxially grown insulating layer as possible replacement of SOI, a scheme investigated as future generation of high efficient and high density CMOS on SOI. Since our scheme is epitaxial, three- dimensional integrated circuits (3D-ICs) may finally be realized in silicon-based technology. Therefore it is important to determine how good is the epitaxially grown silicon beyond a relatively thick Si-O superlattice. This work was supported by Grant(R05-2002-000-00565-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

NS-TuP3 Synthesis of Nanocrystalline Semiconductors and Phosphors by Thermal Self Assembly, ***M. Abboudi,*** Universite Abdelmalek Essaadi, Morocco; *S.Y. Seo, J. Bang,* University of Florida; *A. Benali,* Universite Abdelmalek Essaadi, Morocco; *P.H. Holloway,* University of Florida

A new method has been used to produce luminescent and semiconducting nanopowders by thermo-decomposition of precursors prepared in situ by a direct solid state reaction. This represents a new self assembly approach for the synthesis of nanocrystalline materials. Oxide phosphors prepared by this method include ZnGa@sub2@O@sub4@ doped with europium or manganese, and Y@sub2@O@sub3@ doped with europium. All the synthesized powders have been characterized by X -Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The photoluminescence and the cathodoluminescence from these phosphors with an average particle size of @<=@ 50nm have been studied with varying doping concentrations. Optimized concentrations will be reported and the luminescent spectra shown to be characteristics of the normal transitions for the dopants. The relative luminescence efficiencies will be shown to be good for these nanoparticles. We have also prepared nanocrystalline GaN powders, and will report on the defect structure from luminescence data. Finally, synthesis of Fe@sub2@O@sub3@ with particle diameters @<=@ 25nm, and Ce@sub0.8@Gd@sub0.2@O@sub1.9@ with a specific surface area of 29 m@super2@ per gram will be reported. Potential applications of these nanoparticles to phosphors, catalysts, photovoltaics, data storage, fuel cells and sensors will be discussed.

NS-TuP4 The Effects of Molybdenum-Oxide and Diamond on Field Emission, ***T. Tyler***, *D. Jaeger, A. Kvit,* North Carolina State University; *V. Zhirnov,* Semiconductor Research Corporation; *J. Hren,* North Carolina State University

Refractory metals such as molybdenum and tungsten are frequently used in field emission applications, most often in the form of single tips or arrays of tips. Such field emitters have been studied in great detail over the past thirty years. The addition of an 'intentional' coating material (e.g. dielectric deposits such as aluminum-oxide or diamond) to improve emitter performance has been widely studied as well. However, there has been a lack of control of substrate effects (e.g. the presence and nature of oxides) in combination with coating effects. Carefully controlled morphological and compositional information is now required for a more complete analysis.

We report here on combined studies of field emission, with high-resolution transmission electron microscopy (HRTEM), with computer simulations of local electric fields. Current versus voltage data is obtained during field emission, while HRTEM is used to determine morphology and composition (using electron energy loss spectroscopy). Computer simulations of electrostatic effects, employing finite element methods, are then conducted using the morphologic and compositional information of the composite emitter structure, obtained from HRTEM. The magnitude and distribution of the surface potential barrier and the local field strength at the apex of the field emitter can thus be determined. The results also can provide information on the materials' electronic properties, such as the dielectric constant, trap density, and carrier velocity. The non-destructive nature of these experiments makes comparison studies possible; e.g. molybdenum needles, both oxidized and non-oxidized, are compared with needles coated with layers of nano-diamond.

NS-TuP5 Formation of Nanoporous Noble Metal Films by Electrochemical Dealloying of PtxSi1-x, ***J.C. Thorp****, K. Sieradzki, N. Dimitrov, S.T. Picraux,* Arizona State University

Electrochemical dealloying of metallic alloy mixtures provides a novel way to form nanoporous structures. In the present study we demonstrate the extension of this concept to metal-silicon alloys on silicon platforms for PtxSi1-x. The PtxSi1-x (x = 50 and 25%) alloys are formed by deposition and thermal treatment. Thermal reaction of Pt films is used to form PtSi silicide layers and co-deposition for more silicon rich alloys. The films (200 to 800 nm thick) are then dealloyed in concentrated HF by an electrochemical process that leaches out the silicon. Anodic polarization curves are used to establish the optimum potential for dealloying, for example near + 400 mV (SCE) for PtSi with current densities of approximately 10 mA/cm2. Rutherford Backscattering Spectrometry (RBS) demonstrates the formation of a pure Pt layer on the metal silicide layer as dealloying process progresses and thus provides a direct observation of the dealloying kinetics. The resulting morphology of the nanoporous noble metal structures is determined by scanning electron microscopy. Results are presented for various Pt silicon alloys and dealloying conditions, and preliminary results will be discussed for Au silicon alloys. These nanoporous noble metal thin film structures provide high surface area electrodes on Si. Such nanostructures are of interest for microscale electrochemical sensing and microfuel cells.

NS-TuP8 Solvothermal Synthesis of Nanocrystalline @gamma@-Fe@sub 2@O@sub 3@ in Toluene, ***C.-S. Kim****, J.-H. Park, B.K. Moon, H.J. Seo,* Pukyong National University, Korea*; B.-C. Choi,* Pukyong National University, Korea, South Korea

The synthesis of @gamma@-Fe@sub 2@O@sub 3@ nanoparticles has been performed in solvothermal route. The nanocrystalline particles were obtained after synthesis using two different temperatures of 130°C and 180°C for 10 hrs in an autoclave, where iron pentacarbonyl is thermally decomposed in toluene solutions in the presence of trimethylamine N-oxide as an oxidant. X-ray diffraction and transmission electron microscopy shows that the product has uniform maghemite structure with average particle size below 30nm. The specific surface area of the @gamma@-Fe@sub 2@O@sub 3@ nanocrystalline powder was investigated using BET surface area analyzer. Influence of synthesis conditions such as synthesis temperature and molar ratio of precursor to solution on the size and size distribution of the product was also discussed.

NS-TuP9 Nanopipes in Single Crystal Transition-metal Nitride Layers, ***D. Gall,*** Rensselaer Polytechnic Institute

Nanopipes are 1-nm-wide open pores that extend through the entire thickness of epitaxial NaCl-structure transition-metal nitride layers. They form due to a combination of anisotropic surface diffusion and atomic shadowing effects. Their shape, orientation, and arrangement can be controlled by ion-irradiation and deposition angles. CrN, TaN, ScN, and TiN layers were grown on MgO(001) at 600-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N@sub 2@ and N@sub 2@+Ar discharges at 3-20 mTorr. These deposition conditions result in a highly anisotropic surface diffusion with hop-rates that are 7 orders of magnitude smaller on (111) versus (001) surfaces. This anisotropy leads, during growth under limited adatom mobility conditions, to kinetic surface roughening and the development of deep surface cusps which cause atomic shadowing and the formation of nanopipes that are elongated along the [001] growth direction. The nanopipes have rectangular cross-sections and form self-organized arrays aligned in orthogonal [100] and [010] directions, precisely replicating the in-plane correlation of the surface morphology. Non-normal deposition increases the level of atomic shadowing and introduces a controlled tilt to the nanopipes. Increasing the N@sub 2@@super +@-ion irradiation flux or decreasing the N@sub 2@ partial pressure (and, hence, the steady-state N coverage) during growth provides a corresponding increase in cation surface mobilities leading to smoother surfaces, less atomic shadowing, and partial or full suppression of nanopipe formation.

NS-TuP10 Nanopatterning of Hydrogen Silsesquioxane Resist*, **M.J. Word**, I. Adesida,* University of Illinois at Urbana-Champaign

Creating nano-scaled structures in semiconductor materials generally begins with the use of high-resolution lithography techniques and resists. Electron beam lithography is capable of creating isolated structures less than 10 nm in width when utilized with high-resolution resists such as hydrogen silsesquioxane (HSQ).@footnote 1@ In addition to these isolated structures, it is also important to characterize the resist when more complex and denser structures are required. In our study we characterized the resolution of HSQ resist in the form of densely packed gratings. We began by examining the surface of very thin films of HSQ resist down to a thicknesses of 100 Å in order to determine the limits for successful processing using lithography techniques. Using a JEOL JBX-6000FS electron beam lithography machine operating at 50 kV with a current of 20 pA, we then exposed samples of HSQ at various film thicknesses with gratings having periods as small as 20 nm. We use the results to characterize the resolution limits of HSQ with respect to film thickness, dosing, and grating periodicity. In addition, we discuss the transfer of nanometer-scale patterns into InP and other semiconductor materials with exposed HSQ gratings acting as the etch mask. @FootnoteText@ @footnote 1@ H. Namatsu, J. Vac. Sci. Technol. B 19, 2709 (2001). .

NS-TuP11 On the Study of Growth Behavior of Carbonaceous Tips by Electron Beam Induced Deposition using Preprocessing Methods*, **S.H. Kim**,* Korea Electronics Technology Institute, South Korea*; Y.J. Choi,* Korea Electronics Technology Institute, South korea

For the investigation of high aspect ratio structures with SPM, the cantilevers with very sharp and long tips are useful. The carbon nanotube(CNT) tips and electron beam deposited(EBD) tips are effective candidates for the high aspect ratio tips. Although EBD tips are duller than CNT tips, they have an advantage of simple fabrication process over the CNT tips. EBD tips can be simply fabricated by aligning the electron beam directly down the vertical axis of Si cantilever and then irradiating a single spot on the cantilever for a proper time in the dominant atmosphere of residual gases generated by the oil of the diffusion pump of the Scanning Electron Microscope(SEM).@footnote 1-2@ The height and the base diameter of the EBD tips can be controlled by adjusting the control parameters of the SEM. However, the EBD tips cannot grow over 1µm in the residual gas atmosphere. We could enhance the height of tips by dipping the catilever into the organic solvents which contain aromatic or aliphatic hydrocarbon, drying it in the vaccum chamber and irradiating electron beam. With this process, we could acquire the tip whose base diameter is 0.180µm and effective length is 3.18µm . In addition, we observed that the growth behavior of the tips are different in accordance with the species of the chemicals and we will discuss the effects of the organic solvents on the growth of the tips. @FootnoteText@ @footnote 1@ Albert Floch, Jordi Servat, J. Vac. Sci. Technol. B, Vol 14, No. 4 Jul/Aug (1996). @footnote 2@M.Wendel, H.Lorenz, and J.P.Kotthaus, Appl. Phys. Lett. 67(25) (1995).

NS-TuP12 Probing Adhesion and Friction on Nanostructured Surfaces with Chemical Force Microscopy, ***C.L. Berrie****, J.E. Headrick,* University of Kansas

Chemical functionalization of AFM probe tips allows regions of different composition on the surface to be identified even in the absence of topographic variations. Unfortunately, many of the established chemical-functionalization methods lead to a significant increase in the size and curvature of the tip radius, which effectively sacrifices the resolving ability of the AFM measurement. In this work, we have chemically-modified commercially-microfabricated Si3N4 AFM tips with a variety of self-assembled alkylsilane monolayers having distinct terminal functionalities, such as -CH3, -CH2Br and -COOH, using a fabrication process that minimizes undesirable resolution-loss due to tip growth. We have measured the adhesion forces and friction loops between these functionalized tips and various substrates, including nanostructured substrates where the chemical composition of the surface varies on the nanometer length scale (for example from hydrophobic to hydrophilic). The nanostructured surfaces are created using the AFM. These results will help us to understand the resolution limits of these techniques by allowing the investigation of the sensitivity of the technique to pattern size.

NS-TuP14 In-situ Tip Preparation and Nanoscale Surface Modification using STM Manipulation*, **V. Iancu**, A. Deshpande, S.-W. Hla,* Ohio University

Single atom manipulation@foontote 1,2@ with a scanning tunneling microscope (STM) tip on crystal surfaces requires an extremely fine control over the tip-atom-surface junction. The shape of the STM-tip and the chemical elements that constitute the tip-apex are vital for a successful atom manipulation with atomic scale precisions. Here we report an in-situ tip preparation technique useful to fabricate stable STM-tips with a known chemical element at the tip-apex. The experiments are conducted at an ultra-high-vacuum conditions on a Ag(111) surface at 4.8 and 75 K sample temperatures. During the experiment, the STM-tip, made of polycrystalline tungsten wire, is gently dipped into the substrate and the tunneling voltage is increased to 3 V. The penetration depth is precisely controlled. The shape of the holes created by the tip dipping indicates that the tip becomes sharper by repeating the procedure. This is due to the local heating during the tip-sample mechanical contact that re-shapes the structure of the tip-apex. In addition, variation of the tip-height and tunneling voltage during the procedure results in different impact force. By applying suitable impact force with the STM-tip, atomic scale surface steps and Ag islands can be created locally. This entire procedure will be useful to conduct new nanoscale experiments or to test the strength of the material at an atomic level. @FootnoteText@@footnote 1@S.-W. Hla, K.-F. Braun, K.-H. Rieder, "single atom manipulation mechanisms during a quantum corral construction",Phys. Rev. B rapid communication (2003) in press.@footnote 2@S.-W. Hla, L. Bartels, G. Meyer, K.-H. Rieder,"Inducing all steps of a chemical reaction with the scanning tunneling microscope tip: Towards single molecule engineering", Phys. Rev. Lett. 85 (2000) 2777-2780.

NS-TuP15 Tomographic Reconstruction of Doping Profile and Device Structure in Si MOSFET Devices with a sub 10 nm Spatial Resolution*, **R.K. Bansal**, J.M. Fitz-Gerald, R. Hull, D.H. Anjum,* University of Virginia

Due to a phenomenal reduction is the size of semiconductor devices over the last two decades there is a need to develop better characterization methods which can probe the devices in three dimensions with a high spatial resolution. The present work aims at tomographic reconstruction of the device structure and doping profile in semiconductor devices with sub-10 nm resolution. This involves using a Focused Ion Beam (FIB) to sputter away layers of atoms and subsequently image the cross-section of the device using a high resolution scanning electron microscope (SEM). This process is repeated, followed by concatenation of these images in the computer, to obtain a three dimensional reconstruction of the device. The SEM used for this work is the state-of-the-art JEOL 6700F field emission SEM which has a spatial resolution of 1nm. Also under investigation is the possibility of observing the spatial dopant distribution in the device and the enhancement of the doping contrast by using hydrogen surface passivation. This study is currently being done on short channel length (50nm -1µm) MOSFETs with strained and unstrained Si channel and can be extended to other devices and material systems.

NS-TuP16 Imaging of DNA Strands with the Low Energy Electron Point Source (LEEPS) Microscope*, **A. Eisele**,* Universität Marburg, Germany*; B. Völkel, M. Grunze,* Universität Heidelberg, Germany*; A. Gölzhäuser,* Universität Marburg, Germany

A low energy electron point source (LEEPS) microscope is used to image freestanding DNA multistrands. These span 100 nm wide openings in a thin silicon sample holder. The holographic images are analyzed by assuming a mask model and vacuum wave propagation. We extract the correct source-to-object distance by the analysis of cuts through numerical reconstructions in the object region with an accuracy of 40 nm. Upon variation of the lateral and axial source position, the reconstructions show reproducible object structures and focus behavior. The smallest reproducibly resolved features have dimensions of 1 nm. Due to the low energy (40 eV) of the field emitted electrons, LEEPS microscopes generate images with a much higher contrast than conventional electron microscopes.

NS-TuP18 Second Harmonic Piezoresponse Force Microscopy: A Probe of High Order Ferroelectric Processes*, **R. Shao**,* University of Pennsylvania*; S.V. Kalinin,* Oak Ridge National Laboratory*; D.A. Bonnell,* University of Pennsylvania

Piezoresponse Force Microscopy (PFM) has been widely accepted as an important technique for imaging ferroelectric domains. The principle of PFM is the detection of the electromechanical response to an ac voltage applied at a tip/surface contact. There are two unresolved issues associated with PFM. The first is the degree of perturbation to ferroelectric domain polarization imposed by the ac voltage. The second is a dilemma involving switching mechanisms during acquisition of the hysteresis loop. To address these issues, we have measured the second harmonic of the electromechanical response to the ac imaging voltage on various ferroelectric materials as a function of both frequency and amplitude of the voltage. A theoretical model has been established that relates the ferroelectric relaxation to the second harmonic response. The approach is extended to an imaging technique, Second Harmonic Piezoresponse Microscopy, that maps the distribution of relaxation times on surfaces by acquiring the spatial distribution of the second harmonic response.

NS-TuP19 Lithographic Patterning using Near-field Scanning Optical Microscopy*, **R.E. Hollingsworth**,* ITN Energy Systems, Inc*; C. Veauvy, M. Treaster, J.D. Beach, R.T. Collins,* Colorado School of Mines

We report the development of a near-field scanning optical microscope (NSOM) designed specifically for direct write lithography on 4" substrates. Direct write lithography is ideally suited to research use where rapid turn around, flexible pattern generation and much lower cost than production tools are very important. At present, electron beam lithography is the most commonly used direct write technique , although scanning probe microscopes are receiving increasing attention. The advantages of NSOM lithography over these other direct write approaches are the ability to use conventional optical photoresists and to combine near-field with far-field optical exposure. As an optical technique, NSOM also avoids concerns of high-energy electron damage and vacuum compatibility inherent to e-beam lithography. Our approach uses state of the art mechanical translation stages that take steps a fraction of the typical NSOM resolution. This allows patterning over typical wafer dimensions with none of the stitching errors inherent in other techniques. The microscope also functions in standard NSOM characterization modes allowing, for example, nanoscale topography and reflectance to be measured and used in feature characterization and pattern registration. In this presentation, we will discuss the microscope design, performance tests, and photoresist process development for 100nm scale features and for pattern transfer into substrates and films. Microscope use in example applications such as quantum point contacts, surface plasmon enhanced near-field optics, and nucleation sites for seeded film growth will be presented.

NS-TuP20 Electroless Metal Discharge Layers for Electron Beam Lithography*, **S.L. Brandow**, M.-S. Chen, W.J. Dressick, R. Bass,* Naval Research Laboratory*; E. Dobisz,* Hitachi Global Storage Technologies

Substrate charging during e-beam lithography on non-conductive materials can lead to severe problems in pattern placement accuracy and critical dimension (CD) error. Current methods of controlling charge include the use of conducting polymers or evaporated metal films as charge dissipation layers. We report an alternative approach utilizing ultrathin (i.e., 15-30 nm) Cu films deposited by electroless metal deposition. Our method involves the sequential chemisorption of an aminosiloxane film to the substrate of interest, binding of a colloidal Pd/Sn electroless catalyst, and brief immersion in an electroless Cu bath to deposit the ultrathin Cu film. This ligand based approach permits sufficient control of Cu thickness and uniformity to satisfy electrical conductivity, adhesion, and transparency constraints required for discharge layers. The deposition process is performed under ambient, aqueous conditions which are track-line compatible and thus should have cost advantages over conventional CVD based metallization processes. The grounded Cu film, deployed here as a resist underlayer, eliminates the 0.1 - 0.4 micron subfield stitching errors normally observed in the absence of the Cu film during resist patterning on a glass or insulating substrate. The Cu is readily removed using a nitric acid wet etch following patterning.

NS-TuP21 Metal Pattern Transfer from Microstructured Self-Assembeld Monolayer Templates to Polymer Substrates by an Imprinting Method*, **S. Imura**, N. Saito, H. Sugimura, O. Takai,* Nagoya University, Japan

Nanoimprint lithography is expected to play a crucial role in device nanoprocessing. The method has been employed in order to transfer a minute structure on a mold to a polymer film. Besides fabrication of such 3D polymer nanostructures, nanopatterning a functional material other than polymers through nanoimprint is of further interest. Here we show the first demonstration of metal pattern formation by a imprinting method in which a metal micropattern deposited on a microsturctured template was directly transferred onto a polymer substrate. First, a microtemplate was fabricated as follows. An organic self-assembled monolayer was formed from 1-undecanol on a Si substrate of which surface oxide was removed by HF etching. This monolayer was micropatterned by a photolithographic method.@footnote 1@ Due to irradiation at a wavelength of 172 nm, the monolayer was photochemically decomposed and the underlying Si was oxidized. Consequently, a micropattern on a photomask was printed on the sample as a micropattern consisting of the unirradiated monolayer and photochemically formed SiO@sub2@. Next, this microtemplate was immersed in a tin solution, a palladium solution and a Ni electroless plating solution, in that order. Ni was deposited selectively on the unirradiated monolayer while the oxide surface remained undeposited. Finally, this Ni micropattern deposited on the template was transferred onto a polymer substrate. The template was heated to a temperature of 180 °C and pressed into a polymethylmetacrylate (PMMA) substrate at a pressure of 10 MPa. The Ni micropattern was successfully transferred from the template to the PMMA substrate. @FootnoteText@ @footnote 1@H. Sugimura et al. Langmuir 16, 885 (2000).

NS-TuP22 Photolithographic Structures with Precise Controllable Nanometer-Scale Spacings Created by Molecular Rulers*, **M.E. Anderson**, L.P. Tan, M. Mihok, H. Tanaka, M.W. Horn, P.S. Weiss,* Pennsylvania State University

The combination of conventional lithographic techniques with chemical self-assembly allows for the creation of nanostructures whose spacing and edge resolution reach nanometer-scale precision. The controlled placement and thickness of self-assembled multilayers composed of alternating layers of @alpha@,@omega@-mercaptoalkanoic acids and coordinated metal ions form precise "molecular ruler" resists to produce tailored, lithographically defined patterns.@footnote 1,2@ This resist is selectively deposited onto initial parent gold structures, metal is deposited, and the resist is lifted off, thereby leaving daughter structures whose spacing from the parent depends on the thickness of the resist. For future device fabrication with this technique, it would be advantageous to position these gaps selectively on the surface. We report here a method to accomplish this purpose by combining photolithography and molecular rulers. After forming the molecular resist, conventional photoresist is spin-cast onto the wafer and the photomask is aligned with the parent structure to place daughter structures only in selected locations. After exposure, development, metal deposition, and lift-off of both the photoresist and molecular resist, the final product is a wafer with daughter structures and gaps selectively oriented to create the desired hierarchical nanostructures. @FootnoteText@@footnote 1@ A. Hatzor and P.S. Weiss, Science 291, 1019 (2001). @footnote 2@ M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, H. Tanaka, M. W. Horn, and P. S. Weiss, Journal of Vacuum Science and Technology B 20, 2739 (2002).

NS-TuP23 Formation and Characterization of Nanopores*, **T. Schenkel**, V.R. Radmilovitch, A. Persaud, S.-J. Park,* Lawrence Berkeley National Laboratory*; J. Nilsson,* Lawrence Livermore National Laboratory

The ability to form holes in membranes with diameters of only a few nanometers (1 to 10 nm) is of interest in many fields of nanometer scale science including single molecule studies, ion proximity lithography, and single atom doping. We report on studies of nanopore formation by local deposition of material in a dual beam focused ion beam system (FIB). Large holes with diameters of tens of nanometers are closed by the local deposition of platinum and TEOS oxide. We compare results from electron beam and ion beam assisted deposition of materials. Hole structure evolution is monitored in situ during hole closing by SEM. Hole profiles, local crystalline structure and materials composition are characterized ex situ by TEM. Nanopores with diameters in the 5 nm range have been formed in low stress silicon nitride membranes. We will discuss process reproducibility, and mechanisms of local structure evolution.@footnote 1@ @FootnoteText@ @footnote 1@ This work was performed at the National Center for Electron Microscopy at the E. O. Lawrence Berkeley National Laboratory and was supported by the National Security Agency and Advanced Research and Development Activity under Army Research Office contract number MOD707501, and by the U. S. Department of Energy under contract No. DE-AC03-76SF00098.

NS-TuP24 Probe-Scanned Traces with Chemical Reversibility on Organosilane Self-Assembled Monolayer Surfaces*, **N. Saito**, S.L. Lee, H. Sugimura, O. Takai,* Nagoya University, Japan

Amino-terminated self-assembled monolayers (SAMs) on silicon substrate have a potential as templates for biosensor or molecular devices. Since amino groups are able to link with target molecules such as deoxyribonucleic acid (DNA) and antibody-forming cell, many researchers had investigated amino-terminated SAMs. To fabricate components of future micro-devices, such templates must offer high chemical reactivity which is restricted to specific micro-regions. Thus, the amino-terminated regions must be prepared on given points of a substrate. Such a microstructure can be accomplished by maskless lithography techniques such as focused ion beam lithography and electron beam lithography. However, these lithography techniques cause a great deal of damage to the amino-terminated surface of a SAM due to the excessive energy applied. Considering this, we determined we had to develop a soft chemical lithography process for the reversible oxidation-reduction reaction of amino groups. Scanning probe lithography (SPL) is based on electrochemical theory and can be employed to realize such a soft process by controlling the applied potential. SPL had been applied in many cases, however, for the elimination of SAMs. In our present research, we have attempted, through chemical lithography, to produce amino-terminated regions on a sample surface without changing any other part of molecule. Amino-terminated SAM samples were prepared from p-aminophenyltrimethoxysilane though chemical vapor deposition. The amino-terminated surfaces were converted into nitroso-terminated surfaces at positive bias voltages. Moreover, the nitroso-terminated surfaces were reconverted into amino-terminated surfaces. The changes of functional groups on the surfaces were traced by Kelvin probe force Microscopy and atomic force microscopy.

NS-TuP25 Exploration of Chemical Bonding Forms for Producing Organic Monolayers Directly Attached to Silicon*, **N. Maeda**, N. Saito, H. Sugimura, O. Takai,* Nagoya University, Japan

Self-assembled monolayer (SAM) formed through the chemical reaction between 1-alkene and hydrogen-terminated silicon (Si-H) is an attractive material for molecular electronic devices, since such a monolayer is directly attached to Si without inserting an oxide layer. This is advantageous for electronic applications of the SAMs and is distinct from an organosilane SAM on Si which needs the oxide interlayer. Furthermore, such a directly-bonded SAM is chemically durable to HF solution more than the organosilane SAM.@footnote 1@ However, an understanding of chemical reactivities of Si-H surfaces to organic molecules is still in an insufficient level. Here we report on SAM formation on Si-H from various precursor organic molecules including 1-hexadecen, phenylacetylene, 1-undecanol, 4-bromomethylbiphenyl, p-phenylenediamine, terephthaldialdehyde,etc. Si-H samples were prepared through the etching of Si(111) substrates in 5%-HF. A Si-H sample was then refluxed at a temperature ranging from 100 to 180 °C for several hours in a precursor liquid or a organic solution of a precursor under an atmosphere purged with N@sub 2@. The treated sample was examined with a water contact angle measurement, X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy in order to confirm SAM formation. In the case of 1- hexadecen, phenylacetylene, 1-undecanol, there were no oxidized Si peaks in XPS. This indicates that densely packed monolayers were formed so that the Si substrates were protected form oxidation. However, in the case of the other precursors, the Si substrates oxidized showing that such monolayers were less densely packed. @FootnoteText@ @footnote 1@N. Saito, S. Youda, K. Hayashi, H. Sugimura and O. Takai, Chem. Lett. 31, 1194 (2002).

NS-TuP26 Fabrication of Cylindrical Cu Nanorods on an Indium-Tin-Oxide Substrate*, **S. Asakura**, K. Oda,* Waseda University, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; A. Fuwa,* Waseda University, Japan

Increasing attention has recently been paid to the fabrication of copper (Cu) arrays of nm-scale in order to realize an ultrahigh-density electron emission source. Among the several methods, the use of diblock copolymer (BC) thin film is promising, since an ordered nanoporous structure can be easily obtained from the copolymer thin film by chemical treatment. Here we report the fabrication of cylindrical Cu nanostructures onto an indium-tin-oxide (ITO) substrate through an electrodeposition using a BC thin film as a template. First, a mixture of polystyrene (PS, 70 wt.%)/polybutadiene (PB, 30 wt.%) BCs and dehydrated toluene was stirred for 2 h at room temperature. Next, the solution was spin-coated on the ITO surface and dried in air for 24 h at a temperature of 140 °C. Due to this treatment, the PB component formed cylindrical domains in a matrix of the PS component as confirmed by an optical microscope. Subsequently, the sample was photoirradiated with vacuum ultraviolet (VUV) light of 172 nm in wavelength for 30 min at 10@super 3@ Pa. As a control experiment, identical BC thin film/ITO sample was sonicated in dehydrated toluene for 30 min. Finally, each sample was treated in an electroplating solution to deposit Cu on it. Using a scanning electron microscope, we confirmed that the Cu deposition selectively occurred inside the cylindrical nanopores where the PB domains were photochemically eliminated. The cylindrically shaped Cu nanorods on the ITO surface were less than 800 nm in diameter and several hundreds nm in length. Our result presented here demonstrated that the PB domains were removed completely due to VUV irradiation and the PS matrix served as a mask to prevent Cu deposition. On the other hand, in the case of the chemical treatment, no Cu deposition was observed. This indicates that the PB domains still remained on the ITO surface. Our VUV treatment was found to be effective for preparing the nanoporous structures in the BC thin film.

NS-TuP27 Organic Self-Assembled Monolayers Covalently Linked to Diamond Electrode Surfaces*, **R. Ohta**, N. Saito, Y. Inoue, H. Sugimura, O. Takai,* Nagoya University, Japan

Diamond has excellent properties as an electrode material for electrochemical sensors, besides its well-known properties as the hardest material in nature. It has a wide potential window and chemical stabilities in various environments. Chemical functionalization of diamond surfaces is a powerful means in order to provide chemical selectivity and sensitivity to the diamond surfaces. Thus, it is a crucial technique for developing diamond-based chemical sensors. However, in actual applications of a modified diamond electrode, its surface is needed to be durable chemically and mechanically. Organic molecular monolayers covalently linked to diamond surfaces meet these demands and promising candidates. In this research, we have studied both vapor phase and liquid phase processes for the modification of hydrogen-terminaed diamond to several organic molecules such as 1-undecanol and 1-hexadecen as well as that of hydroxyl-terminated diamond to organosilane molecules such as alkylsilane and aminosilane. The molecules were fixed onto the diamond surfaces through covalent bonds such as C-O-C, C-C and C-O-Si and consequently formed self-assembled monolayers. The monolayers were characterized by scanning probe microscopy, X-ray photoelectron spectroscopy and infrared spectroscopy. These results will be discussed with the electrochemical behavior of the modified-diamond surfaces. Micropatterning of the diamond surfaces will be also presented.

NS-TuP28 Photochemical Reaction of Organosilane Self-Assembled Monolayers as Studied by Scanning Probe Microscopy*, **H. Sugimura**, N. Saito, I. Ikeda, Y. Ishida, K. Hayashi, O. Takai,* Nagoya University, Japan

Photopatterning of organosilane self-assembled monolayers has attracted attention due to a wide variety of applications of micopatterned monolayers as micro templates for immobilizing biomolecules, nanoparticles, polymers and so forth. For such advanced applications of the micropatterned monolayers, the study on photochemical reactions proceeding on the monolayers due to photo irradiation is indispensable. In this study, we used two types of the monolayers prepared on Si substrates from octadecyltrimethoxysilane (ODS) and chloromethylphenyltrimethoxysilane (CMPhS). Each monolayer was micropatterned by irradiating the monolayer through a photomask with a light at 172 or 244 nm in wavelength in the presence of atmospheric oxygen molecules. Although, the CMPhS monolayer could be micropatterned by both the light at 172 and 244 nm, patterning of the ODS monolayer was capable only by the light at 172 nm. Generation of activated oxygen atoms through the excitation of the atmospheric oxygen molecules had a crucial role in photopatterning at 172 nm, while excitation of aromatic rings was the key process for patterning of the CMPhS monolayer at 244 nm. Photochemical reactions proceeded on the monolayers were further studied in minute scale through changes in friction and surface potential due to photo-irradiation by means of scanning probe microscopy, that is, lateral force microscopy and Kelvin-probe force microscopy, respectively. These results will be discussed with results obtained from spectroscopic studies such as X-ray photoelectron and infrared absorption spectroscopies.

NS-TuP29 Self-organizing Processes in Connection with Nanocluster States*, **W. Schommers**, M. Rieth,* Forschungszentrum Karlsruhe, Germany*; S. Baskoutas,* University of Patras, Greece

In the past experimental as well as theoretical investigations have shown that the structure of metallic nanoclusters most often deviates significantly from those of the bulk. With the help of molecular dynamics calculations we demonstrate how the transition from bulk structured materials to nanostructured clusters might take place, e.g., during a production process. In connection with such structural transitions one result is rather interesting: the occurrence of meta-stable cluster states. The conditions under which such meta-stable nanostructures might be possible and how their life-time could be influenced is systematically investigated. Such structurally meta-stable atomic compounds are commonly known in connection with huge complicated inorganic molecules. Especially in biology such meta-stable molecules are most often observed to store energy or to act as propulsion system in one way or another by changing parts of its structure. Our molecular dynamical investigations have shown that specific metallic nanoclusters behave similar. In this connection we also tried to answer the following questions: How is the dynamics of nanoclusters changed when they transform from the metastable to the stable state? Is this behavior restricted to specific materials? And what is the underlying mechanism?

Organic Films and Devices
Room Hall A-C - Session OF-TuP
Poster Session

OF-TuP3 Real Time Observation of Surface Stress during Dithiol Adsorption in Gas Phase*, **A.N. Itakura**,* National Institute for Materials Science, Japan*; R. Berger,* Max Planck Institute for Polymer Research, Germany*; S. Igarashi,* Japan Science and Technology Corporation, Japan*; M. Kitajima,* National Institute for Materials Science, Japan

Self-assembled monolayers (SAM) such as alkanethiol, HS-(CH@sub2@)@sub n-1@-CH@sub 3@ for n=4,6,8,12, on Au induce compressive surface stresses during the self-assembly, and the saturation value of the stress is proportional to the length of alkyl chain.@footnote 1@ We observed the compressive stress for dithiol HS-(CH@sub2@)@sub n@-SH for n=6,8,10, adsorption on Au in gas phase. Contrary to the alkanethiol adsorption, the saturation value of the compressive stress showed smaller value for longer alkyl chain. The compressive stress for dithiol adsorption may be induced by the bonding between S and Au substrate. Dithiol adsorbes on Au surface as a lie-down phase, while alkanethiol as a standing phase. Density of the S-Au bonds should be lower for longer chain of dithiol, resulting in the reduction of the stress. @FootnoteText@ @footnote 1@ A.N.Itakura, R.Berger, T.Narushima and M.Kitajima, Appl.Phys.Lett.80, 3712 (2002)

OF-TuP4 XPS Studies of Charge Transfer between Dye Molecules and Polymer Chains in Dye Molecule Doped Conducting Polymer Films*, **H. Kato**, S. Takemura,* Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecules such as methylene blue (MB), safranine T (ST) and brilliant green (BG) were prepared by electrochemical doping and diffuse injection methods. Polymeric structure, charge transfer and interaction between the dye molecule and PT polymer chain in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. Vibrational states of the doped dye molecule and polymer backbone were also investigated by FTIR RAS and ATR in order to examine the dopant configuration into polymer chains. XPS measurements clarified the identification of doping species into the polymer chains varied with synthetic methods and conditions. Dye molecules such as MB, ST and BG were doped in polymer films as two types of states such as cation-like and salt-like. In the case of BG, XPS core-level analysis of S 2p split indicates simultaneous doping of BG cation and HSO4- in the hybrid films prepared by electrochemically reduced and dye diffused injection methods. The higher binding energy peak corresponds to HSO4- while lower binding energy peak can be assigned to the S sites of polymer backbone. Synthesized film samples were categorized into two types by the difference of S 2p core-level energy shift. In the cation-like doped sample, the energy shift of the lower peak of S 2p suggests the charge transfer between BG molecules and polymer chains creating a n-type conducting polymer state. The relation between dopant species with different configuration and dopant-chain charge transfer will be also discussed.

OF-TuP5 XPS Studies of Organic-Inorganic Interface Interaction between Conducting Polymer Chains and Si Sublayers*, H. Kato, **S. Takemura**,* Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) and polypyrrole (PP) films were grown on Si substrates. PT/Si and PP/Si interfaces were fabricated by electrochemical method. Thin polymer film growth was obtained by controlling the applied voltage to the anode Si wafer in an electrochemical cell. Obtained film thickness was thin enough to be penetrated by XPS measurement to detect the organic-inorganic interface. Polymer chain configuration was also investigated by FTIR. XPS measurements were conducted closely investigating the core-level energies and spectral profiles of the atomic components. An affinity between a deposited polymer film and a Si substrate was strong compared with the case of film growth on metal oxide substrates such as ITO and SnO2. Si 2s and 2p core-level spectra which were basically composed of different Gaussian components reflect different valence states of Si interacting with upper polymer layers in comparison with the core-level spectra of non-deposited Si substrate expecting bonds between polymer chains and Si substrate layers. The lower binding energy peaks observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT suggesting Si-C and Si-F bonds created at the PT/Si interface. In adition to the organic-inorganic bonding, the polymer chain configuration was also investigated by FTIR. The polymer chain orientation on a Si substrate will be discussed comparing with the data obtained by RAS and ATR techniques detecting ring stretching modes of the polymer chain. The polymer chain linkage which reflects symmetric and asymmetric vibration modes will be also discussed.

OF-TuP6 Vibrational Spectroscopy and Charge Transport Characteristics of Metal-Molecule-Metal Junctions*, **J.L. Lazorcik**, J.G. Kushmerick, R. Shashidhar,* Naval Research Laboratory

We report the current-voltage characteristics and inelastic electron tunneling spectra of self-assembled monolayers in a crossed-wire tunnel junction. Inelastic electron tunneling spectroscopy (IETS) enables in situ vibrational characterization of metal-molecule-metal junctions. The well defined spatial orientation of molecules in a self-assembled monolayer enables the selection rules for IETS to be explored. Results for an insulating alkane-thiol and two @pi@-conjugated molecular wires, oligo(phenylene ethynylene) and oligo(phenylene vinylene), will be presented.

OF-TuP7 Photolithographycally Defined Micropatterned Organosilane Monolayer as a Template Surface for Guided Self-Assembly of Charged Microparticles*, A. Takahara, **T. Koga**, M. Morita, H. Otsuka,* Kyushu University, Japan

Two-dimensional arrangement of microparticles on the substrate surface might be a promising method to fabricate functional materials. In this study, micropatterned fluoroalkylsilane/aminosilane monolayer was prepared as a template surface for site-specific arrangement of sulfonated polystyrene (PS) microparticles. Micropatterning of organosilane monolayer was carried out by area-selective irradiation of vacuum ultraviolet-ray through the photomask. Si wafer substrates with micropatterned organosilane monolayer were then exposed to the dispersed aqueous solution of sulfonated PS microparticles. Atomic force microscopic (AFM) observations revealed that the PS microparticles were area-selectively adsorbed onto the aminosilane phase. The site-specific adsorption of PS microparticles onto the aminosilane phase was ascribed to the electrostatic interaction between sulfonic acid groups of PS microparticles and amino groups of aminosilane phase. The height of adsorbed PS microparticles is in good agreement with the diameter of PS microparticle. This result suggested that the sulfonated PS particles formed a monolayer on the substrate surface. This consideration was supported by the result of adhesion force measurements. Adhesion force measurements clearly showed the specific interaction between sulfonic acid group of cantilever tip and amino group of aminosilae patterned surface. Compared with fluoroalkylsilane phase, strong adhesion force was observed on the aminosilane phase. On the other hand, very weak adhesion force originated from repulsive interaction was observed between sulfonic acid group of cantilever surface and that of PS microparticles. It is considered that the micropatterned surface prepared by present method can be applied for area-selective arrangement of two kinds of microparticles onto the substrate surface.

OF-TuP8 Electrical and Optical Characteristics of Indium Tin Oxide Thin Films Deposited by an Oxygen Beam Assisted Deposition Technique on Organic Electroluminescent Device (OLED)*, **N.G. Cho**, Y.H. Lee, J.H. Lee,* Sungkyunkwan University, South Korea*; Y.W. Ko, J.H. Lee,* Electronics and Telecommunications Research Institute (ETRI), Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

To fabricate active matrix organic electroluminescent devices (OLED), a transparent conducting material such as indium tin oxide(ITO) has to be deposited on the organic material of the devices and the organic materials are easily damaged by the oxygen atom, ion bombardment, heating, etc. during the deposition processing of ITO. Therefore, it is very difficult to deposit ITO on the OLED to form a transparent electrode. Also, it is difficult to maintain both electrical conductivity and transparency of ITO without generating damages to OLED when a conventional ITO deposition technique such as sputter deposition is used. Therefore, in this study, a dual oxygen ion, neutral beam assisted evaporator system has been used to deposit ITO films on the OLED to investigate as a possible transparent and conductive ITO deposition technique without generating damage to OLED. The characteristics of the deposited ITO on OLED was investigated using a four-point probe and a UV-spectrometer to measure the resistivity and transmittance of ITO films, respectively. The change of surface roughness after ITO deposition was investigated using an atomic force microscopy. Also, current-voltage(I-V) characteristics of the fabricated OLED with the ITO electrode were measured by HP-4145A semiconductor parameter analyzer.

OF-TuP9 Contour TPD of N,N'-disalicylidene-1,2-propanediamine Thin-films*, **C.C. Chusuei**,* University of Missouri-Rolla*; J.A. Schreifels,* George Mason University

A simple method for obtaining a comprehensive overview of large (m/e > 200) molecular weight compounds desorbing from the surface during temperature programmed desorption (TPD) experiments is presented. Standard 2D TPD methods require a priori knowledge of surface reactions and typically therefore is limited to a few pre-selected mass-to-charge ratios (< 10). Our method precludes this necessity since wide mass ranges (m/e = 25) can be monitored in a single experiment. Desorbing organic films can be represented in the form of contour TPD (CTPD) plots. In our example, the desorption of N, N'-disalicylidene-1,2-propane -diamine, an important jet fuel additive used in aircraft, is adsorbed onto oxidized and oxide-free 304 stainless steel surfaces. The utility of CTPD for providing mechanistic insight into thermal decomposition pathways is demonstrated. Four chemical species were observed at m/e = 107, 133, 232 and 290 respectively, and mechanistic pathways for their formation are presented. Conventional 2D TPD spectra can be extracted from the CTPD by taking vertical slices of the contours.

OF-TuP10 Organic Electroluminescent Devices Fabricated by Ink-jet Printing*, **S.J. Jo**, S.M. Jeong,* Yonsei University, Korea*; H.K. Baik,* Yonsei University, Korea, South Korea*; S.H. Choi, W.H. Koo,* Yonsei University, Korea*; K.M. Song,* Kon Kuk University, Korea*; S.J. Lee,* Kyungsung University, Korea

Organic Electroluminescent Devices for full color were fabricated by ink-jet printing methods. ITO used as anode was treated by atmosperic plasma for hydrophilic surface. Also polyimide as a bank was treated by atmospheric plasma for hydrophobic surface. In this experiment, we investigate characters of OLED and the influence of atmospheric plasma treatment.

Contacts to Organic Materials Topical Conference
Room Hall A-C - Session OM-TuP

Poster Session

OM-TuP1 Study of Surface Photovoltage Effects in Doped Organic Molecular Thin Films*, **C. Chan**, W. Gao, A. Kahn,* Princeton University

We investigate photoemission-induced surface photovoltage (SPV), i.e. non-equilibrium resulting from photoexcitation and separation of carriers, in organic films. We focus on electrically doped molecular films that exhibit interface depletion regions@footnote 1@ and can sustain charge separation and SPV. We combine ultraviolet photoemission spectroscopy (UPS) to measure the HOMO and vacuum levels under illumination, and contact potential difference (CPD) measurement with a Kelvin probe to measure the vacuum level in the dark. Zinc phthalocyanine (ZnPc) and N,Nâ€™-diphenyl-N,Nâ€™-bis(1-naphthyl)-1,1â€™biphenyl-4,4â€™â€™diamine (@alpha@-NPD) p-doped with the acceptor molecule, tetrafluorotetracyanoquinodimethane (F@sub 4@-TCNQ), are investigated.@footnote 1,2@ UPS and CPD measurements are performed as a function of film thickness deposited on Au. CPD measurements reproduce with excellent accuracy the UPS-observed shifts of the molecular energy levels, in particular through a depletion region ~30-50Å near the metal-organic interface of the doped organic films. The excellent agreement shows that: (1) efficient p-doping occurs even in the dark in these two organic systems; (2) SPV is negligible in both doped and undoped organic films. The undoped films do not have depletion regions where charge separation can occur. In the doped films, electrons separated in the interface depletion region recombine in the metal before generating significant SPV, whrereas the holes readily recombine throughout the film. @FootnoteText@ @footnote 1@ W. Gao and A. Kahn, Organic Electronics 3, 53 (2002) @footnote 2@ W. Gao and A. Kahn, J. Appl. Phys. (accepted for publication; July 1, 2003).

OM-TuP2 Adsorption of PTDCA on Si(100)*, B. Grandidier, **T. Soubiron**, J.P. Nys, M. Dubois, C. Delerue, D. Stievenard,* IEMN-CNRS, France

Submonolayer coverages of perylene-tetracarboxylic-dianhydride (PTCDA) molecules have been investigated with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). At low coverage, comparisons between the STM images and calculations of the electronic structure of the molecule show that the molecule adsorbs mostly in a planar configuration with its axis parallel to the Si dimers. Different configurations are observed and associated with physisorbed and chemisorbed states of the adsorbates. At higher coverage, X-ray measurements indicate that only a fraction of the molecules are chemisorbed and that the bonding occurs through the dicarbonyl functional groups, preserving the pi-conjugation of the molecules. While PTCDA selectively reacts with the Si dimers, steric hindrance is found to be the major cause to hamper the formation of an ordered film.

OM-TuP3 Potential Imaging of Metal-organic Semiconductor Interfaces using Kelvin Probe Force Microscopy*, O. Tal,* Tel Aviv University, Israel*; W. Gao, L. Friedman, A. Kahn,* Princeton University*; Y. Rosenwaks,* Tel Aviv University, Israel

Understanding and improving the performance of organic electronic devices depends, to a great extent, on the elucidation of organic materials interfaces with inorganic and organic solids alike. Therefore these interfaces are the focus of this work. We present a study of two dimensional (2-D) potential profiles across metal-organic film interfaces (metal- Au or Al, organic film - tris(8-hydroxyquinolino) aluminum [Alq@sub 3@]) with nanometer spatial resolution provided by Kelvin probe force microscopy (KPFM) in a nitrogen environment. The contact potential difference (CPD) is measured across Al/Alq@sub 3@/Al, Au/Alq@sub 3@/Au and Au/Alq@sub 3@/Al sandwich-like structures following cleavage under the inert atmosphere. The CPD profiles are in a very good agreement with vacuum level profiles estimated by calculation, which are based on ultraviolet photoemission spectroscopy (UPS) measurements. Preliminary measurements of these structures and "device-type" structures under operating conditions will be presented and discussed. This work is the first step in providing a new and unique type of information on the electronic structure of metal-organic and organic-organic interfaces, as determined by KPFM and additional techniques.

OM-TuP4 Conductive Core-Shell Nanoparticles: An Approach to Self-Assembled Mesoscopic Wires*, G. Kaltenpoth,* *M. Himmelhaus,* Universität Heidelberg, Germany*; L. Slansky,* Daimler-Chrysler AG, Germany*; F. Caruso,* University of Melbourne, Australia*; M. Grunze,* Universität Heidelberg, Germany

Conductive core-shell nanoparticles were prepared by coating negatively charged monodisperse polystyrene (PS) latex spheres with a thin layer of polyethyleneimine (PEI). Subsequently, gold colloid with 3 nm in size was electrostatically adsorbed onto the PEI-coated spheres, and finally, an electroless gold plating step was repeatedly carried out to yield a high gold coverage and thus a conductive gold shell. The metallic behavior was investigated by XPS and UV-vis. In the XPS Au4f peak, a shift due to charging effects was observed at low metal coverage, which decreased with increasing gold decoration, and vanished with the formation of a conductive metal shell. The UV-vis spectra show a coverage-dependent shift and broadening of the Au plasmon resonance. The self-assembly of the metal coated spheres into continuous lines was investigated to explore the applicability of such particles to realize self-assembled electrical circuits. It was found that the particles selectively adsorb to the carboxyl-terminated areas of line patterns fabricated by microcontact printing of alternating carboxyl- and methyl terminated alkanethiolates on gold.

OM-TuP5 The Enhancement of Passivation Effect and Long Time Stability on Aluminum Cathode Deposited by Adatom Mobility Enhancing Technique in Organic Electroluminescent Display*, S.M. Jeong*, *W.H. Koo, S.H. Choi,* Yonsei University, Korea*; S.J. Lee,* Kyung Seong University, Korea*; K.M. Song,* Kon Kuk University, Korea*; H.K. Baik,* Yonsei University, Korea, South Korea

Highly stable and electroluminescent devices based on spin-coated PPV thin films have been achived. The improvement of lifetime is derived from aluminum cathode deposited by adatom mobility enhancing technique. There are much less pinhole defects because of fine grain size caused by high surface mobility and contact area between Al and PPV increase. It is believed that the passivation effect and minimizing thermal degradation is induced by much less pinhole defect and large contact area between Al and PPV.

OM-TuP6 Hole-injection and Transport in Arylamines Films Sandwiched between Metal Contacts*, G. Szulczewski*, *J. Li, K.-Y. Kim, J. Sun, S.C. Blackstock,* University of Alabama

We have synthesized a series of electron-rich arylamines to systematically control their electronic properties, i.e. dipole moment and ionization potential. Films of these molecules were made by solution and/or vapor deposition techniques on Ag and Au substrates and characterized by cyclic voltammetry and x-ray photoelectron spectroscopy. We have measured current-voltage curves of monolayer and multilayer films to study hole-injection and transport. We find that these molecules rectify current under forward bias above a threshold voltage. A plot of the threshold voltage against the measured electrochemical oxidation potential yields a straight line with an excellent correlation coefficient, R = 0.98, and slope greater than unity. We will discuss how the how the molecular properties influence charge-injection at the metal-molecule interface. We acknowledge the National Science Foundation for support of this work through the Materials Research Science and Engineering Center grant # DMR0213985.

Plasma Science and Technology
Room Hall A-C - Session PS-TuP
Poster Session

PS-TuP1 Silicon Dioxide Etching Processes Employing Electron Beam Excited Plasmas*, M. Ito,* *K. Takeda, Y. Tomekawa, M. Iwawaki, T. Shiina, Y. Okamura,* Wakayama University, Japan*; M. Hori, T. Goto,* Nagoya University, Japan

Optical devices or micro total analysis system fabricated by using micromachining techniques attract much attention because of their usefulness. In the fabrication processes, micromachinings of non-planer thick dielectric materials such as optical fibers and thick quartz parts are necessary. In such processes, the fast atomic beam etching and ion beam etching are employed because the RF self-biasing in the conventional reactive ion etching (RIE) is not applicable to non-planer dielectric materials such as silicon dioxide (SiO@sub 2@). However, the etch rates of these processes are typically around few tens nm/min, which are very low compared with the RIE and so the higher etch rate is strongly required to reduce the processing time. Therefore, the biasing effect is necessary to etch the SiO@sub 2@. On the other hand, an electron beam excited plasma (EBEP) has an excellent potential for applying self-bias to the non-planer dielectrics by using the electron beam. The SiO@sub 2@ etching characteristics using EBEP have been never reported although the SiO@sub 2@ is useful for the devices using micromachining techniques. Therefore, we have demonstrated the SiO@sub 2@ etching processes using self-biasing induced by an electron beam of the EBEP without any additional bias power supply. As a source gas, the CF@sub 4@ diluted by Ar (CF@sub 4@/Ar) was employed. The etch rate of 117 nm/min has been obtained. From the plasma diagnostics using a Langmuir probe and an optical emission spectroscopy, it has been found that the higher electron beam current for generating plasmas improves the plasma density and sheath potential, resulting in higher etch rate of SiO@sub 2@. Moreover, novel pulsed EBEPs have been applied for the SiO@sub 2@ etching process. The plasma diagnostics have been carried out. These results indicated that the electron beam excited plasmas has a great potential for application to micromachining processes.

PS-TuP2 A Novel Si/SiO@sub 2@ Etching Technique for Minimizing Charge-induced Microscopic Non-uniformity in Plasma Etching*, K.H. Baek*, Samsung Electronics, South Korea*; D.H. Lee, S.J. Jung,* Sungkyunkwan University, South Korea*; C.J. Kang,* Samsung Electronics, South Korea, Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

In this study, microscopic non-uniform etching characteristics solely caused by positive ions were investigated and a novel etching technique using energetic and directional neutrals was introduced as an alternative of reducing those charge-induced phenomena. To systematically investigate microscopic non-uniform etching characteristics, various samples designed to evaluate microscopic etching characteristics were prepared and etched in a homemade ICP(inductively coupled plasma) etching system, ion beam etching system, and neutral beam etching system. By analyzing all the results, we could clarify role of positive ions in the non-uniform etching phenomena and get an idea on reducing them. To realize the idea, we revised our previous neutral beam etching system so that it could improve flux and directionality of neutrals. By using this system, successful etching results for poly-Si and SiO2 nearly without the charge-induced phenomena were achieved, even though the results etched in the other systems show those non-uniform etching characteristics. Thus, we recommend energetic and directional neutrals as a potential etching source for the next generation technology era.

PS-TuP3 Effects of Substrate Temperature and Ultraviolet Radiation on the Etching of Copper Films using Inductively Coupled Chlorine-based Plasmas*, K.H. Jang,* Sungkyunkwan University, South Korea*; H.R. Kim, W.J. Lee,* IMG, LG-Production Engineering Research Center*; G.Y. Yeom,* Sungkyunkwan University, South Korea

Copper(Cu) is one of the potential materials in thin film transistor liquid crystal display (TFT-LCD) because of its lower bulk resistivity and lower cost than aluminium alloy, chromium, tungsten, and nickel at room temperature. Cu etching for TFT-LCD is currently performed using wet etching methods, however, for the fabrication of high resolution display devices, the use of plasma etching process is indispensable. In reality there are several problems to be solved before Cu plasma etching to be applied to TFT-LCD processing. The main problems are the formation of involatile etch products, lower etch rates, and high surface roughness after removing the etch products. For example, many works on Cu etching using chlorine-based plasma have been studied, however, slow etch rates and thick involatile Cu etch products remaining during the etching were reported especially for the integrated circuit (IC) manufacturing. Therefore, in this study, using an inductively coupled chlorine-based plasma, the effects of substrate temperature and ultraviolet radiation effects were investigated to obtain Cu etch rates higher than 200 nm/min and to remove the involatile etch products by changing substrate temperature and ultraviolet photon density and strength. To understand the Cu etching characteristics, we used the optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) and measured the substrate temperature and ultraviolet intensity and wavelength. Also, a scanning electron microscope (SEM) was used to observe etched Cu electrodes profile.

PS-TuP4 The Electrical Properties of SBT Thin Films Etched in BCl@sub 3@/Cl@sub 2@/Ar Plasma*, **J.K. Kim**, C.I. Kim, K.T. Kim, D.P. Kim,* Chung-Ang University, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) thin films have a lot of good features such as high resistance to polarization fatigue due to the charge-compensating role of the (Bi@sub 2@O@sub 2@)@super 2+@. The 200-nm SBT thin films were deposited on the Pt electrode by metal organic deposition (MOD). Until now, there is no report on the etching characteristics of SBT thin films in BCl@sub 3@/Cl@sub 2@/Ar inductively coupled plasma (ICP). Therefore, SBT thin films were etched in BCl@sub 3@/Cl@sub 2@/Ar with using ICP etching system. The etch rates and selectivity of SBT thin films were investigated as functions of gas mixing ratio, rf power, dc-bias voltage and pressure. With adding 20% BCl@sub 3@ in Cl@sub 2@/Ar plasma, increasing rf power and dc bias voltage, and lowering pressure, the etch rate of SBT increased. The etching byproducts were investigated with using quadruple mass spectroscopy (QMS). The heterogeneous reaction of plasma on the surface of the etched SBT was investigated with x-ray photoelectron spectroscopy (XPS). The etching profiles of samples have been investigated with using scanning electron microscopy. The chemical states on the etched surface were investigated with XPS. After the etching, the electrical properties of SBT capacitors were characterized in terms of hysteresis curves, leakage current and switching polarization. After etching in BCl@sub 3@/Cl@sub 2@/Ar plasma, the remanent polarization decreased and the leakage current increased. After the annealing at 600°C in an O@sub 2@ atmosphere for 10 min, the ferroelectric properties were significantly recovered. The degradation of electrical properties after the etching was considered due to the physical effect of ion bombardment and chemical residue contamination.

PS-TuP5 Modeling of Etching Mechanism of PZT in Cl@sub 2@ Plasma with the Addition of Ar, O@sub 2@*, **S.M. Koo**, C.I. Kim, D.P. Kim, K.T. Kim,* Chung-Ang University, Korea

Ferroelectric Lead Zirconate Titanate (Pb(Zr,Ti)O@sub 3@) thin films have been widely known as capacitor materials in nonvolatile ferroelecric random access memory (FRAM). the desirable properties such as high permittivity, high remnant polarization, fast switching speed, high Curie point and resistivity. Now, 32Mbit FRAM has been developed and some companies attempt to use FRAM as mobile phone memory. But the larger FRAM capacity, the smaller feature size. Therefore, in order to accomplish the integration of such devices, the etching process of PZT thin films with high etch rate, vertical etch profile, low by-product must be developed. PZT thin films were prepared on Pt/Ti/SiO@sub 2@/Si substrates by sol-gel processes. Pt top electrodes were deposited on PZT thin films by using rf magnetron sputtering. SiO@sub 2@ was deposited on Pt top electrodes. SiO@sub 2@ layer was etched in CF@sub 4@/Ar inductively coupled plasma with PR mask. We continued etching Pt/PZT/Pt layer without removing PR and SiO@sub 2@ patterns. PZT thin films were etched with two steps. First, it was etched with Cl@sub 2@/Ar inductively coupled plasma, then instead of Ar, it added O@sub 2@ to Cl@sub 2@ plasma. We observed the effect of etching profile in PZT thin films during etching in Cl@sub 2@/Ar, Cl@sub 2@/O@sub 2@ plasma. The ferroelectric and electrical properties were measured with a precision workstation. We obtained stable value of remanent polarization and good fatigue resistance for PZT with SiO@sub 2@ mask as compared with Pt dot, which was used as physical mask during etching process. The structural damages to the near surface of PZT are evaluated by x-ray diffraction (XRD). The chemical deformation of etched surface was surveyed x-ray photoelectron spectroscopy (XPS).

PS-TuP6 Etching Characteristics of LNO (LaNiO@sub 3@) Thin Films Using Inductively Coupled Plasma*, C.I. Kim, **J.W. Yeo**, K.T. Kim, D.P. Kim,* Chung-Ang University, Korea

Among the ferroelectric thin films that have been widely investigated for ferroelectric random access memory (FRAM) application, the LaNiO@sub 3@ (LNO) thin film is known to play a role to improve fatigue and imprint of ferroelectric capacitor. And LNO thin film is expected as an effective electrode for the growth of highly oriented ferroelectric thin films because it shows a pseudocubic perovskite structure (a = 3.84 Å) and an n-type metallic behavior without any doping procedure. Although, there are several advantages and Dry etching, which shows anisotropic etching properties, has become one of the critical processes for pattern transfer in ultra large scale integration, very few studies on the etch properties of LNO electrode thin films have been reported. In this study, LNO thin films were etched by BCl@sub 3@/Ar plasma with inductively coupled plasma etching system. The etch rates of LNO thin films and selectivity of LNO to SiO@sub 2@ were investigated as functions of gas mixing ratio, rf power, dc-bias voltage, pressure and gas flow. To understand the effects of etching parameters, the atoms of B, Cl and the ions of Ar were investigated in BCl@sub 3@/Ar plasma using optical emission spectroscopy and Langmuir probe. The etching byproducts were investigated with using quadruple mass spectroscopy. The heterogeneous reaction of plasma on the surface of the etched LNO was investigated with x-ray photoeletron spectroscopy and secondary ion mass spectroscopy. The etching profiles of samples have been investigated with scanning electron microscopy.

PS-TuP7 Plasma Etching of Cantilever Epitaxy Sapphire Substrates*, **K.C. Cross**, K.H.A. Bogart, C.C. Mitchell, R.D. Briggs,* Sandia National Laboratories

Growth of GaN-based wide bandgap semiconductors by MOCVD is performed on sapphire, silicon carbide, or silicon substrates due to the lack of bulk crystalline GaN. Cantilever epitaxy (CE), a new lateral overgrowth method, utilizes sapphire substrates patterned by plasma etching. CE is advantageous because it requires only one growth run to achieve <5E7 dislocations per cm@super2@, nearly one to two orders of magnitude lower than standard planar growth. The sapphire (Al@sub2@O@sub3@) material is exceedingly difficult to etch due to the large Al-O bond strength (122.4 kcal/mol). We have developed a method for plasma etching of sapphire. The etching mask for the sapphire is a quad-level film stack consisting of a release layer, hardbaked photoresist, silicon nitride, and imaging resist, and is etched in an ECR plasma with O@sub2@/Ar chemistry. The sapphire is etched in an ICP system with high rf source and substrate powers, low pressure and temperature, and chlorine-based chemistry. Typical etching rates are 580 Å/min with a selectivity of 0.3, for etch depths of 2-4 µm. Issues that have been difficult to overcome include etch uniformity over 50 mm, critical dimension control, and profile control. Data and optimization of the etching process will be presented. Results from experiments to characterize the etching process as a function of rf source power, substrate bias, pressure, temperature, and gas chemistry will also be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

PS-TuP8 Effect of O@sub 2@/Cl@sub 2@ Gas Mixing Ratio on Dry Etching Characteristics and Electrical Properties of Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ Films*, **D.P. Kim**, C.I. Kim, K.T. Kim,* Chung-Ang University, Korea*; A.M. Efremov,* Ivanovo State University of Chemistry and Technology, Russia

Recently, Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ (BLT) has been considered a predominant candidates for ferroelectric random access memory because of its high resistance to polarization fatigue due to Bi@sub 2@O@sub 2@ layers, which reduce space charges and the unpinning of domain walls. There are a lot of reports on deposition BLT thin films, but there is no report on the etching characteristics and electrical properties of BLT in Cl@sub 2@/O@sub 2@ plasma. The BLT of 200 nm was spun-coated on a Pt/Ti/SiO@sub 2@/Si substrate by MOD. Pt thin films, which used as top electrode, were deposited on BLT. BLT thin films were etched in Cl@sub 2@/O@sub 2@ using ICP because it is easy to control energy of infringing ions to the substrate. When Cl@sub 2@-based gas mixtures were used with Ar and O@sub 2@, the etch products remaining on the substrate could be observed after etching because of their very low vapor pressure. The etch rates and selectivity of BLT thin films were investigated as a function of gas mixing ratio, rf power, dc-bias voltage, and pressure. With adding 20 % O@sub 2@ in Cl@sub 2@ plasma, increasing rf power and dc bias voltage and lowering pressure, the etch rate of BLT increased. To understand the effects of etching parameters on the etch rates of BLT thin films, the atoms of Cl and O investigated using optical emission spectroscopy and Langmuir probe. The surface of the etched BLT was investigated with x-ray photoelectron spectroscopy. To estimate electrical properties of BLT after etching process, the etched species were characterized with measuring leakage current using semiconductor parameter analyzer [HP4145B] and P-E loops of Pt/BLT/Pt capacitor using precision work station. In Cl@sub 2@/O@sub 2@ plasma, we obtained higher low remnant polarization value and lower leakage current density compared with Cl@sub 2@/Ar plasma. @FootnoteText@ Acknowledgement: This work was supported by grant No. R01-2001-00268 from the Korea Science & Engineering Foundation.

PS-TuP10 Production of Electron-Temperature-Controllable ECR Plasma for Thin Film Deposition*, **N. Itagaki**, H. Muta,* Kyushu University, Japan*; N. Ishii,* Tokyo Electron Co. Ltd., Japan*; Y. Kawai,* Kyushu University, Japan

In semiconductor processing, it is required to control the electron temperature (T@sub e@) in the plasma for progress of microelectronic devices and minimization of substrate damage. An electron cyclotron resonance (ECR) plasma source has attracted much attention for its high electron density that can be achieved at low gas pressure. However, in a conventional ECR plasma produced by 2.45 GHz microwave, T@sub e@ is relatively high and quite hard to be controlled in a wide range. Recently, we have clarified that T@sub e@ in a 915 MHz ECR plasma depends on the spatial profiles of the microwave power absorption by both the measurement of electromagnetic waves and the calculation of microwave power absorptions. Since the power absorption profile is influenced by the effective resonance zone width (@DELTA@z@sub res@, above-mentioned results implies that T@sub e@ can be controlled by varying @DELTA@z@sub res@ which is determined from the magnetic field gradient and the microwave frequency. In this report, the spatial profiles of wave patterns were measured at different @DELTA@z@sub res@ to make clear the relationship between the power absorption profiles and @DELTA@z@sub res@. Furthermore, we tried to control T@sub e@ by changing the magnetic field gradient in order to examine whether or not the above-mentioned way to control T@sub e@ is an effective method. As a result, the power absorption profiles were confirmed to change with @DELTA@z@sub res@, which indicated that T@sub e@ could be controlled by varying @DELTA@z@sub res@. In fact, we observed that T@sub e@ varied from 1.9 eV up to 3.5 eV with increasing the magnetic field gradient at the resonance point from 0.3 G/mm to 1.4 G/mm for N@sub 2@ plasma. The experiments on thin film deposition were also performed to investigate the relationship between T@sub e@ in the plasma and the quality of prepared films, which will be presented at the conference.

PS-TuP11 Fabrication of Carbon Nanowalls Using RF Plasma-Enhanced Chemical Vapor Deposition Assisted by Hydrogen Radical Injection@footnote 1@*, **K. Shiji**, M. Hiramatsu, T. Kadoya, H. Amano, Y. Ando,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan

Carbon nanostructures are of tremendous interest from both a fundamental and an applied prospective. Recently, fabrication of two-dimensional carbon nanostructures (carbon nanowalls) was reported.@footnote 2@ The large surface area of carbon nanowalls may provide us various new applications. In the case of film formation using plasma-enhanced chemical vapor deposition (PECVD) technique, surface morphology can be effectively controlled not only by optimizing the substrate temperature and bias, but also by the inclusion of specific reactive species as appropriate to the film growth and nucleation. Previously we demonstrated the diamond growth using a unique PECVD system that consists of a parallel-plate radio-frequency (rf, 13.56 MHz) capacitively coupled plasma (CCP) assisted by a hydrogen (H) radical source.@footnote 3@ In this work, carbon nanowalls were successfully fabricated on silicon (Si) substrate using C@sub 2@F@sub 6@ rf-CCP assisted by H radical injection from H@sub 2@ inductively coupled plasma (ICP). Partial pressures of C@sub 2@F@sub 6@ and H@sub 2@ were 20 and 80 mTorr, respectively, and the total pressure was 100 mTorr. The rf powers of CCP and ICP were 100 and 400 W, respectively, and the substrate temperature was 500 °C. Growth experiments were conducted for 2 hours. Carbon nanowalls were grown vertically on the Si substrate without catalyst. The thickness of these carbon nanowalls grown was 10-30 nm, and their height was about 300 nm. The aggregation of carbon nanowalls would be useful as templates for the fabrication of other types of nanostructured materials. In the case of the deposition without ICP, on the other hand, carbon nanowalls were not fabricated. @FootnoteText@ @footnote 1@This work was supported by 21st century COE program, Nano Factory.@footnote 2@Y.H. Wu, et al., Adv. Mater., 14 (2002) 64. @footnote 3@M. Hiramatsu, et al., Rev. Sci. Instrum., 67 (1996) 2360.

PS-TuP12 Surface and Gas-phase Reactions in Plasma CVD using Cu(EDMDD)@sub 2@ as Source Material*, **K. Takenaka**, M. Takeshita, M. Kita, K. Koga, M. Shiratani, Y. Watanabe,* Kyushu University, Japan*; T. Shingen,* Asahi Denka Kogyo K.K., Japan

We have demonstrated 1) deposition of Cu films which have a low resistivity of 1.85 µ@ohm@cm and a strong adhesion strength above 10 MPa to the TiN layer, and 2) conformal deposition of smooth Cu films of 20 nm in thickness in trenches 0.5 µm wide and 2.73 µm deep using H-assisted plasma CVD (HAPCVD), which has an advantage of controlling independently concentrations of Cu-containing radicals and H atoms.@footnote 1@ To obtain information on surface and gas-phase reactions in HAPCVD, we have studied electron impact dissociation processes of Cu(EDMDD)@sub 2@ as well as nucleation and island growth of Cu, which are closely related with smoothness of Cu films and their adhesion strength to their under-layer. Quadrupole mass spectroscopic measurements show that Cu(EDMDD)@super +@ is the dominant ionic product from Cu(EDMDD)@sub 2@ due to an electron impact at electron energy of 70 eV. Based on this result together with the ion-core model, Cu(EDMDD) is suggested to be the main neutral radical from Cu(EDMDD)@sub 2@ due to electron impact dissociation. In-situ FT-IR measurements also show that supply of H atoms to the surface of deposition film is quite effective in reducing its impurity concentration. Nucleation density has little dependence on the kind of materials of under-layer such as TiN, TaN, WN, and Si. The nucleation rate increases from 2.3x10@super 14@ m@super -2@s@super -1@ at the substrate temperature T@sub s@ = 120°C to 4.1x10@super 14@ m@super -2@s@super -1@ at T@sub s@ = 220°C with increasing T@sub s@, while a maximum nucleation density of 3x10@super 16@ m@super -2@ is obtained at T@sub s@ = 150°C. The maximum density is more than two orders of magnitude higher than that for thermal CVD, and the high density is considered to contribute to smoothness and high adhesion strength of Cu films. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Proc. of ISTC 2002 (in press).

PS-TuP13 Sub-Millimeter Absorption Measurements of Temperature and Density in Fluorocarbon Plasmas*, **E.C. Benck**, K. Siegrist, D. Pusquellic,* National Institute of Standards and Technology

Sub-millimeter (300 GHz to 1 THz) absorption spectroscopy is being developed as a diagnostic for measuring radical densities and temperatures in processing plasmas for microelectronics. Most molecules, radicals, and ions have transitions suitable for detection at these frequencies and the necessary spectroscopic data is available in the literature for determining the absolute radical densities. Initial measurements are being conducted with a backward-wave-oscillator (BWO) source and a liquid-He-cooled bolometer detector. The narrow linewidth (< 10 kHz) of the BWO is ideally suited for measuring the translational temperatures of radicals through the Doppler broadening of the absorption lineshape. Previous temperature measurements in an inductively coupled Gaseous Electronics Conference (GEC) Reference Reactor found all the radicals to have a translational temperature close to room temperature. Other spatially resolved plasma diagnostics, such as laser-induced fluorescence, in similar inductive sources found significantly higher rotational temperatures within the plasma. The disagreement between the diagnostic methods is being investigated by measuring the radial density and temperature distributions. Initial results indicate that the low temperatures being measured with the BWO are probably due to the geometry of the GEC Reference cell which has a large volume of gas surrounding the plasma. Therefore the line-integrated absorption signal of the BWO is being dominated by the cooler, denser gas surrounding the plasma.

PS-TuP14 Plasma Frequency Measurements for Absolute Plasma Density by Means of Wave Cutoff Method*, J.H. Kim,* Korea Research Institute of Standards and Science, Korea*; Y.H. Shin, K.H. Chung,* Korea Research Institute of Standards and Science

A plasma oscillation method@footnote 1@ and a plasma absorption method@footnote 2,3@ have been used for measurements of absolute electron density in a plasma. In this report, a newly designed method for precise measurements of absolute electron density in the plasma using plasma frequency is described. A microwave perturbation of a frequency is introduced to plasma from a network analyzer and transmits in the plasma. The transmitted wave at a distance from a radiating antenna is monitored using spectrum analyzer as scanning the perturbing frequency. The transmitted wave rapidly decays by wave cutoff at the plasma frequency, which gives the absolute electron density. The propagating waves of some frequency including plasma frequency are characterized. The measured plasma frequency by this method is coincident with that obtained by the plasma oscillation method. The measured plasma densities are also compared with those got by using a double Langmuir probe over wide parameter range (gas composition, input power and gas pressure). @FootnoteText@ @footnote 1@T. Shirakawa and H. Sugai, Jpn. J. Appl. Phys. Vol. 32, 5129 (1993). @footnote 2@H. Kokura et al., J. Appl. Phys. Vol. 38, 5262 (1999). @footnote 3@K. Nakamura et al., J. Vac. Sci. Technol.A 21, 325 (2003).

QSA-10 Topical Conference
Room Hall A-C - Session QS-TuP
Aspects of Quantitative Surface Analysis

QS-TuP1 Test Studies on Charging, Charge Compensation and XPS Binding Energy Referencing for Al-Ox on Al and SiO@sub 2@*, M.H. Engelhard,* *D.R. Baer, D.H. Kim, D.J. Gaspar,* Pacific Northwest National Laboratory

The ability to determine absolute binding energy remains a challenging problem for X-ray Photoelectron Spectroscopy analysis of insulating or partially insulating specimens. Many studies have demonstrated a variety of difficulties with most approaches. Because our work involves study of many oxide and insulating materials, we have developed a number of approaches for dealing with charge compensation and charge referencing. To extend our understanding of charging in XPS, we have been examining how specific properties of a specimen influence the different approaches to dealing with surface charging. In this paper we add carbon over-layer thickness to measurements that examined the impact oxide layer thickness. Oxidized Al films and SiO2 samples that have been coated with different amounts of evaporated carbon. We have examined the peak widths and apparent binding energies as a function of charge compensation conditions for a Phi Quantum 2000 and Kratos Axis 165 XPS spectrometers. Results assist understanding of the charging process and indicate methods for charge compensation and referencing.

QS-TuP2 A Multi-modal Imaging and Visualization System for 3-D Materials Characterization*, J.E. Fulghum,* *K. Artyushkova, J. Farrar,* University of New Mexico*; L. Broadwater,* Kent State University*; J. Fenton, S. Pylypenko, D. Barbash,* University of New Mexico

Rapid image acquisition has transformed laboratory XPS imaging from a novelty to an increasingly routine analysis method for surface chemical characterization on the scale of microns. A variety of techniques, including FTIR, AFM and confocal microscopy (CM) have fields-of-view which are comparable to imaging XPS, making correlative analyses possible. With appropriate sample marking, information can be acquired from the same area on samples using multiple techniques. Correlating and combining this information allows us to model chemical changes within the sample through visualization techniques. The end result will be a three-dimensional model of the complex chemical structures and morphologies formed in multicomponent, heterogeneous samples. An additional goal is to utilize multivariate analysis methods to extract quantitative data from images and link them to chemical information. Proper integration of useful data from the separate techniques is essential. A comprehensive image analysis system - the Active Knowledge Mesh Model (AKM) - is currently under development in our laboratories. Image analysis involved in AKM has several steps, depending on the properties of the images and prior knowledge of the system and the experiment. Correlating the data from multiple modalities requires experimental matching and marking, image registration, multivariate image analysis, image quantification and image fusion. A prototype interface of AKM architecture involving all these steps will be shown. This work has been partially supported by NSF ALCOM (DMR89-20147), NSF CHE-0113724 and UNM.

QS-TuP3 Measurement of Overlayer Properties Using Angle Resolved XPS*, P. Mack, B. McIntosh,* ***R.G. White,*** Thermo Electron*; J. Wolstenholme,* Thermo Electron, UK

Ultra-thin films (<10 nm) are encountered, for example, as gate oxides on transistors, self-assembled monolayers or surface contamination layers. Angle resolved XPS (ARXPS) can provide a convenient and non-destructive method for measuring thickness and distribution of the component materials within these layers. It will be shown that methods based on sputtering or single angle XPS measurements may produce misleading results. The equation commonly used for the calculation of overlayer thickness will be shown to have limitations that depend upon both the material and the overlayer thickness. Advanced methodologies for the determination of layer thickness from ARXPS data will be described and will be shown to overcome these problems. These methods include the simultaneous calculation of thickness of each layer in a multi-layer stack by fitting. The methods for measuring concentration depth profiles will be discussed. In some applications, it is essential to know the dose of an element within an ultra-thin layer, for example the distribution of nitrogen in a transistor gate oxynitride. It will be shown that large errors can be expected if such measurements are attempted using XPS without knowing the distribution of the nitrogen within the layer. Using ARXPS, the nitrogen distribution can be measured and a more accurate dose calculated from this distribution. Application of ARXPS to thin films will be shown to be a powerful technique for the measurement of dose distribution and thickness but care must be taken to ensure that all of the required parameters are taken into account.

QS-TuP4 Experimental Determinations of Electron Inelastic Mean Free Paths in Ten Elemental Solids from Elastic Peak Intensities*, S. Tanuma,* *T. Kimura,* National Institute for Materials Science, Japan*; K. Goto,* Nagoya Institute of Technology, Japan*; S. Ichimura,* National Institute for Advanced Industral Science, Japan

The values of electron inelastic mean free paths (IMFPs) are very important physical quantity for surface analyses by AES and XPS. In usual, they have been determined from the theoretical calculations because the reliable experimental determinations of IMFP is rather a complicated work. The elastic-peak electron spectroscopy (EPES) is an efficient tool for experimental determination of IMFPs. This method, however, requires a reference specimen to obtain the values of IMFPs and gave different values according to the used reference specimen. On the other hand, absolute elastic-peak measurement method, which is carried out with a novel cylindrical mirror analyzer equipped with a Faraday cup, does not need the reference specimen. However, this method needs the surface plasmon excitation correction. Then, we have measured the IMFPs for Si, Zn, Cu, Ag, Ta, W, Au, Mo, Fe and Pt using Ni reference in the range 50 -2000 eV and compared with the IMFPs determined from theoretical calculations and absolute elastic-peak method using Oswald surface excitation correction. The experimental elastic peak intensity rations of above elemental solids to Ni-reference are in excellent agreement with those of Monte Carlo calculations from TPP-2M and from theoretical IMFPs (Penn algorithm) in the 200 - 5000 eV energy range. Under 200 eV, however, the measured intensity rations of them did not coincide well with the calculated result, which was mainly due to the surface excitation effects and the uncertainty of used elastic scattering cross sections.

QS-TuP6 An Analysis of Rotating-Compensator Ellipsometers for Metrology*, D.E. Aspnes,* *M. Asar,* North Carolina State University*; T. Mori,* Tohoku University, Japan*; K.A. Ebert,* Thermawave, Inc.

Increasing demands on accuracy are moving spectroscopic-ellipsometry technology from rotating-analyzer and -polarizer (RAE, RPE) configurations to rotating-compensator (RCE) designs. The additional 4@omega@t component generated in the transmitted intensity by an RCE makes it intrinsically more powerful for analysis, yet questions concerning relative performance, optimum configurations, and optimal component settings remain. Here, we discuss aspects relevant for achieving maximum accuracy for nm-scale thin-film metrology. First, calculations show that precisions on sample parameters obtained by an RCE are often better than those attainable with an RAE or RPE even for compensator retardations near 180 degrees, thereby resolving the optimum-sensitivity issue. Second, a comparison of RAE and RCE data obtained on a bench system that was operated as an RAE for over 25 years revealed a previously unsuspected polarizer-leakage artifact that affected the RAE data to about 1%, highlighting the more powerful diagnostic capabilities of an RCE. Third, we treat depolarization artifacts in general, using a system-transfer-matrix approach that also allows sample parameters to be extracted from RCE data without having to Fourier analyze the transmitted intensity. Finally, we analyze monoplate and biplate compensators, in particular discussing the multiple-internal-reflection artifacts that lead to the appearance of interference oscillations in spectra obtained with systems using biplate compensators. The optimum ellipsometer configuration is an RCE operating with a monoplate compensator.

QS-TuP7 Characterization of Buried Nanowire by X-ray Standing Wave Method, ***A. Saito,*** Osaka University and RIKEN harima Institute, Japan; *K. Matoba, J. Maruyama,* Osaka University, Japan; *W. Yashiro,* National Institute of Advanced Industrial Science and Technology, Japan; *T. Ohashi, H. Takaki, K. Takami, M. Akai-Kasaya, Y. Kuwahara,* Osaka University, Japan; *Y. Yoda, O. Sakata,* Japan Synchrotron Radiation Research Institute; *K. Miki,* National Institute for Materials Science, Japan; *M. Aono,* Osaka University, Japan

A perfect bismuth atomic nanowire on a clean Si(001) surface has recently attracted great interests.@footnote 1@ The STM studies showed that this wire is qualitatively different from the other atomic wires that are formed by group-III or -V elements at the initial stage of growth on Si(001): the Bi wire is free of kinks or defects, the width of 1 nm is kept for more than 400 nm long, and the wire appears to be rigidly embedded within the surface, not as adsorbates. Although X-ray photoelectron diffraction and the theoretical analysis were applied to reveal the Bi wire structure in UHV condition, the wire in the buried interface can be hardly estimated because of the methodological difficulty, despite its importance in application. X-ray standing wave (XSW) method is suitable for this ordered, dilute, and embedded system. This method is based on to excite selectively a specific element and to control the X-ray wave field in the substrate crystal under diffracting condition. Since the spatial controllability of the wave field is precise in about 0.001 nm (0.01Å), the atomic site of the element can be determined quantitatively with respect to the substrate Si lattice plane. In this paper, we present the XSW analysis of the Bi nanowire, where the Bi atomic site was estimated and compared among three different conditions (UHV, amorphous Si cap, epitaxial Si cap). The same analytical method was available for characterization of the low-dimensional system with the different capping layers by use of the third generation synchrotron radiation source. @FootnoteText@@footnote 1@J.H.G.Owen et al.,Phys.Rev.Lett.88,(2002) 226104.

QS-TuP8 Phase Separation at the Surface of PLLA/P104 Blends, ***J. Yu***, *J.A. Gardella,* State University of New York at Buffalo

Blends of Pluronic P104, poly(ethylene oxide) (A) poly(propylene oxide) (B) ABA block copolymer surfactant, and PLLA, poly(L-lactic acid), are considered as a delivery matrix for active proteins, nutrients, and essential amino acids in the application as Synthetic Basement Membrane for tracheal wound repair. The amphiphilic block copolymer Pluronic P104 was investigated using X-ray photoelectron (XPS), FTIR and NMR. In blends of different bulk compositions the enrichment of each component was examined by XPS and the thickness of each layer was listed to study the relationship between the bulk composition and surface segregation.

QS-TuP9 Factors Influencing Angle Dependent XPS to Si Oxide Films, ***N. Sanada***, *A. Tanaka, A. Yamamoto,* ULVAC-PHI, Inc., Japan

The chemical structure and thickness of an ultra thin film with 1 to 3 nm on a crystalline semiconductor is of interest because its application in semiconductor industries such as gate oxide (including silicon oxy-nitride and high-k gate oxide) thin films and ultra thin passivation films. An XPS measurement is the peculiar nondestructive technique on the chemical in depth analysis of ultra thin films. In addition, XPS has advantages in reproducibility and sensitivity in theory compared with other non-destructive surface analysis techniques. By this means, XPS is anticipated as a tool to evaluate the chemical in depth analysis of the ultra thin films, especially in a measure of the industrial demand. We have gauged several latent variables in XPS measurements, for examples, photoelectron diffraction of crystalline silicon substrate, acceptance angle of the photoelectron analyzer, X-ray probe stability, and damages in the XPS measurement. Those issues are evaluated as a matter of fluctuation of the film thickness. The photoelectron diffraction of the substrate silicon is the heavy factor to fluctuate the analysis results. A commercial XPS instrument which has an acceptance angle with 4 degree in polar angle and 20 degree in azimuthal angles, even has 6% fluctuation in Si 2p photoelectron intensity of the substrate silicon at 45 degree in polar angle, which is confirmed by an experiment and a calculation. On the other hand, XPS measurement is evident to be reliable by avoiding the particular measurement angle and using an instrument with a wide acceptance in azimuthal angle. Finally, we applied the angle dependent XPS analysis to two-layered high-k gate oxide thin film with identical constituent elements for both layers. Those results will be discussed in detail.

QS-TuP10 Comparison of Model Predictions and Experimental Measurements of Linescans Across an Interface by Auger Electron Spectroscopy, ***S.A. Wight***, *C.J. Powell,* National Institute of Standards and Technology

In order to determine the lateral resolution in scanning Auger microscopy of a practical sample, measurements and simulations have been made of variations in Auger signals across a selected interface. The interface for these experiments consisted of a selected line of chromium oxide over chromium on an indium-tin oxide coated quartz substrate. Auger electron spectra were collected between 300 eV and 600 eV as the beam was stepped across the interface in a direction perpendicular to the interface. The spectra at each point in the linescan were then processed to extract the relative contributions of the spectra for the two materials measured far from the interface. The normalized data were plotted against beam position on the sample to visualize the sharpness of the interface and to obtain a measure of the lateral resolution for the Auger signals. This procedure was repeated for multiple accelerating voltages of the primary electron beam. The experimental linescans were compared with simulated linescans for an ideal interface based on a simple model that represents contributions to the Auger signal from ionizations caused by the primary electrons and backscattered electrons. Preliminary results show qualitative agreement. We also show that the radius of the analysis area varies appreciably with parameters describing the Auger signal due to backscattered electrons.

QS-TuP11 Quantitative Image Analysis of Low-energy Electron Diffraction Patterns to Obtain Surface Geometries of Amines Adsorbed on the Si(100)-(2x1) Surface, ***J.K. Dogbe***, *S.M. Casey,* University of Nevada, Reno

Experimental and computational low-energy electron diffraction (LEED) intensity vs. voltage (IV) curves were used to analyze the surface geometries of amines adsorbed on the Si(100)-(2x1) surface. Both the clean silicon surface and the ammonia-covered surface were used as calibration systems. For silicon, the LEED IV curves obtained agree well with literature data to within experimental uncertainty. The results for ammonia adsorption are compared to results from recent photoelectron diffraction studies of this surface. Results of LEED IV probing of methylamine adsorption will be presented and compared to computational treatments of probable reaction pathways for this class of molecule on silicon.

QS-TuP12 Physically Measuring Thickness' of Thin Films via Atomic Force Microscopy: Design and Use of The Abruptor, *G. Acosta,* ***D. Allred***, *R. Davis,* Brigham Young University

In our research of thin films (typically our films are 2.5-15 nm thick), we invest a great deal of time and energy in characterizing our films' physical and optical properties. We have found that it is imperative to have the ability to determine, with confidence, the thickness of our films when we try to describe a material's optical performance, especially true for work in the extreme ultraviolet. Unfortunately, we've learned this is not as simple a task as it would seem. Methods that are optical in nature used to determine how thick a film become more difficult to employ and less effective for very thin films. We would much rather be able to use an AFM to physically measure a film's thickness. Having spent two years refining such a technique, we are happy to report the method we have developed. Our technique involves using a rigidly supported, stainless steel razor blade to mask the substrate during deposition, leaving a distinct, abrupt edge when removed. The device is named the Abruptor. In addition to now being able to determine the thickness of our films, we also offer a side note regarding hydrocarbon contamination of substrates (on the sub-nanometer scale) from exposure to ambient.

Advanced Surface Engineering
Room Hall A-C - Session SE-TuP

Poster Session

SE-TuP1 Synthesis and Elastic Properties of Polycrystalline Thin Films with Cr2AlC Structure, *J.M. Schneider,* ***Z. Sun***, *R. Mertens, F. Ãœstel,* RWTH-Aachen, Germany; *R. Ahuja,* Uppsala University, Sweden

We report the synthesis and characterization of polycrystalline thin films with Cr2AlC structure by magnetron sputtering. Ab initio total energy calculations using the Projector Augmented-Wave (PAW) was used to investigate the electronic structure. Our estimated d spacing values agree well (within 3 to 6 â€°) with glancing incidence X-rax diffraction data of the as deposited films. No peaks other than the ones of Cr2AlC were observed.

SE-TuP2 Growth of PACVD c-BN Films and c-BN/Diamond Bilayers*, M.S. Wong,* National Dong Hwa University, Taiwan, ROC, Taiwan, R.O.C*; J.B. Cheng,* ***T.S. Yang****, S.S. Chu,* National Dong Hwa University, Taiwan, ROC

The synthesis of c-BN films was carried out by the reaction of BF3 and N2 in the hydrogen and argon mixture using microwave plasma-assisted chemical vapor deposition (PACVD). The effects of N2/BF3 ratios, hydrogen addition, DC substrate-bias voltage and diamond as bufferlayer on the formation of c-BN were investigated. As-grown films are characterized by FTIR, grazing-incidence XRD, and SEM. The composition of gas mixture and energy of ion bombardment are critical to the formation of c-BN phase in the BN films. Under optimal growth conditions and using nanocrystalline diamond film as bufferlayer, the growth of high c-BN content up to ~85 % c-BN was achieved.

SE-TuP3 Kinetics of Boron Nitride Thin Film Formation using Low Energy Ion Beam Assisted Deposition*,* ***W. Otaño,*** University of Puerto Rico at Cayey

Cubic boron nitride (cBN) is a superhard material, which is defined as a material with microhardness over 40 GPa, and offers the best combination of high hardness, low friction coefficient, resistance to oxidation, and resistance to chemical degradation with iron-based materials. Other applications of cBN take advantage of its high density, high thermal conductivity, good transparency in the visible and infrared portion of the spectrum, and high electrical resistivity. Cubic BN is also a wide band gap semiconductor, which can be n- and p-type doped. Several models have been proposed to describe the nucleation and growth of cBN thin films based on the observation of the necessity of energetic bombardment of the growing film for the stabilization of the cubic phase. These models include the concept of thermal spikes, the subplantation model, stress-induced stabilization, and resputtering of the BN hexagonal phase. Several authors have been able to correlate the energetic bombardment with P/a, the total momentum imparted to the growing film per arriving boron atom. In this report, the use of a high intensity, low energy ion source, incorporated to an ion beam assisted deposition system to study the kinetics of the cBN thin film nucleation at bombarding ion energies in the 50-100 eV range will be discussed. It will be shown that the control of the ion bombardment and of the incoming boron atom flux is critical for the kinetics of formation of the boron nitride films. The implications for the nucleation process of the BN cubic phase and a comparison with systems using high deposition rates will be discussed.

SE-TuP4 Mechanistic Studies of the Wet Chemical Oxidation of Hydrogen-terminated Si(100)*,* ***C.A. Shea****, K.T. Queeney,* Smith College

Wet chemical cleaning of the Si(100) surface is a critical step in wafer processing for microelelectronics. Oxidation of HF-etched (hydrogen-terminated) Si(100) surfaces occurs both intentionally (via peroxide solution) and uninentionally (e.g. during rinsing steps) and can affect both the chemistry and the morphology of the underlying substrate. We have used a combination of surface infrared spectroscopy and contact angle measurement to follow both the microscopic and macroscopic evolution of the H-terminated Si(100) surface during aqueous oxidation. Ex-situ transmission IR experiments allow us to elucidate the role of solution species including dissolved oxygen and OH@super -@ on both the rate and the mechanism of oxidation by following changes in both the Si-H and Si-O regions of the infrared spectrum. Contact angle hysteresis provides a measure of surface heterogeneity during these processes; comparison with the more uniform Si(111) surface provides a benchmark for the degree of inhomogeneity inherent to the rougher H:Si(100) substrate.

SE-TuP5 Rheological Modeling of Fracture Mechanics of Hard Coatings on Soft Substrates at Hertzian Indentation*, M.V. Kireitseu,* ***L.V. Kireitseu,*** Institute of Mechanics and Machine Reliability, Belarus

The present work described rheological modeling of novel coating «chrome carbide nanoparticles – aluminum oxide – soft aluminum substrate» and «steel – viscous-elastic polymer – aluminum – aluminum oxide» at their Hertzian indentation. When the hard aluminum oxide-based coatings are brought into contact with a ceramic or a metal indenter, different stress-deformation modes can be developed between the materials. Strains and forces will depend upon the state of the surfaces, its roughness and the fundamental mechanical properties of the two solids that are both indenter and substrate. Mechanical behaviour between the coatings and another solid indenter are discussed from a theoretical consideration of the mechanical constants (elasticity, plasticity and viscosity) of the coatings and experimentally by relating loading forces and stresses to the interface resulting from the contact. Rheological models were proposed for the coatings and were confirmed by in-suit experiments using principal Hertzian theory. An experimental evidence showed good agreement between the models and mechanical behavior of the coatings. Load rating tests revealed ultimate stresses and stress-deformation modes for both the coatings and their particular layer. The models and its behavior under a few fundamental conditions of loading (triangle, pulse, sinusoidal etc.) are discussed. @FootnoteText@ none

Surface Science

Room Hall A-C - Session SS-TuP

Poster Session

SS-TuP1 Ultrastable Besocke Type Scanners*,* ***N. Pertaya****, K.-F. Braun, K.H. Rieder,* Freie Universit@um a@t Berlin, Germany

A widespread used construction for the coarse approach mechanism in scanning probe microscopy is the Besocke beetle type. Using stick-slip motion the scanner can thereby be positioned on the nm scale covering usually a range of several mm horizontally and vertically. This apparent advantage of a high flexibility is bought on the expense of a reduced mechanical stability. Mechanical resonances around one kHz are attributed to so-called rattling modes (dependent on the contact forces between moving and fixed parts), other modes result from the scanner itself, and limit the performance of the microscope.@footnote 1@ Here we present a detailed analysis of the vibrational response of a beetle type scanner and based on this a very stable optimized scanner setup. Three scanners were assembled using different type of and differently dimensioned piezoceramics. Type (a) and (b) are using tube piezos of different length and thickness. Covering the same scanning area the overall size was reduced and the lowest measured mechanical resonance shifted from 300 to 900 Hz. In a recent setup (c) shear stack piezoelectric elements (PI - ceramics) were used, which resulted in a shift of the lowest resonance frequency to 6 kHz. Freshly cleaved graphite surface was imaged using a mechanically cut golden tip. Typically atomic-resolved images obtained under ambient conditions show a triangular lattice or a honeycomb array respectively. @FootnoteText@@footnote 1@S. Behler, M.K. Rose, D.F. Ogletree, M. Salmeron, Rev. Sci. Instr. 68, 124 (1997).

SS-TuP2 Studying Surface Phenomena by Pulsed Heating of Microdevices*,* ***O.C. Thomas****, R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology

MEMS microheater devices have been operated with periodic (2-40 Hz), short duration (5ms) temperature pulses to investigate the relationship between surface adsorbate concentrations and surface electronic behavior of high surface area, oxide films. Tin oxide films were grown by CVD on microscale (40 µm X 100 µm), thermally isolated bridge structures that possess embedded polysilicon heaters and surface electrodes. These structures permit the rapid thermal cycling and real time conductometric measurement of the deposited oxide films. In air devoid of reducing analyte, the application of short, high temperature (500°C, 5 ms) heating pulses results in the generation of surface bound O@super -@ from surface adsorbed O@sub 2@, and as a consequence a tin oxide film that is both highly resistive and highly sensitive to reducing gases. Exposure of such a film to trace concentrations of reducing gas results in large conductometric changes (from 1x10@super -7@ @OMEGA@@super -1@ in dry air to 2.5x10@super -4@ @OMEGA@@super -1@ in 10 ppm MeOH; measured at 25 °C). In the presence of reducing gases, the heating pulses activate the titration of the surface bound O@super -@ by the reducing species. Modulating the period between heating pulses from 25 ms to 500 ms reveals an increase in room temperature conductance, which is interpreted in terms of the adsorption dynamics of the reducing species. Results on a number of reducing gases show conductance vs. period profiles, which may be explained in terms of both molecular adsorption dynamics and stoichiometric capacity for reduction. These results provide a basis for analyte recognition and a level of mechanistic insight about interfacial transduction processes.

SS-TuP3 A Novel Study using XANES Spectroscopy, XPEEM, and Nanoindentation Techniques to Correlate the Microchemistry and Nanomechanical Properties of Zinc-dialkyldithiophosphate Tribofilms on Steel Surfaces*, **M.A. Nicholls**, P.R. Norton, M. Kasrai, G.M. Bancroft,* The University of Western Ontario, Canada*; T. Do,* Atomic Energy of Canada*; G. De Stasio,* The University of Wisconsin, Madison

Additives with special functions have long been components of engine oils, designed to improve the performance and prolong the life of an engine. One particular additive, zinc-dialkyl-dithiophosphate (ZDDP) has been added to improve the lifespan of an engine by reducing wear at high pressure contacts. ZDDPs have been found to break down under the extreme conditions in an engine and produce products that, under high pressure and temperature, form a sacrificial polyphosphate film that reduces wear. This film has been studied thoroughly for decades, but the origins of its effectiveness still remain a mystery. Advanced synchrotron radiation techniques such as X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron emission microscopy (XPEEM), are now providing the detailed chemical and spatially resolved chemical analysis required to help understand how these films form. In combination with nanoindentation techniques, it is now possible to measure the chemical and nanomechanical properties of these films on the same length scales. We describe how XANES can determine the polyphosphate chain-length in a film, and also illustrate the interaction of ZDDP decomposition products with steel surfaces. Further, XPEEM and nanoindentation have been used to correlate, for the first time, the spatially-resolved chemistry and mechanical properties of the same, selected regions of an antiwear film at a resolution of approximately 200 nm.

SS-TuP4 Monosaccharide Adsorption on Hydrophobic and Hydrophilic Surfaces*, **J.W. Clemens**, M.A. Cobleigh, K.T. Queeney,* Smith College

The adsorption of encapsulated bacteria to both natural and synthetic surfaces is governed by extracellular polysaccharides. In order to gain insight into the interactions of these large starch molecules with such surfaces, and specifically to separate out effects of their primary and secondary structure, we have undertaken a comprehensive study of the adsorption properties of the constituent monosaccharides of xanthan gum, a model bacterial polysaccharide. A combination of surface infrared spectroscopy and atomic force microscopy is used to investigate the adsorption properties of glucose, mannose and glucuronic acid on silicon and functionalized silicon surfaces. Access to the full mid-IR frequency range allows us to analyze both the OH-stretching region, in order to probe the role of hydrogen-bonding in adsorption, and the fingerprint region of the molecules, which is more sensitive to configurational changes in the molecules upon adsorption. Combining this information with AFM images allows us to correlate spectroscopic signatures associated with sugar-surface and sugar-sugar interactions.

SS-TuP5 Effect of Multidirection Ion Beam Treatment and Alignment Property of Nematic Liquid Crystal*, **S.J. Rho**, H.J. Ahn, K.C. Kim, H.K. Baik, J.Y. Hwang, Y.M. Jo, C.J. Park, D.S. Seo,* Yonsei University, South Korea*; K.M. Song,* Konkuk University, South Korea*; S.J. Lee,* Kyungsung University, South Korea

We have investigated the alignment properties of liquid crystals induced by multi- directional ion beam irradiation on the a-C:H flims. Ion beam treatment of alignment layer is the new method which does not contact with alignment layer and prevent from debris or electrostatic discharge. Amorphous carbon (a-C:H) films for alignment layer were deposited by remote plasma enhanced chemical vapor deposition and were modified by an Ar ion beam at an films. For the multi-domain of LCD, the direction of ion beam exposure was changed about 0deg, 90deg, 180deg, 270deg and at each step, ion beam is overlapped It is experimentally found that the aligning direction of the liquid crystal depend on the final irradiating direction of ion beam and by these results, we analyzed the structural transition of a-C:H layer after ion beam irradiation. Raman, IR, and AFM data were used for analysis of theses phenomena. Also we prove the merit of ion beam method, which decrease the masking step for multi-domain of LCD manufacturing.

SS-TuP6 Dynamic Mechanical Analyses of Polymers*, T.J. Mullen,* U.S. Naval Research Laboratory*; S.A. Syed Asif,* Hysitron, Inc.*; **K.J. Wahl**,* U.S. Naval Research Laboratory

Thin polymer films are of considerable interest for applications in electronics packaging, biomedical devices, MEMS devices, lubrication, antifouling and adhesives. However, evaluating the mechanical properties of polymer thin films is difficult due to the low elastic moduli and substrate influence. In this paper, we present an approach for measuring the dynamic mechanical properties of thin, compliant polymer films using AC force-modulation coupled with a hybrid scanning indenter. This combination allows surface sensitive, quantitative mechanical properties measurements at a single point as well as while scanning. Dynamic response of the indenter is monitored during tip-sample approach, enabling sensitive detection of the surface, and during contact for evaluation of storage and loss moduli of polymer samples. Examples of dynamic mechanical properties analyses using force-displacement curves, frequency sweeps, and imaging will be presented for polyethylene, poly(dimethylsiloxane) (PDMS) and other polymer surfaces.

SS-TuP7 Patterning and Selective Metallization of Polymer Films Bearing Chloromethylphenyl Groups*, **W.J. Dressick**, M.-S. Chen, T.L. Schull, S.L. Brandow,* Naval Research Laboratory

The ability to spatially control polymer surface reactivity without affecting bulk properties for the selective deposition of materials, such as metals, ceramics, or other chemical and biological species, is critically important for microelectronics, optics, and sensor technologies. We have been investigating the top-surface imaging of thin polymer films containing surface chloromethylphenyl groups to address this challenge. Recently we demonstrated that solvent-templated nanocavities could be formed in chloromethylphenyl-based films that are capable of non-covalently binding reactive adsorbates. Exclusion of the adsorbate from aqueous solution and binding within the film nanocavity are driven by favorable hydrophobic interactions between the adsorbate and the aromatic residues of the polymer film. Spatial control of adsorbate entrapment is demonstrated using a variety of patterning tools (e.g., microcontact printing, deep UV, proximity x-ray, high-energy e-beam, and low voltage scanning tunneling microscope) to selectively inhibit entrapment through chemical modification of the films or displacement of entrapped adsorbate from film nanocavities. Spatial control of adsorbate binding allows the subsequent selective deposition of Pd-based catalytic nanoparticles of controlled size for electroless metal deposition. Fabrication of nanoscale structures in metal with good control of feature critical dimensions is demonstrated. Details of the largely aqueous based process will be presented and factors contributing to feature critical dimensions and optimization of ligand physisorption will be discussed.

SS-TuP8 Surface Lattice Dynamics of KCl(001) by Helium Atom Scattering*, **R. Fatema**,* Florida State University*; F.A. Flaherty,* Valdosta State University*; S.A. Safron, J.G. Skofronick, D.H. Van Winkle,* Florida State University

High-resolution helium atom scattering (HAS) has been employed to investigate the surface lattice dynamics of the KCl(001) surface, produced by cleaving a single crystal sample in ultra high vacuum (UHV). Several branches of the surface phonon dispersion have been mapped out in the and high symmetry directions, across the surface Brillouin zone (SBZ). These include the low-energy Rayleigh wave, a "crossing mode" which increases in energy from the SBZ boundary to the zone center, and optical modes which appear dispersionless across the SBZ. These results are compared with "shell model" calculations and with experimental results, which were reported previously. The implications of these results for the use of KCl(001) as a substrate for films of soft materials is also discussed.

SS-TuP9 The Effect of Water Vapor on the Surface Composition of Alkali Halides*, **S. Ghosal**,* University of California, Irvine*; F.G. Requejo,* University of La Plata and CONICET., Argentina*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; J.C. Hemminger,* University of California, Irvine

We present here results from our studies on the aqueous ionic solvation of alkali halide surfaces. Using a novel high pressure X-ray Photoelectron Spectroscopy (XPS) system based on the ALS synchrotron radiation source we have for the first time made dire ct experimental measurements of the surface composition of alkali halide crystals while in contact with water vapor pressures approaching and at the point of dissolution. The salt crystals were cleaved in vacuum and then analyzed by XPS as the water vapor pressure was increased. Our results show that the anion/cation ratio at the interfacial region initially decreases with increasing water vapor pressure. At higher water vapor pressures, approaching the dissolution point of the salt, the surface compositi on behavior varies depending on the particular salt. These results are further supported by Scanning Polarization Force Microscopy experiments. The primary focus of the study was to determine the structure and composition of the interfacial region between the salt and air as a function of water vapor exposure. This is of particular interest since the solid/vapor interfacial composition of salt solutions and salt particles has implications for heterogeneous atmospheric chemistry involving sea salt aerosols.@footnote 1@ @FootnoteText@

@footnote 1@Finlayson-Pitts, B. J.; Hemminger, J. C. J. Phys. Chem. 2000, 104(49), 11463.

SS-TuP10 Secondary Phases on Oxide Surfaces*, **C.B. Carter**, S.R. Gilliss,* University of Minnesota

The wetting of a ceramic surface by a secondary phase is a technologically relevant problem that is encountered under many situations. Processing of ceramics using liquid-phase sintering relies on the wetting of the ceramic powder compact by a lower melting additive. The additive may be a non-metallic glassy phase, as in oxide ceramics, or can be a liquid metal as in the case of Co additives for WC ceramics. The wetting of ceramics by liquid metals is also encountered in joining applications like active metal brazing. Wetting and dewetting of liquid metals and glasses on ceramic substrates has been investigated using a combination of microscopy techniques. The influence of surface structure on dewetting behavior and the influence of the dewet droplets on the morphology of surface steps has been shown with the aid of experimental observations from many systems. The role of chemistry and kinetics on the wetting behavior will also be discussed. The manner in which the secondary phase wets the crystalline ceramic at processing temperatures dictates the microstructure and therefore the properties of the material. Model systems of anorthite and sapphire and silica and rutile will be emphasized. Thin films (100 nm) of the secondary-phase (anorthite or silica) are deposited onto a single-crystal substrate of sapphire or rutile by pulsed-laser deposition. The specimens are then heat-treated in air at high temperature (1400°C-1650°C). At high-temperature and during cooling steps and facets form on the oxide surface and the secondary-phase may dewet or continue to wet the surface. The effect of the secondary-phase on the kinetics of step/facet formation and an analysis of the wetting behavior will be presented. The degree of dissolution and reprecipitation of the substrate material within the secondary phase has been monitored by X-ray energy dispersive spectroscopy and electron energy-loss spectroscopy and will be discussed.

SS-TuP11 Evidence of Surface Pre-melting of Bi Ultrathin Film on Si(111)*, **S. Yaginuma**,* Tohoku University, Japan*; T. Nagao,* Tohoku University and PRESTO, JST, Japan*; J.T. Sadowski, Y. Fujikawa, T. Sakurai,* Tohoku University, Japan

Semimetal bismuth has attracted much attention because of its various unique transport properties. Recently, we have successfully fabricated high-quality Bi (001) films on the Si (111)-7x7 substrate. The Bi (001)/Si (111) system self-organized into an atomically flat single crystal Bi (001) film, experiencing the unique orientation flipping from interconnected close-packed Bi {012} films to the two-dimensional (2D) Bi (001) films, which then grew into a nearly perfect uniform film by layer by layer growth. Temperature-dependent spot-profile-analysis low-energy electron diffraction (SPA-LEED) study revealed that suitable annealing of the as-deposited Bi (001) films resulted in an increase of the peak intensity and a change in the spot profile, marked improvement in the crystallinity and surface roughness. The resulting surface was ideally flat over the ~100 nm range. With this ideal 2D system, we further performed the systematic SPA-LEED experiment as a function of annealing temperature and estimated the surface Debye temperature to be approximately 90 K. In addition to the expected Debye-Waller decrease, a steeper decrease in the spot intensity was observed above 350 K in a reversible manner without hysteresis. Since the separate in-situ STM observations have clarified the decrease in step density, this anomalous thermal behavior of the diffraction peak intensity is attributed to the surface pre-melting instead of the surface roughening. By fitting the data with the logarithmic growth law, the correlation length of this phase transition was determined within the length of one bilayer. Negligible thickness dependence reflects the layered structure of Bi with mobile bilayer stacking. A possible mechanism of the surface pre-melting of the Bi (001) films will be discussed.

SS-TuP12 Crater Wall Shape Evolution During Annealing Induced Flattening of Si(001)*, **B.J. Gibbons**, J.P. Pelz,* The Ohio State University

We have studied high temperature annealing induced flattening of large (up to 50 µm@super 2@) "craters", formed using a new double wet thermal oxidation process on silicon (001). This process was used to eliminate the initial "trenching" around the perimeter of the crater floor that can occur during normal dry etching procedures. It has been suggested that such trenching can interfere/delay the process of flattening.@footnote 1@ Surprisingly, we have found that trenches are formed during extended annealing even if not initially present, as well as a "peak" around the upper crater wall perimeter. Above the roughening temperature (~ 1200 °C for Si(001)) the profile of the crater wall can be described using a continuum model.@footnote 2@ For temperatures below roughening the trench and peak features can be qualitatively described using microscopic step models,@footnote 3@ although a good quantitative description has not yet been achieved. To date we are able to remove the initial sample miscut over an area of up to 30 x 40 µm@super 2@, leaving behind a region with concentric closed steps formed by pit nucleation.@footnote 4@ We will discuss the optimum conditions for creating large flat regions "blindly", as well as ongoing electromigration experiments in the presence of a Si flux. @FootnoteText@@footnote 1@Tanaka, et al., Appl. Phys. Lett., 69(9), 26 Aug. 1996 @footnote 2@W.W. Mullins, J. Appl. Phys. 28(3), Mar 1957 @footnote 3@Liu, et al., J. Vac. Sci. Technol. B 14(4), Jul/Aug 1996) @footnote 4@J.-F. Nielsen, et al., Phys. Rev. Lett. 87(13), 24 Sep. 2001

SS-TuP13 Structure-optimized CoSi@sub 2@-buried-metal-layer Substrates for IRRAS Fabricated by Wafer-bonding*, **S. Yamamura**,* The Graduate University for Advanced Studies, Japan*; S. Yamauchi,* DENSO Research Laboratories, Japan*; S. Watanabe,* Fujitsu Laboratories Ltd., Japan*; T. Urisu,* Institute for Molecular Science, Japan

The conventional IRRAS (infrared reflection absorption spectroscopy) is applicable only for the metal substrates. So, the IRRAS using buried metal layer (BML) substrates has been developed to apply this technique to the semiconductor surfaces. To obtain high sensitivity in BML-IRRAS, it is essentially important to control the top Si layer thickness less than 200 nm. In this work, we have successfully fabricated a BML substrate with 200 nm thick top Si layer by wafer-bonding for the first time using a SOI wafer having controlled thickness (260 nm) of Si layer. Comparing with the ion implantation method, the wafer bonding method has advantages of (1) atomically flat top Si surface, and (2) unnecessariness of epitaxial growth process, which is essentially required in the ion implantation method to remove the ion implantation damage. The fabrication process is as follows; (1) overlapping of a Co (~ 200 nm thickness) deposited Si wafer on the SOI wafer with face to face, (2) annealing at 800°C for 30 min under N@sub 2@ atmosphere, (3) polishing of the back side Si layer of SOI to ~ 100 nm, followed by complete removal by 10 % KOH solution etching at 70°C for 3 ~ 4 h, and (4) the residual top SiO@sub 2@ layer was removed by etching using 2.5 % HF solution, and the Si(100)/CoSi@sub 2@/base Si(100) BML substrate was obtained. The preliminary formation of thin (100 nm) SiO@sub 2@ layer on the SOI surface was effective to reduce the interface roughness between the top Si and the CoSi@sub 2@ layers. The self-assembled alkyl monolayer was deposited on the BML substrate, and its IRRAS was observed in the wide frequency range from stretching to bending regions.

SS-TuP14 Relating Polarization to Optical Absorption and Ablation of Silicon/Silicon Oxide Surfaces*, Y.N. Picard, H. Liu, J.C. Pentland, J.P. MacDonald, J. Nees, G. Mourou, **S.M. Yalisove**,* University of Michigan, Ann Arbor

A significant benefit of machining materials using lasers with pulse lengths on the order of femtoseconds, rather than nanoseconds or picoseconds, is the reduced size of the damage region associated with the machined areas. However, depth of absorption, absorption mechanisms, and nano-scaled modifications of the near surface are still not fully understood and characterized when machining at or just below the ablation theshold of the material using femtosecond lasers. The direction of the laser electric-field vector relative to the sample surface is estimated to be directly proportional to the magnitude of optical absorption, and as a consequence, the ablation threhold of the material. Our recent studies have demonstrated a factor of 3 difference in the estimated ablation threshold for S versus P polarization (referenced to the sample surface plane) when machining silicon at grazing incidence (86°) in air. We extend these studies to grazing incidence machining of silicon with no native oxide on the surface as well as silicon with different oxide thickness, all under vacuum. We use a Ti:sapphire laser with 800 nm wavelength, 120 femtosecond pulses to irradiate the surface at both S and P polarizations. The intensity of the laser irradiation ranges from below to above the ablation threshold for silicon (~200mJ/cm@super 2@). We present results from clean Si (native oxide removed by HF etching or Shiraki method) as well as those from Si with a native oxide and thermally grown oxide layers. Samples are machined inside a vacuum chamber capable of reaching a pressure of 10@super -11@ Torr. For silicon samples with no oxide present on the surface, surface structure during irradiation is monitored using reflected high energy electron diffraction (RHEED). SEM and AFM results show differences in the size and morphology of the damage region, which are then correlated to the ablation threshold.

SS-TuP15 Controlling Silicon Surface Morphology with Aqueous Etching: The Surprising Effect of Barriers*, **H. Bao,** S.P. Garcia, M.A. Hines,* Cornell University

For reasons that are not completely understood, nanoscale surface morphology can influence the electronic, chemical and mechanical properties of a variety of devices. Thus, the ability to fabricate atomically smooth micron-scale regions of silicon would b e beneficial to many technologies. In this research, we use chemical etching to force the atomic height steps on a vicinal surface bunch into "macrosteps" -- micron-high macroscopic steps that separate terraces of near-atomic flatness. Interestingly, we f ind that the orientation of the macrosteps does not always correspond to the vicinal step direction. Instead, the orientation of the macrosteps can be controlled by lithographically patterned etch barriers. A variety of surface morphologies created by the barriers are presented and characterized by a combination of optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). In some cases, the patterned barriers lead to large, nearly atomically flat regions. In other cases, macrosteps are curved and oriented by the barrier structure.

SS-TuP16 Low-Dimensional Plasmons in a Metallic Strip Monolayer on a Semiconductor Surface*, **T. Inaoka,*** Iwate University, Japan

The Si(111)-@sr@3x@sr@3-Ag surface can be formed by depositing one monolayer of Ag atoms on a Si(111)-7x7 surface. One of the surface-state bands at this surface provides an ideal two-dimensional system of conduction electrons (2DES). The 2DES is confined in a @sr@3x@sr@3-Ag domain surrounded by atomic steps or out-of-phase boundaries. In this work, we consider a strip domain with finite width and infinite length. By means of the time-dependent local-density approximation, we investigate low-dimensional plasmons (LDPLs) in a metallic strip monolayer on the semiconductor surface, namely, LDPLs in a 2DES confined in a strip region. We analyze the energy-loss intensity, the energy dispersion, and the induced charge distribution of the two plasmon modes at each wave number q along the strip. When wavelength @lambda@ (= 2@pi@/q) of the mode is considerably smaller than the strip width D, the higher-energy mode (HEM) has its induced charges extending widely in an interior region, showing a definite character of the area plasmon (APL). Its energy is quite close to that of the two-dimensional plasmon in an infinite area (pure 2DPL). However, as the mode energy deviates upward from that of the pure 2DPL with increase in @lambda@, the induced charge distribution of the APL evolves into a standing-wave pattern with its free end at the edge. In contrast, the lower-energy mode (LEM) has its induced charges localized near the strip edge, exhibiting a definite character of the edge plasmon. When @lambda@ is small compared with D, the induced charge density of the LEM decays slowly on the inside of the strip owing to the influence of the HEM (APL) close to the LEM in energy. At larger @lambda@ values, the quick attenuation of the induced charge density inside the strip involves conspicuous oscillations due to the interference of electronic waves impinging on and reflected from the edge.

SS-TuP17 Conductance Switching of Single Molecules in Alkanethiolate Self Assembled Monolayers*, **A.M. Moore,** Z.J. Donhauser,* The Pennsylvania State University*; J.M. Tour,* Rice University*; P.S. Weiss,* The Pennsylvania State University

Phenylene ethynylene oligomers (OPE) have been studied as candidates for molecular electronic devices using scanning tunneling microscopy (STM). These molecules were inserted into host alkanethiolate self-assembled monolayers (SAMs) for isolation and individual addressability. OPE molecules were probed using STM and exhibited reversible conductance switching, which is observed as a change in the topographic height of the molecule in the STM images. The rate of active switching has been shown to be mediated by the structure of the host matrix. Using shorter chain alkanethiolate SAMs we have shown multistate switching of these molecules and have suggested molecular motion changing the molecule to substrate contact conductance. Analysis of this switching mechanism has involved changing functionality, bonding, size and rotational freedom of the molecules under study.

SS-TuP18 The Interaction of Water with Oligo(Ethylene Glycol)-Terminated Self-Assembled Monolayers on Gold and Silver Investigated by IR and Vibrational Sum-Frequency Spectroscopy*, **R.-Y. Wang**, M. Himmelhaus, J. Fick, S. Herrwerth, W. Eck, M. Grunze,* University of Heidelberg, Germany

Oligo(ethylene glycol)-terminated self-assembled monolayers (SAMs) have been the topic of intense research over the last years, due their unique protein repulsion properties.@footnote 1,2@ Recently, in particular, the structure of the films in contact to aqueous solutions has been in the focus of interest.@footnote 3,4@ In the present study, we used infrared reflection absorption spectroscopy (IRRAS) and vibrational sum-frequency spectroscopy (VSF) to investigate water-induced structural changes in methyl (1-mercaptoundec-11-yl) hexa (ethylene glycol)- terminated alkanethiol (EG6OMe) monolayers self-assembled on gold and silver. The spectra were recorded right after preparation of the films and after their exposure to water. In the case of gold as a substrate, the layers were also investigated during water contact. The spectra show that water causes pronounced disorder in the EG6OMe monolayers, which is only partially reversible after drying of the films under vacuum conditions. @FootnoteText@@footnote 1@ K. L. Prime and G. M. Whitesides, J. Am. Chem. Soc., 115, 10714,1993@footnote 2@P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, and P.E. Laibinis, J. Phys. Chem. B102, 426-436, 1998 @footnote 3@M. Zolk, F. Eisert, J. Pipper, S. Herrwerth, W. Eck, M. Buck, and M. Grunze, Langmuir, 16,5849-5852,2000@footnote 4@D. Schwendel, T. Hayashi, R. Dahint, A. Pertsin, M. Grunze, R. Steitz, F. Schreiber, Langmuir 19, 2284, 2003.

SS-TuP19 Switching Dynamics of Ladder Molecules in Low Defect Self Assembled Monolayers*, **A.A. Dameron,*** The Pennsylvania State University*; J.W. Ciszek, J.M. Tour,* Rice University*; P.S. Weiss,* The Pennsylvania State University

We have fabricated 1-adamantanethiolate self assembled monolayers (SAMs) on Au(111) and characterized them with scanning tunneling micrsocopy.@footnote 1@ Adamantanethiol molecules have a bulky cage structure and orient in both fcc and hcp packing structures. The adamantanethiolate SAMs display fewer defect sites and less prominent domain boundaries than alkanethiolate SAMs. The switching dynamics of 2-thioacetylphenanthrene ("ladder molecules") and 4-thioacetyl-biphenyl molecules were studied by insertion of the molecules into both adamantanethiolate and short chain alkanethiolate SAMs. The switching dynamics in the two SAMs are similar; in both cases the molecules insert primarily into the defect sites in the monolayer and display switching between two states. @FootnoteText@@footnote 1@ L. F. Charles, M. S. Thesis, The Pennsylvania State University (1999).

SS-TuP20 Photodegradation Phenomena of Si-C Linked Monolayer Induced by 126, 172 and 254 nm Ultraviolet Light*, **K. Oda,*** Waseda University, Japan*; N. Shirahata,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan*; Y. Yokogawa, T. Kameyama, A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan

Micropatterned Si-C linked monolayers have recently attracted attention for their use as templates to fabricate electronic- and bio-devices in micro~nanometer-scale. Among numerous approaches, photolithography is one of the most promising techniques in order to design and fabricate the microtemplates arbitrarily. However, there have no papers describing photodegradation mechanism of Si-C linked monolayers. In order to optimize the micropatterning of the monolayers, further understanding of the photochemistries which proceed when the monolayers are exposed to various kinds of ultraviolet (UV) light sources is vital. In this study, we report the photodecomposition of a Si-C linked monolayer of 1-octadecene (ODM) induced by three types of UV light sources, i.e., 126 and 172 nm vacuum UV (VUV), and conventional 254 nm UV light. This ODM was attached to Si substrate terminated with hydrogen (Si-H) through Si-C bond. As control experiments, we have similarly examined the photodegradation of a self-assembled monolayer (SAM) of n-octadecyltrimethoxysilane (ODS) formed onto Si substrate covered with native oxide (SiO@sub 2@/Si) through Si-O-Si bond. Due to the formation of ODM and ODS-SAM, the Si-H and SiO@sub 2@/Si substrates became highly hydrophobic with their water-contact angles changing from about 80 and <5 ° to 110°, respectively. After 254 nm UV-irradiation for the appropriate period in air, the hydrophobic surfaces became completely hydrophilic one. However, photodecomposition rates of these monolayers were quite different, although our monolayers thicknesses were nearly identical. The rate of ODM was found to be about one-sixth as fast as that of ODS-SAM. This marked difference in photodecomposition rate may be responsible for the nature of the Si-C bonds, that is, the difference in electron distribution in the bonds, in ODM and ODS-SAM.

SS-TuP22 Atomic Structure of InGaAs Surfaces*, **A. Riposan,** J. Mirecki Millunchick, B.J. Dall, C.A. Pearson, B.G. Orr,* University of Michigan

The atomic structure of compound semiconductor alloy surfaces is important for heteroepitaxial growth, as it has an impact on the subsequent microstructure of the film. We examined the morphology and surface reconstruction of In@sub x@Ga@sub 1-x@As alloy layers during growth and after annealing. Films of different compositions were grown by molecular beam eptiaxy on GaAs and InP (001) substrates to thicknesses less than the critical thickness for 3D islanding, and examined using in-situ Scanning Tunneling Microscopy (STM). The surface reconstruction of lattice matched In@sub 0.53@Ga@sub 0.47@As/InP alloys is highly disordered; nearly 25% of the surface is covered with a 4x3 reconstruction and 15% with a c(3x4). Models developed based on the STM data suggest that these reconstructions are terminated by both cation and anion dimers. The surface reconstruction during the growth of alloys under compressive misfit strain was 2x3 according to reflection high energy electron diffraction. However, STM shows that the surfaces are covered with a number of differently reconstructed domains. The majority of the surface of In@sub 0.27@Ga@sub 0.73@As/GaAs layers is covered by a disordered c(3x4), while 34% of the surface consists of short segments of @alpha@2(2x4) with in the terrace. The reconstruction of In@sub 0.81@Ga@sub 0.19@As/InP surfaces, which have the same amount of lattice mismatch, consists of @beta@2(2x4) regions resting upon an underlying 4x3. The coverage of the @beta@2(2x4) decreases from 50% to 34% after a 25 minute anneal at the growth conditions. This behavior is consistent with the decrease of the surface In concentration during annealing, suggesting that the @beta@2(2x4) regions on this surface are related to In surface segregation.

SS-TuP23 Low Energy Li Ion Scattering from Iodine Adatoms on Si and SiO@sub 2@ Surfaces*, Y. Yang*, *J.A. Yarmoff,* University of California, Riverside

We recently showed that the neutralization of alkali ions backscattered from halogens adsorbed on metal surfaces depends sensitively on the internal polarization of the adatom. Charge-resolved time-of-flight spectra collected from backscattered @super 7@Li@super +@ ions display consistently larger neutral fractions for scattering from the halogen adatoms than that from the substrate. An increased neutral fraction indicates that the potential at the halogen site is reduced from that of the substrate, which is surprising considering that the halogen adatom is overall negatively charged. We thus propose that there is a region of positive charge at the very top of the adatom, which is consistent with the results of density functional theory. The positive region is presumably formed as the electron charge is attracted to its image in the metal substrate. This internal electronic structure of the halogen adatom was verified by measurements of the angular dependence of the neutralization. The neutral fraction of Li scattered from the halogens decreases as the exit beam moves off-normal, demonstrating that the charge associated with the adsorbate is non-uniform and that ion scattering is sensitive to this internal structure. Surprisingly, we found the same behavior for iodine adsorbed on Si surfaces, although the image charge in the substrate and the consequent charge rearrangement might be expected to be weaker. This implies that the iodine adatoms above a Si substrate are internally polarized. We are currently exploring the role of the substrate by investigating the neutralization of alkali ions scattered from Si wafers that are oxidized in situ prior to iodine exposure. This will allow us to determine how the conductivity of the substrate is involved in facilitating the internal charge rearrangement.

SS-TuP24 Chemistry of Bifunctional Nitro Group-containing Molecules on Silicon: a Cryogenic Approach to Selective Self-assembly in Vacuum*, S. Bocharov*, *A.V. Teplyakov,* University of Delaware

Surface chemistry of alkyl and aryl compounds containing nitro-group on Si(100)-2x1 has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy, Auger electron spectroscopy, and temperature-programmed desorption/reaction mass spectrometry. Despite theoretical prediction for essentially barrierless interaction of nitromethane with this silicon surface, all the nitroderivatives studied physisorb molecularly within a monolayer coverage on Si(100)-2x1 at 95 K. Surface chemical reaction involving nitro-group occurs around 140 K regardless of the nature of the alkyl/aryl substituent studied. Thus, a significant energy barrier, approximately 8 kcal/mol, is established for the interaction of these molecules with the Si(100)-2x1 surface. An opportunity of selective self-assembly using the advantage of cryogenic conditions to control the kinetics of surface reactions will be discussed. Further surface annealing studies suggest that all nitrogen and oxygen atoms remain on a surface even at the temperatures as high as 900 K, while some carbon is removed as a corresponding hydrocarbon molecule.

SS-TuP25 Adsorption and Reaction of Amines on Germanium and Silicon Surfaces*, P. Prayongpan*, *C.M. Greenlief,* University of Missouri, Columbia

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

SS-TuP26 Adsorption of 1,3-butadiene on Si(001) 2x1 Surface*, J.Y. Baik*, Korea Research Institute of Chemical Technology and Sungkyunkwan University, Korea*; H.-N. Hwang,* Korea Research Institute of Chemical Technology*; K.-S. An,* Korea Research Institute of Chemical Technology, Korea*; E.S. Cho,* Sungkyunkwan University, Korea*; K.J. Kong, Y. Kim,* Korea Research Institute of Chemical Technology*; J.-Y. Park,* Sungkyunkwan University, Korea

Recently unsaturated organic molecules playing a role of multifunctional layer adsorbed on Si(001)2x1 surface has come into the focus of research in semiconductor fabrication and semiconductor devices. The well-known unstable @pi@ bond of up and down dimer atoms of Si(001)2x1 surface, ethylene-like(C@sub 2@H@sub 4@), is reactive with the unsaturated organic molecule through charge transfer in order to minimize the total energy on the surface. 1,3-butadiene(C@sub 4@H@sub 6@) among these molecules leads to the [4+2] reaction forming the organic molecule/Si hybrid of six-membered cycle with the Si dimer even at room temperature. And also, it was reported that the [2+2] reaction could occur at less possibility than the [4+2] reaction. In this study, the adsorption and thermal behaviors of 1,3-butadiene on the Si(001)2x1 surface were investigated by high-resolution photoelectron spectroscopy(HRPES), scanning tunneling microscopy(STM) and thermal desorption spectroscopy(TDS) with theoretical calculations. In STM images, three different-typed adsorptions were observed and well identified as the [4+2], the [2+2], and the end-edge bridge reaction by the STM simulation. For C 1s core level spectrum reported as only one asymmetric component, despite of two kinds of quite different chemical surroundings, it was found that the broad spectrum consisted of two components with abnormally small core level shift based on the calculation. In addition, TDS shows successive desorption of 1,3-butadiene and acetylene molecules with increasing the substrate temperature, different to previous reported hydrogen desorption by C-H bond breaking, without acetylene desorption.

SS-TuP27 Adsorption and Thermal Decomposition Reaction of Vinylacetic Acid on Si(100)2x1 Surface*, K.-S. An*, *J.Y. Baik,* Korea Research Institute of Chemical Technology, Korea*; H.-N. Hwang, Y. Kim,* Korea Research Institute of Chemical Technology*; C.-Y. Park,* SungKyunKwan University, Korea*; C.C. Hwang, B. Kim,* POSTECH, Korea

Covalent attachment chemistry of organic molecules on silicon surfaces has been of recent interest in surface science. Several molecule attachment chemistry on the Si(001)2x1 surface has been reported for organic molecules including various single and multi-functional groups such as alkene, hydroxyl, thiol, amine, and carboxyl groups, etc, which can be applied important building blocks for organic molecule/Si surface. In this study, the adsorption and thermal decomposition of vinylacetic acid (VAA) on the Si(001)2x1 surface is investigated using photoelectron spectroscopy and thermal desorption specroscopy. Vinylacetic acid is a typical monomer having both vinyl (C=C) and carboxyl groups (COOH) with alkyl chain, which can well adsorb on the Si dimer as the [2+2] cycloadditional and dissociative reaction, respectively. Curve fitting of the Si 2p core level spectra taken after VAA exposures shows the development of two new surface components, S@sub O@ and S@sub H@, shifted by +0.93 and +0.40 eV, respectively, with respect to the bulk component. From the result, it is found that VAA adsorbs on the Si(001)2x1 surface, not through the cycloaddition reaction with vinyl group (C=C) but through the dissociative adsorption of RCOOH (R = CH@sub 2@CHCH@sub 2@) into RCOO(ad) and H(ad) without breaking the Si dimer. The dissociative adsorption is confirmed by the analysis of the C 1s and O 1s core level spectra. Based on the line-shape changes of the Si 2p, C 1s, O1s core level spectra and TDS measurement with increasing the substrate temperature after the VAA saturation, the thermal decomposition and desorption behaviors of the VAA molecules are also investigated.

SS-TuP28 Plasmons in Ag Ultrathin Films on Si(111) Studied by Energy Loss Spectroscopy with High Momentum Resolution*, **T. Nagao,*** Tohoku University and PRESTO, JST, Japan*; S. Yaginuma, T. Sakurai,* Tohoku University, Japan

Self-organized metallic overlayers deposited on semiconducting substrates constitute an interesting class of materials since one can explore a variety of physics related to low dimensionality and size effects. The collective behavior in electron systems (plasma oscillation, or plasmon) confined in atomically thin region is expected to be very different from plasmons in three-dimension. In the present talk, we report on the thickness dependence of the plasmon dispersion curve of several- monolayers-thick Ag films supported on Si(111), by use of high-momentum-resolution HREELS. The films were prepared by "electronic growth" scheme with lateral grain size larger than 70 nm characterized by the spot profile analysis using the spectrometer in high-resolution LEED mode. In addition to the surface plasmon peak, a steeply dispersing peak was observed around the (00) Bragg spot, which rapidly decays in intensity and broadens in a very narrow momentum window of 0.04 [1/A] as a function of momentum transfer. The energy dispersion curve of this mode was explained in terms of a quasi-2D mode of thin film plasmon and its loss energy approaches the value of 1900eV which is close to the interfacial plasmon mode at the semiinfinite Ag/Si system. The details of the analysis together with the development of the spectrometer will be presented. We also plan to present some data of sheet-type plasmons in surface-state bands at silicon surfaces.

SS-TuP29 Semiconductor Surface Reconstructions of the Si(100) Surface at 5K*, B. Grandidier, L. Perdigao, D. Deresmes,* ***M. Dubois****, C. Delerue, G. Allan, D. Stievenard,* IEMN-CNRS, France

The reconstruction of the Si(100) is related to the formation of dimers to lower the surface energy. Their bonding consists of a weak double bond so that the symmetric configuration is not held and give rise to buckled dimers. As several types of reconstructions have been predicted, with well defined electronic properties, we have studied the reconstructions of the Si(100) surface by scanning tunneling microscopy (STM) and spectroscopy at 5K. At low positive sample voltages, when well-ordered surfaces are prepared, two phases, the c(2x4) and the p(2x2) reconstructions, are visible. By increasing the number of surface defects, a third arrangement, the p(2x1) asymmetric reconstruction, appears. Scanning tunneling spectroscopic measurements indicate that all the surfaces are semiconductor. However at higher positive voltages or at negative voltages, the appearance of the dimers change into a symmetric features. While spectroscopic data show that the tip does not induce a modification of the surface reconstruction whatever the sample voltage and the reconstruction types of the surface, the voltage-dependent STM images are investigated by theoretical calculations for the p2x2 arrangement.

SS-TuP30 Surface Oxidation of Silicon Blisters formed by Hydrogen Ion Irradiation*, **S. Igarashi**, A.N. Itakura,* National Institute for Materials Science, Japan Science and Technology Corporation, Japan*; M. Kitajima,* National Institute for Materials Science, Japan*; K. Hojou,* Japan Atomic Energy Research Institute

Blister is a local protrusion of solid surface induced by gas ion irradiation. Si (100) substrate was irradiated with H@super +@ (ion energy of 10 keV and fluence of 1x10@super 22@ ions/m@super 2@) at an angle of 30 deg. to the surface normal. The blisters of several µm in diameter at the bottom were formed. After the ion irradiation, the substrate was exposed to an O@sub 2@ gas. By means of scanning Auger microscopy, we observed that the rims of the blisters have higher oxygen intensities than the flat surfaces and the tops have lower than the flats. The blistering is considered to create local stress on surface layers; the surface layers should be stretched laterally at the top of blisters and are compressed at the rim, relative to the flat surfaces. The O distribution clearly consists with the stress distribution of the surface. Our results demonstrate a patterned oxidation of Si surface applying its reactivity depending on the surface stress.

SS-TuP32 Synthesis of a Sinter Resistant Mixed-oxide Support for Au Nanoclusters*, **B.K. Min**[1], A.K. Santra, D.W. Goodman,* Texas A&M University

The synthesis of a sinter-resistant oxide support for Au clusters has been explored using scanning tunneling microscopy (STM). Nano-sized Au clusters supported on a reducible oxide such as TiO2 are active catalysts for CO oxidation; however, rapid deactivation occurs at reaction conditions due to an increase in the cluster size. To prevent this deactivation, a sinter-resistant oxide support has been synthesized by patterning oxide domains consisting of small islands of a strongly-interacting support (TiO2) on second weakly-interacting oxide (SiO2). The size of the TiO2 domains can be controlled by the amount of Ti deposited. The Au nanoclusters preferentially decorate the TiO2 domains and are resistance to sintering when exposed to elevated pressures of O2, CO, and mixtures of the two gases under reaction conditions.

SS-TuP33 Dissociation of Methyl Iodide on the Al(111) Surface - An STM and DFT Study*, **S. Mezhenny**[2],* University of Pittsburgh*; D.C. Sorescu,* U.S. Department of Energy*; P. Maksymovych, J.T. Yates, Jr.,* University of Pittsburgh

The reaction of methyl iodide (CH@sub 3@I) with the Al(111) surface was studied by room temperature scanning tunneling microscopy (STM) and by first principles calculations. It was found that at 300K CH@sub 3@I decomposes on the Al(111) surface forming methyl, CH@sub 3@, methylidyne, CH, and adsorbed iodine. CH@sub 3@ groups were observed to occupy atop sites by STM, while CH species occupy hollow sites. Total energy density functional theory calculations have shown that CH@sub 3@ species occupy atop Al sites (E=45.3 kcal/mol), CH species adsorb on fcc hollow sites (E=155.0 kcal/mol), while individual iodine atoms can bind on both top or hollow sites with adsorption energies 54-56 kcal/mol.

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

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

AVS 50th Anniversary Plenary Session
Room 310 - Session AP-WeM

Surfaces, Processing, and Materials

Moderator: J.H. Weaver, University of Illinois at Urbana-Champaign

8:20am **AP-WeM1 Controlling Surface Reactions***, **G. Ertl**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**
Reactions at solid surfaces determine the mechanisms of heterogeneous catalysis and form hence the basis of numerous technologically important processes. Studies with well-defined surfaces enable detailed insights into the underlying elementary steps and their control down to atomic length and femtosecond time scales. Nonlinear kinetics coupled to adsorbate diffusion may give rise to phenomena of spatio-temporal self-organisation which may be affected by various feedback strategies. In this way not only options for improving catalytic activity, but also models for structure formation in living systems are established.

9:00am **AP-WeM3 Continuity in Plasma Processing: Yesterday's Accomplishments, Today's Innovations and Tomorrow's Challenges@footnote 1@***, **M.J. Kushner**,* University of Illinois, Urbana-Champaign **INVITED**
Plasma processing has provided impressive capabilities for converting either inert or weakly reactive materials into activated species which produce light, modify or create materials or activate other processes. The impact of plasma processing for modification of high technology materials owes its success, in part, to a legacy of research on what at first look seems like unrelated topics, such as lighting, lasers and upper atmospheric physics. These projects created a continuity of knowledgebases of experimental and computational techniques and fundametal data which have provided the foundation for today's advances in plasma based technologies. For example, advanced microdischarge plasma sources such as plasma display panels can trace their origins to dielectric barrier discharges for ozonizers. This legacy of "continuity," leveraging knowledge bases to move forward plasma based technologies, provides insights to how plasmas will impact future high technology applications in microelectronics fabrication, sensors, biotechnology, lighting, and materials processing. That continuity and expectations for future developments in the field will be discussed. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation, Semiconductor Research Corporation, 3M Inc. and AFOSR.

9:40am **AP-WeM5 The Promise of Solid State Lighting: Status, Trends, and Remaining Challenges***, **M.G. Craford**,* Lumileds Lighting **INVITED**
LED technology developments over the past decade have enabled the use of LEDs in a variety of colored and white lighting applications. With further improvement LEDs appear to have the potential to become an important technology for large area general illumination. White LEDs with outputs of more tha 100 lumens are already available commercially. LEDs are expected to save energy, be environmentally friendly, and provide a variety of other features, including long lifetime, compact size, and programmable color control, which enable design options for new approaches to lighting. In this presentation the LED technology status and trends will be described and LEDs will be compared to conventional lighting technologies. Developments that will need to occur for LEDs to be a viable contender for large area general illumination will be discussed.

10:20am **AP-WeM7 Epitaxial Ferromagnetic Heterostructures Based on Semiconductors: Towards a New Spin-Based Electronics***, **M. Tanaka**,* University of Tokyo, Japan **INVITED**
Creating a new spin-based electronics (often called "spin-electronics" or "spintronics") is one of the hot topics in the current solid-state physics and electronics research. In order to utilize the spin degree of freedom in solids, particularly in semiconductors the current electronics is based on, we need to fabricate appropriate materials, understand the spin-dependent phenomena, and control the spins. In this talk, I will review the recent developments of epitaxial ferromagnetic heterostructures based on semiconductors towards spintronics. This includes the semiconductor materials and heterostructures having high ferromagnetic transition temperature (III-V based alloy magnetic semiconductors, Mn-delta-doped magnetic semiconductors, and related heterostructures), spin-dependent transport and tunneling, spin-dependent bandgap engineering, their device applications (tunneling magnetoresistance devices and three-terminal devices). Future issues and prospects will be also discussed. @FootnoteText@ The author thanks the collaborations and discussions with S. Sugahara, A.M. Nazmul and Y. Higo, S. Ohya, and T. Matsuno. The work at the Univ. of Tokyo was partially supported by PRESTO of JST, IT Program of MEXT, Toray Science Foundation.

Applied Surface Science
Room 324/325 - Session AS-WeM

High-K Materials Interface Analysis

Moderator: H.G. Tompkins, Consultant

8:20am **AS-WeM1 Spectroscopic Characterization of High-k Dielectrics: Applications to Interface Electronic Structure and Stability Against Chemical Phase Separation***, G. Lucovsky, **Cristiano Krug**,* North Carolina State University **INVITED**
The lowest conduction band states of high-k transition metal and rare earth dielectrics are associated with localized anti-bonding d*-states. Combining X-ray absorption spectroscopy, XAS, with vacuum ultra-violet spectroscopic ellipsometry, VUV SE, photoconductivity, PC, and internal photoemission, IPE, provides a way to study final state effects, in particular different d*-states, and d*-s*-state splittings which can then be compared with ab initio calculations on small clusters. These studies prove important insights into empirical correlations between i) band gaps, and ii) conduction band offset energies with respect to crystalline silicon and atomic d-state energies which apply to both transition metal and rare earth dielectrics, including binary oxides, and silicate and aluminate alloys. These results provide important insights into optimization of silicate and aluminate alloys for minimum direct tunneling at a given equivalent oxide capacitance. Combining Fourier transform infra red spectroscopy, FTIR, and derivative X-ray photoelectron spectroscopy, XPS, with extended X-ray absoroption fine structure spectroscopy, EXAFS, provides an unambiguous way to differentiate between chemical phase separation with different degrees of crystallization in Zr and Hf silicate gate dielectrics, and at their interfaces with Si. This is of importance for semiconductor device processing since chemical phase separation at 900C (1000C) in silicon dioxide-rich Zr (Hf) silicates not detectable by X-ray diffraction, XRD, reduces gate dielectric capacitance, and therefore can reduce current drive in field effect transistors, FETs.

9:00am **AS-WeM3 Effect of Nitrogen on Interface Stability of Plasma Enhanced Chemical Vapor Deposition of Hafnium Oxide on Si(100)***, **P. Chen**, H. Bhandari, T.M. Klein,* The University of Alabama
Hafnium oxide is a potential high dielectric constant material for use in field effect transistor gate applications. Interface quality, especially for chemical vapor deposited films, is a concern, however, and is the motivation for the introduction of nitrogen. Plasma enhanced chemical vapor deposition (PECVD) was used to grow hafnium oxide thin films on Si using Hf tert-butoxide and N@sub 2@O or N@sub 2@ remote plasma. Upto 6 at.% N was obtained using a N@sub 2@/He plasma. Angle resolved x-ray photoelectron spectroscopy indicates the nitrogen is located at the oxide/Si interface. Stability of the interface is enhanced with nitrogen treatment showing a smaller increase in film thickness after annealing in argon.

9:20am **AS-WeM4 High-k Al@sub 2@O@sub 3@-HfO@sub 2@ Layers for CMOS Applications Studied by XPS and ToF-SIMS***, **R.G. Vitchev**, L. Houssiau, J.J. Pireaux,* Facultes Universitaires Notre-Dame de la Paix, Belgium
High-k metallic oxides are considered as promising candidates to replace SiO@sub2@ as a gate dielectric in the future CMOS devices. Al@sub 2@O@sub 3@-HfO@sub 2@ mixed oxide layers deposited by Atomic Layer Chemical Vapor Deposition on differently pretreated silicon wafers (0.5 nm and 1 nm SiO@sub 2@ grown by rapid thermal oxidation as well as HF-last Si surface) were characterized by single- and two emission angle XPS and by ToF-SIMS dual beam depth profiling (250 eV Xe@super +@ and Cs@super +@ sputtering beam, 15 keV Ga@super +@ analysis beam). The composition and the depth distribution of constituent elements were measured for mixed oxide layers deposited with different number of cycles (and hence with different thickness) and different Hf/Al cycle ratios. It was found that the Hf/Al content ratio for the thinnest films was much higher than for the thicker films with the same cycle ratio. The surface region of the thicker films was enriched in Al (and depleted in Hf) indicating a preferential deposition of HfO@sub 2@ at the film/silicon interface. The depth distribution of impurities was also measured and compared. The interfacial SiO@sub 2@ layer thickness was determined as well as the oxidation state of Si atoms in it. Changes of the interfacial SiO@sub 2@

layer thickness and chemistry after prolonged air exposure were followed. Work performed under EU-CUHKO project.

9:40am **AS-WeM5 Materials Characterization and Processing Effects on Hafnium-based Gate Dielectrics**, ***W.R. Nieveen***, Charles Evans & Associates/Evans Analytical Group; *P.S. Lysaght,* International SEMATECH; *G. Goodman, I. Mowat, B. Schueler,* Charles Evans & Associates/Evans Analytical Group; *J.A. Bennett, B. Foran, M. Gardner, R.W. Murto, H.R. Huff,* International SEMATECH

Introduction of high-k gate dielectrics into semiconductor processing is proving to be a formidable challenge due to the electrical performance requirements and insufficient understanding of the variations in physical characteristics as a function of thermal processing. Relevant device parameters including gate leakage current density, EOT, V@sub t@ instabilities, V@sub fb@ shift, and electron and hole mobility are affected by process conditions that alter the materials properties. Such physical parameters include phase orientation, oxygen coordination, onset temperature of crystallization, etc. Optimization of process parameters, which affect the material properties and lead to improved device performance with good integration properties, is todays challenge in high-k materials. In this work, we focus on advanced material characterization of various hafnium-silicon-oxygen composition systems and correlate the physical data with specific aspects of transistor performance. A comprehensive and complimentary set of Hf silicate samples, exposed to an incremental range of thermal process treatments, are characterized by XPS, HRTEM, HAADF, EELS, conductive AFM, and SIMS. Fundamental issues associated with phase separation in Hf-Si-O (and HfSiON) systems are discussed within the context of relevant capacitor and transistor device performance. We will discuss the correlation of physical material parameters measured by various analytical techniques with process conditions, and electrical parameters and measurements.

10:00am **AS-WeM6 Synchrotron UPS and EXAFS Analysis of High-k and Si Interfaces**, ***Y.-S. Lin***, *R. Puthenkovilakam, J.P. Chang,* University of California, Los Angeles

Ultra-thin dielectric films with high permittivity such as ZrO@sub 2@, HfO@sub 2@, and HfO@sub x@N@sub y@ have numerous applications in advanced microelectronics, especially on silicon substrates for gate dielectric application in metal-oxide-semiconductor (MOS) devices. In this work, we combine synchrotron based ultra-violet electron spectroscopy (UPS) and extended x-ray absorption fine structures (EXAFS) analysis to characterize the interface of ZrO@sub 2@, HfO@sub 2@, and HfO@sub x@N@sub y@ on silicon. Specifically, the interfacial composition and chemical coordination of the deposited metal oxides and oxynitrides films on silicon are determined. By tuning the photon energy in UPS analysis, we determined the composition of the interfaces between high-k dielectrics and silicon and their corresponding valence band structures. The experimental results were compared to first principle calculations using density functional theory to validate the measurements and elucidate the effect of chemical coordination at the interface on the electronic structure, band gap, and band offsets. The energy shifts measured in oxygen s and p states compared favorably with first principle calculations and closely related to the bonding to metal atoms. The Fourier transformed EXAFS spectra also agreed very well with the first principle prediction and allowed the determination of interatomic spacings and the chemical nature of the nearest and second-nearest neighboring atoms. Based on the experimental validation, we used density functional theory to calculate the electronic band gaps, conduction and valence band offsets, and interface states for dielectric/Si interfaces, and found that these properties are greatly affected by the metal, oxygen, and nitrogen coordinations.

10:20am **AS-WeM7 Determination of ToF Medium Energy Backscattering Capabilities for Interfacial Analysis**, ***R.D. Geil,*** *B.R. Rogers, D.W. Crunkleton, Z. Song, R.A. Weller,* Vanderbilt University

Time-of-flight medium energy backscattering (ToF-MEBS) is a unique surface analysis technique developed at Vanderbilt initially for determining levels of transition metal contaminants on silicon surfaces. The technique's high sensitivity and depth resolution makes it highly suitable for the analysis of ultra-thin films, such as gate dielectrics. The interface between the gate dielectric and silicon is of particular interest because it is a dominant factor in determining the overall electrical properties of the gate structure.@footnote 1@ In order to determine the extent of information about the lower interface region of a gate dielectric that ToF-MEBS can provide, we have studied a well-characterized material system, SiO@sub 2@/Si. Thermally grown SiO@sub 2@ films with thicknesses ranging from 2-10 nm were analyzed to determine how interfacial information degrades with depth into the sample. Thickness and stoichiometric information at the bulk and interfacial regions were determined. Channeling in the direction of the Si substrate was performed to suppress background. TEM analysis was performed on the films to confirm ToF-MEBS thickness values. Spectroscopic ellipsometry was also used for thickness comparisons. XPS analysis provided extra interfacial and compositional information. @FootnoteText@ @footnote 1@ Wilk, G.D., R.M. Wallace, and J.M. Anthony, High-K Gate Dielectrics: Current Status and Materials Properties Considerations. Applied Physics Review, 2001. 89(10): p. 5243-5275.

10:40am **AS-WeM8 Investigation of PECVD TiO@sub 2@ on Silicon**, ***P.R. McCurdy***, *L. Sturgess, S. Kohli, E.R. Fisher,* Colorado State University

Continuous wave (CW) and equivalently powered, pulsed radio frequency plasmas were used to deposit thin films of titanium dioxide on to Si(100) substrates. In these experiments oxygen plasmas were created by feeding oxygen gas through the coil region, titanium (IV) isopropoxide was introduced downstream from the plasma region. These films have been characterized using XRD, XPS, SEM and AES. XRD showed that TiO2 films deposited at substrate temperatures Â³350ÂºC are polycrystalline with an anatase structure, while at lower substrate temperatures the films were amorphous. Results show high quality films were produced with some carbon incorporation. Annealing these films in vacuum at 900 oC show the TiO2/Si interfacial region to be reduced to Ti2O3, while Si is oxidized to SiOx. Upon annealing at a 950oC further reduction of the TiO2 film was noted to include TiO. The 950oC film partially re-oxided upon exposure to atmosphere. XRD of annealed films showed no crystalline structure of these annealed films. SEM of the TiO2 film surfaces showed the as deposited films were smooth and structureless and remained so even when annealed at 850oC. Annealing at 950oC caused the surface to become very rough, resulting in the rupturing of the TiO2 surface thus exposing areas of the underlying Si/SiO2 substrate.

Biomaterial Interfaces

Room 307 - Session BI+SS-WeM

Cell Interactions with Patterned Surfaces

Moderator: M. Textor, ETH Zurich, Switzerland

8:20am **BI+SS-WeM1 Patterned Surfaces using Masking during Plasma Deposition or Pulsed Laser Ablation**, *H. Thissen,* CSIRO Molecular Science, Australia; *J.P. Hayes,* Industrial Research Institute Swinburne, Australia; *P.G. Hartley, G. Johnson,* CSIRO Molecular Science, Australia; *E.C. Harvey,* Industrial Research Institute Swinburne, Australia; ***H.J. Griesser***, University of South Australia, Australia

The patterning of biomaterial surfaces has attracted much recent interest for various fundamental and applied purposes, such as the control of the location and shape of attached anchorage-dependent cells. Patterned surfaces are also of interest for bio-diagnostic arrays, cell culturing and separation, some tissue engineering products, and some biomedical implants. We have used two different approaches for the fabrication of patterned surface chemistries. One approach involves the use of masks during the deposition of thin plasma polymer coatings. The other approach is based on the deposition of multilayer coating structures followed by laser ablation through a mask; the top layer is a non-adhesive coating such as PEG and the laser beam exposes adhesive regions "underneath" by ablating the PEG layer in spatially controlled areas. Cell-adhesive proteins can then adsorb only onto the exposed areas capable of adsorbing proteins. The second approach is very attractive because of its speed and ease of fabrication; ablation of the thin PEG layer using a pulsed 248 nm excimer laser is fast with nanometre thickness control by controlling the number of laser pulses. The patterned surface chemistries and their protein adsorption characteristics were analyzed by several surface analytical techniques and by antibody assay. Cell culture using bovine corneal epithelial cells confirmed that cell attachment is controlled by these surface chemistry patterns. Our work has so far focused on fluoropolymer and Si wafer substrates and the use of plasma polymer interlayers for the covalent anchoring of a cloud point grafted PEG top layer; the use of a plasma polymer interlayer has the advantage of being readily transferable to a variety of substrates both ceramic and polymeric. However, the use of laser patterning is not restricted to those coating structures and can be applied to burn adhesive "holes" into other non-adhesive coatings equally well.

8:40am **BI+SS-WeM2 Patterning Surfaces with "Nonfouling" Oligoethylene Glycol "Bottle Brushes" by Soft Lithography and Surface-Initiated Atom Transfer Radical Polymerization***, **H. Ma**, A. Chilkoti,* Duke University

A "grafting from" strategy is described for creating patterned biologically-nonfouling polymer coatings. Initiators presenting a bromoisobutyrate moiety and a thiol group at two ends of the molecule were synthesized and patterned on gold by soft lithography. The patterned SAM was used as a substrate for surface-initiated atom transfer radical polymerization (SI-ATRP) of oligoethylene glycol methyl methacrylate (OEGMA). The SI-ATRP was carried out in an oxygen-free environment with CuBr/Bipy as catalysts in a water /methanol mixture. Ellipsometry showed that the thickness of the poly(OEGMA) "bottle brush" could be easily manipulated from 0 to 50 nm by control of the polymerization conditions. The patterns were characterized by imaging ToF-SIMS, imaging XPS, and AFM. This "bottle brushes" are exceptionally protein-resistant. Surface plasmon resonance (SPR) spectroscopy showed no adsorption of fibronectin (1 mg/ml), 10% or 100 % fetal bovine serum (FBS) onto those surfaces. NIH 3T3 fibroblasts were confined to regions demarcated by the patterned poly(OEGMA) brushes. The cellular patterns were maintained for over 30 days, which is significantly longer than is possible with EG-terminated alkanethiol SAMs. This "grafting from" strategy is not limited to gold-coated surfaces as demonstrated by SI-ATRP on glass and silicon, and overcomes the intrinsic limitation of low surface density of PEG chains by physisorption or the "grafting to" approach. The poly(OEGMA) grafts synthesized in situ by SI-ATRP recapitulate in a polymer brush some of the key features of oligoethylene glycol-terminated SAMs, namely the high surface density of oligoethylene glycol in a thicker and more robust coating. These patterned "nonfouling" surfaces have utility in the design of experimentally useful model system to investigate the response of cells to chemical and topographical cues, in addition to a wide range of applications in bioanalytical devices.

9:00am **BI+SS-WeM3 Molecular Assembly Patterning by Lift-off (MAPL): A Novel Approach to Produce Biologically Designed Micropatterns for Biosensor Applications and Cell-Surface Interaction Studies***, **D. Falconnet**,* Swiss Federal Institute of Technology (ETH) Zurich*; F. Assi,* Swiss Federal Institute of Technology (ETH) Zurich, Switzerland*; A. Koenig,* Swiss Federal Institute of Technology (ETH) Zurich*; M. Textor,* Swiss Federal Institute of Technology (ETH) Zurich, Switzerland

A new chemical micropatterning technique is presented for cell-surface interaction studies. The MAPL technique allows creating patterns of bioactive molecules (such as biotin, peptides, oligonucleotides) at a controlled surface density and embedded in a background resistant to the adsorption of proteins. A simple photoresist lift-off process is exploited in conjunction with the spontaneous assembly of polycationic poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) onto negatively charged metal oxide surfaces. A positive photoresist on a metal-oxide-coated substrate (e.g. niobium oxide coated on glass) is developed resulting in a micropattern of resist and bare metal oxide areas. Bio-functionalized (e.g., biotin or cell-adhesive peptide) PLL-g-PEG is immobilized at the bare metal oxide regions by spontaneous assembly from aqueous solutions of the polymer. The photoresist is lifted off in an organic solvent without affecting the integrity of the adsorbed functionalized PLL-g-PEG monolayer. Subsequently, the background is backfilled with protein- and cell-resistant PLL-g-PEG. The resulting pattern of bio-interactive and non-adhesive areas shows an excellent contrast on the protein level, demonstrated by fluorescence microscopy using labeled streptavidin to specifically decorate the PLL-g-PEG/PEG-biotin patches. Cell attachment to such micropatterns consisting of PLL-g-PEG/PEG-RGD-peptide was tested using human foreskin fibroblasts. This lift-off-based biochemical patterning is a 'soft', robust, simple and reproducible technique that does not require specialized clean room and heavy etching facilities. It is an interesting alternative to microcontact printing because it circumvents many disadvantages of the printing technique. The high signal-to-noise ratio and the feasibility of tailoring the bioligand (capture molecule) density in the interactive patches make MAPL a promising technique also for biosensor microarray applications.

9:20am **BI+SS-WeM4 Micrometer-scale Fibronectin Patterning for Control of Focal Adhesion Dynamics in Fibroblasts***, **D.S. Rhoads**, R.N. Orth, M. Wu, B.A. Baird, J.L. Guan,* Cornell University

We have developed a new method for analyzing the processes of fibroblast adhesion and spreading using micro- and nanometer-scale fibronectin patterns. Fibronectin is an extracellular matrix protein that provides mechanical stability for cells and tissues, by being a ligand for integrin cell surface receptors which anchor the actin cytoskeleton to the plasma membrane. These anchor points are referred to as focal adhesions, and are composed of numerous scaffolding and signaling proteins in addition to forming focus points of the actin cytoskeleton. Here, we patterned fibronectin using a technique previously shown to produce feature sizes as small as 700nm. The fibronectin features are used to observe small focal adhesions and the morphological effects of minimal activation by fibronectin per cell area. For fabrication of patterned surfaces, polymer-coated silicon wafers were patterned using photolithography and reactive ion etching. Fibronectin was then deposited onto the wafer samples prior to polymer removal and cell application. The resulting patterns contained features ranging from 76 µm to > 1 µm, and were used in cell adhesion and spreading experiments. Cells adhering to the pattern were fixed, permeablized and analyzed by immunofluorescence, using antibodies to fibronectin, f-actin, paxillin, and focal adhesion kinase. Fluorescence microscopy was complemented with scanning electron microscopy to image focal adhesions, stress fibers, lamellipodia and filopodia. From this analysis, we propose that this method for analyzing cellular responses to subcellular cues from their surroundings is a model system for spatially isolating and studying focal adhesions.

9:40am **BI+SS-WeM5 Microengineering Surfaces to Interface with Mammalian Cells***, **C.S. Chen**,* Johns Hopkins University **INVITED**

The interactions between cells and their surroundings provide the basis for the coordinated functions of tissues. To understand and control these interactions, we have developed several microfabrication-based approaches to provide model environments for cells. We will describe these approaches, and how they are beginning to elucidate how cells probe and make sense of their environment through biochemical and mechanical means. Integrating microfabricated devices and cells will pave the way for a new era in biomedical research and medicine.

10:20am **BI+SS-WeM7 Analyzing Lymphocyte Adhesion, Membrane Receptors and Cytoskeletal Rearrangement on Micron Scale Mitogen Patterns***, **R.N. Orth**, M.J.B. Flaminio, J. Kameoka, T.G. Clark, H.G. Craighead,* Cornell University

In this study, we investigated an in vitro immune reaction on a planar surface between T cells, B cells, and micron scale patterned mitogens as a model system for analyzing cell surface ligand responses. To form functionalized biomaterial microdomains, a polymer-coated substrate was patterned using photolithography and reactive ion etching. The samples were incubated in antibody and mitogen solutions prior to polymer removal and cell application. Uniform mitogen patterns ranging from 76 µm to <1 µm were created to target cell surface receptors, upregulate intracellular signaling cascades and cell activity, and stimulate proliferation. Several methods were used to analyze the patterned mitogens' effects on the lymphocytes. Carboxy-fluorescein diacetate, succinimidyl ester (CFSE)-stained lymphocytes harvested from the substrate demonstrated a proliferative response when assayed by flow cytometry. Mouse monoclonal antibodies against equine membrane cell receptors (anti-major histocompatibility (MHC) class II, anti-CD4, anti-CD3, and anti-leukocyte function associated-antigen (LFA)-1) provided a view of stimulated cells' surface receptor distribution. Secondary anti-mouse antibodies with a conjugated 1.5 nm gold sphere were bound to the primary antibodies. The samples were incubated in a silver solution to form 10-100 nm spheres as the silver nucleated off the gold particles. Scanning electron microscopy (SEM) imaging provided high resolution images of the cell surface ligands' spatial distribution as marked by the silver spheres. This patterning technique provided a precise and reproducible means to structure biomaterial surfaces at subcellular resolutions.

10:40am **BI+SS-WeM8 Directed Motoneuron Growth on Self-Assembled Monolayer (SAM) Patterned Surfaces***, **M.G. Poeta**, M. Das, C.A. Gregory, P. Molnar, D.C. Henry, L.M. Riedel, J.J. Hickman,* Clemson University

We are investigating the directed growth of embryonic rat motoneurons on glass substrates and are determining if they exhibit proper morphological and electrophysiological characteristics in this defined environment. This is the first step in recreating the reflex arc, one of the fundamental controls circuits in the body, with biological components on a MEMS chip. Recreating this system in vitro could have significant implications for improving treatment for people with spinal cord injuries, which affect 10,000 people every year in the United States. Throughout the last century, many methods have been developed to direct the growth of different cell types. These include fibroblasts, glial cells and hippocampal neurons grown on spider webs adhered to coverslips, grooves scratched in polystyrene and palladium deposited on petri dishes. In order to direct the growth of the motoneurons, we are using two recently developed patterning techniques, microcontact printing and laser ablation. Microcontact printing is a patterning method where a polydimethyl siloxane (PDMS) stamp is cast from a mold. It is inked in our case with a hydrophilic silane, diethyltriamine trimethoxysilane (DETA), and brought into contact with a substrate. The substrate is then backfilled with a hydrophobic silane, tridecafluoro-1,1,2,2-tetrahydroctyl-1-trichlorosilane (13F). Laser ablation is a patterning method where, again in our system, a substrate is coated with DETA and exposed with an excimer laser fitted with a beam homogenizer through a photomask. The exposed regions are then backfilled with 13F. Embryonic rat motoneurons are plated on these patterned substrates. XPS and contact angle are used to verify the surface modification procedures. We have found that the motoneurons orient themselves along the hydrophilic patterns. We will report on the characterization of these patterns using patch-clamp electrophysiology to measure the electrophysiological characteristics of the cells.

Biomaterial Interfaces
Room 317 - Session BI-WeM

Bionanoscale Analysis: Theory to Experiment

Moderator: R.A. Latour, Clemson University

8:20am **BI-WeM1 Calculation of Free Energy of Peptide-Surface Adsorption Using Molecular Dynamics Simulations***, **V. Raut**, S.J. Stuart, R.A. Latour,* Clemson University

Proteins, which are bioactive molecules, adsorb on implants placed in the body and directly influence biocompatibility. Molecular dynamics (MD) modeling provides one of the most direct methods of analyzing individual molecular-level interactions and can be used to simulate protein adsorption behavior using empirical force fields. In order to correctly simulate protein adsorption behavior, a force field must correctly represent the thermodynamic driving forces governing peptide residue-surface interactions (i.e., adsorption enthalpy, entropy & free energy). However, since existing force fields were developed without consideration of protein adsorption, they may not accurately represent this type of molecular behavior. Therefore the objective of our research is to develop computational chemistry methods to calculate thermodynamic parameters of peptide-surface adsorption and compare them with experimental results for the assessment of force field accuracy. Various MD simulations demonstrating individual residue-surface reactions are being studied. These models represent the behavior of small peptides over functionalized SAM surfaces in a water box with periodic boundary conditions. Statistical mechanics methods are being developed based on positionional probability distributions obtained from MD simulations to enable us to calculate the change in enthalpy, entropy & free energy as a function of distance between the peptide & surface. Comparison of these results with experimental results will enable us to determine the accuracy of available force fields. If necessary, the developed methods will then also serve as a basis for the development of a new force field that is specifically parameterized to accurately simulate protein adsorption behavior.

8:40am **BI-WeM2 Molecular Simulation Studies of Protein and DNA Interactions with Surfaces***, J. Zheng, J. Zhou, J.P. Sullivan, L. Zhang, **S. Jiang**,* University of Washington

Molecular-level understanding of protein behavior on surfaces will facilitate the development of biomaterials with superior biocompatibility and biosensors with high sensitivity and specificity. In this work, we report various molecular simulation studies of non-fouling mechanism, protein orientation/conformation on surfaces, molecular recognition, and DNA chips. First of all, molecular dynamics (MD) simulations are performed to study lysozyme interactions with SAMs presenting oligo (ethylene glycol) (OEG) groups in the presence of explicit water molecules and ions. The behavior of water at protein/SAM interfaces is characterized by self-diffusion coefficient, order parameter, hydrogen bonding, and radial distribution. The effects of surface (charge, hydrophobicity, and defect), solvent, pH, and ion strength will be taken into account. Results from this work will shed light on non-fouling mechanism at the atomic-scale level and guide the design of better biocompatible materials and biosensors. Second, Monte Carlo simulations are performed to study IgG orientation on positively charged NH2 and negatively charged COOH terminated self-assembled monolayers (SAMs) on Au(111). Simulations are confirmed by experimental results from surface plasmon resonance (SPR) biosensor and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Third, MD simulations are performed to study molecular conformation of cytochrome c on charged SAMs in the presence of explicit water molecules and ions. The ability to predict protein orientation and conformation will enable one to control and manipulate protein behavior on surfaces, important for biomaterials and biosensors. Fourth, hybrid molecular simulations are performed to study the unbinding pathway of biotin/avidin interactions at the atomic force microscopy time scale. Finally, MD simulations are performed to study the molecular packing of thiolated ssDNA and dsDNA on Au(111) and then mixed DNA and OEG SAMs.

9:00am **BI-WeM3 Macromolecular Dynamics: Insights from Simulation***, **B.R. Brooks**,* National Institutes of Health **INVITED**

Examples of recent macromolecular simulations will be presented which explore the relationship between modeled systems and real systems probed by experiment. In particular, data from neutron scattering, NMR, and crystallography can be compared and contrasted with corresponding results from molecular dynamics simulation. Also presented will be examples where simulation can provide insights that are difficult to obtain with experiment. There will be some discussion of recently developed methods that enhance our ability to accurately model interfacial systems and interactions between macromolecules. Also, protein conformational change and enzyme catalysis can be examined with a variety of methods. We present several methods, such as the Replica/Path method and extensions of the Nudged Elastic Band method, for examining such events and their application to interesting biological systems.

9:40am **BI-WeM5 Molecular Modeling of Adsorption-Induced Exposure of Integrin Binding Sites in Fibrinogen***, **M.A. Agashe**, S.J. Stuart,* Clemson University*; L. Tang,* The University of Texas at Arlington*; R.A. Latour,* Clemson University

Implants invoke inflammatory responses from the body even if they are chemically inert and non-toxic. It has been shown that a crucial precedent event in the inflammatory process is the spontaneous adsorption of fibrinogen on implant surfaces, which is typically followed by the presence of phagocytic cells. It has been found that interactions between the phagocyte integrin Mac-1 and one short sequence within the fibrinogen D domain (@gamma@190 to 202) partially explain phagocyte accumulation at implant surfaces. However, it is still unknown what makes adsorbed fibrinogen proinflammatory when soluble fibrinogen is not. One premise is that adsorption exposes the normally occult P1(@gamma@190 to 202) and P2 (@gamma@377 to 395) epitopes that reside in the D domains of fibrinogen; these epitopes are also involved in thrombin-mediated conversion of fibrinogen to fibrin. The objective of our research is to use molecular modeling to investigate how surface chemistry influences the adsorption behavior of the D fragment of fibrinogen with a particular focus on characterizing adsorption-induced conformational changes in the P1 and P2 region of this fibrinogen fragment that may lead to epitope exposure for integrin binding. Modeling is being conducted using Insight II software (Accelrys) with the CHARMM force field. The adsorption of the @gamma@ chain of fibrinogen is being simulated on 4 types of SAM surfaces (hydrophobic, hydrophilic, + - charged). An implicit solvent model (generalized Born) is being used to represent the solvent and solvent-mediated interactions during the molecular dynamics simulations. The study of these changes in conformation will help us to understand the likely molecular mechanisms that are responsible for the exposure of the P1 and P2 domains, and how this may be able to be controlled by surface chemistry. This understanding may help in the design of biomaterial surfaces with improved biocompatibility.

10:00am **BI-WeM6 Scaled Interfacial Activity of Proteins at the Liquid-Vapor Interface***, **A. Krishnan**, J. Sturgeon, C.A. Siedlecki, E.A. Vogler,* The Pennsylvania State University

A principal conclusion drawn from observations of time- and concentration-dependent liquid-vapor (LV) interfacial tension @gamma@@sub lv@ of a diverse selection of proteins ranging from albumin to ubiquitin is that concentration scaling substantially alters perception of protein interfacial activity, as measured by the amount adsorbed to the hydrophobic LV surface. Proteins appear more similar than dissimilar on a weight/volume basis whereas molarity scaling reveals a "Traube-rule" ordering by molecular weight, suggesting that adsorption is substantially driven by solution concentration rather than diversity in protein amphilicity. Scaling as a ratio-to-physiological-concentration demonstrates that certain proteins exhibit the full possible range of interfacial activity at-and-well-below physiological concentration whereas others are only weakly surface active within this range, requiring substantially higher solution concentration to achieve maximum adsorption to the LV interface. Important among this latter category of proteins are the blood factors XII and XIIa, assumed by the classical biochemical mechanism of plasma coagulation to be highly surface active, even in the presence of overwhelming concentrations of other blood constituents such as albumin and immunoglobulin that are shown by this work to be among the class of highly-surface-active proteins, at physiologic concentration. A comparison of pendant-drop and Wilhelmy-balance tensiometry as tools for assessing protein interfacial activity shows that measurement conditions employed in the typical Wilhelmy plate approach fails to achieve the steady-state adsorption state that is accessible to pendant-drop tensiometry. A comparison of bovine and human proteins reveals substantial differences in adsorption to the LV interface, apparently arising from as-yet unresolved speciation effects.

10:20am **BI-WeM7 Nanodevices Integrating Biomolecular Motors: Design Strategies and Applications***, **H. Hess**, J. Clemmens,* University of Washington*; C. Matzke, G.D. Bachand, B.C. Bunker,* Sandia National Laboratories*; V. Vogel,* University of Washington

Biomolecular motors are at present the engines of choice for nanodevices.@footnote 1,2@ Their small size, high efficiency, and functional integration allow the construction of hybrid devices, which demonstrate the promise of engineering at the nanoscale. We will discuss the tools employed in designing these devices, which include surface patterning, microfabrication, and genetic engineering. Our recent results@footnote 3@ show that these tools have to be employed in concert, in order to achieve outstanding results. For example, controlled placement of motor proteins on a surface requires non-fouling regions of high quality, as well as fine-tuning of the adsorption properties of the motors by genetic engineering. The design process in general requires an in-depth understanding of the motor properties as well as the properties of the filaments the motor proteins bind to (e.g. microtubules). New measurements aim at determining these properties. We will also present an overview of the applications studied by us, ranging from molecular shuttles@footnote 4,5@ to surface imaging @footnote 6@ and force measurements.@footnote 7@ @FootnoteText@@footnote 1@ H. Hess and V. Vogel, Reviews in Molecular Biotechnology, 82, 67-85 (2001)@footnote 2@ H. Hess, G. Bachand, and V. Vogel in: Encyclopedia of Nanoscience and Nanotechnology. Edited by James A. Schwarz, Cristian Contescu, and Karol Putyera (Marcel Dekker, New York, in print)@footnote 3@ J. Clemmens, H. Hess, J. Howard, V. Vogel, Langmuir, 19, 1738-1744 (2003)@footnote 4@ H. Hess, J. Clemmens, D. Qin, J. Howard, and V. Vogel, Nano Letters, 1 (5), 235-239 (2001)@footnote 5@ H. Hess, J. Clemmens, C. M. Matzke, G. D. Bachand, B. C. Bunker, and V. Vogel, Appl. Phys. A, A 75, 309-313 (2002)@footnote 6@ H. Hess, J. Clemmens, J. Howard, and V. Vogel, Nano Letters, 2 (2), 113-116 (2002)@footnote 7@ H. Hess, J. Howard, and V. Vogel, Nano Letters, 2(10), 1113-5 (2002).

10:40am **BI-WeM8 Nanoparticle Transport Using Microtubules and Motor Proteins***, **B.C. Bunker**, G.D. Bachand, A.K. Boal, S.B. Rivera, T.J. Headley, J.M. Gaudioso, J.M. Bauer, R.P. Manginell,* Sandia National Laboratories*; H. Hess, V. Vogel,* University of Washington

Active transport systems consisting of motor proteins and microtubules can potentially provide a dynamic mechanism for assembling and reconfiguring materials at nanometer length scales. We are interested in using motor protein-microtubule systems to manipulate gold nanoparticles and quantum dots to create programmable or responsive conductive or optical arrays within microfluidic systems. The primary active transport strategy we have investigated involves the use of patterns of tethered motor proteins to transport short functionalized microtubules attached to nanoparticles. This talk will focus on two central issues associated with developing a viable transport system: 1) the development of surface functionalization schemes that optimize the guiding of microtubule shuttles through lithographically-defined networks, and 2) the development of functionalized microtubule configurations that allow nanoparticles to be carried without affecting critical motor protein-microtubule interactions. For guiding, we have obtained the best results using lithographic patterns containing both gold and silica surfaces. The gold surfaces are coated with self-assembled monolayers (oligoethylene glycol and amine terminations are most effective) that are antifouling with regard to proteins, confining the adsorption of motor proteins and their support structures onto exposed silica at the channel bottoms. In terms of microtubule functionalization, we have demonstrated that both gold nanoparticles and CdSe quantum dots can be attached to microtubules using standard biotin-streptavadin linkages. The structures of the nanoparticle-microtubule constructs have been characterized using both transmission electron and atomic force microscopies. Flourescence microscopy results show that the number and spatial distributions of particles must be controlled to achieve active transport. Several successful strategies for controlling such distributions will be described.

Electronic Materials and Devices
Room 321/322 - Session EM-WeM
Multifunctional Electronic Materials

Moderator: C.J. Palmstrom, University of Minnesota

8:20am **EM-WeM1 Peter Mark Memorial Award Address: Epitaxial Complex Oxide Heterostructures: Electrostatic Modulation of Correlated Electron Behavior***, **C.H. Ahn**[1],* Yale University **INVITED**

Complex oxide materials exhibit a tremendous diversity of behavior, including phenomena that have only been observed in oxides, such as high temperature superconductivity. An even richer spectrum of possibilities becomes available if one combines different complex oxides in epitaxial thin film form to create artificially structured, heterogeneous systems. One can use such materials to electrostatically modulate correlated electron behavior, including superconductivity and magnetism, without introducing chemical or structural disorder. It is also possible to combine complex oxides, such as ferroelectrics, with semiconductors to explore new functionality in semiconducting systems.

9:00am **EM-WeM3 MBE Growth and Properties of Fe-, Cr- and Mn-doped TiO2 Rutile and Anatase***, **S.A. Chambers**, S. Thevuthasan, T. Droubay, S.M. Heald, C.M. Wang, A.S. Lea, V. Shutthanandan,* Pacific Northwest National Laboratory*; J. Osterwalder,* University of Zurich, Switzerland*; Y.J. Kim,* Hanbat National University, Korea*; R.P. Sears, B. Taylor, B.S. Sinkovic,* University of Connecticut

Room temperature ferromagnetism in Co-doped anatase TiO@sub 2@ has inspired a number of experimental and theoretical efforts. A high Curie point, good electron mobility, and optical transparency are attractive for use in spin electronics and optoelectronics. A natural question concerns the use of other magnetic dopants. Combinatorial doping of anatase and rutile with Sc, V, Cr, Mn, Fe, Ni, Cu using laser ablation by Matsumoto et al. reveal that only Co-doped anatase is ferromagnetic. However, DFT calculations by van Schilfgaarde for Cr, Mn, Fe and Co in anatase predict that Co, Cr and Fe make the material ferromagnetic, whereas Mn is antiferromagnetic. We are currently exploring Fe and Cr as dopants in MBE-grown TiO@sub 2@ rutile and anatase, and plan to investigate Mn in the near future. The substrates for rutile and anatase films are rutile TiO@sub 2@(110) and LaAlO@sub 3@(001), respectively. Films were characterized with RHEED, XPS, XPD, XAS, EXAFS, XMCD, AFM, SAM, TEM and MOKE. Cr and Mn are more likely to substitute for Ti in rutile than Fe because CrO@sub 2@ and MnO@sub 2@ exhibit rutile structures that are reasonably well lattice matched to TiO@sub 2@. No such phase exists for Fe. Moreover, CrO@sub 2@ is a half-metallic ferromagnet in the bulk. Cr indeed substitutes for Ti in the rutile lattice, and assumes a +3 formal oxidation state for doping levels of a few atomic percent. The first films have been found to be antiferromagnetic. In contrast, attempting to dope rutile with Fe leads to secondary phase Fe@sub 3@O@sub 4@. Fe (II) and Fe(III) are present, as expected if Fe@sub 3@O@sub 4@ is present. In addition, these films exhibit magnetic hysteresis and circular dichroism, but these signals are presumably due to the presence of minority phase Fe@sub 3@O@sub 4@. Cr exhibits a +3 oxidation state and substitutes for Ti for doping levels of a few atomic percent in anatase. Magnetic measurements of these films are pending at the time of writing of the abstract.

9:20am **EM-WeM4 Unusual Behavior of Electrical Conductivity and Thermopower Found in Mn@sub 1.68-X@Cu@sub .6+X+Y+Z@Co@sub .24-Y@Ni@sub .48-Z@O@sub 4@ Thin Films***, **F.S. Ohuchi**, J.G. Moyer, D.A. Kukuruznyak, M.S. Prowse,* University of Washington

The thermopower, S, and electrical conductivity, @sigma@, are measured on variations of a reference composition, Mn@sub 1.68-X@Cu@sub .6+X+Y+Z@Co@sub .24-Y@Ni@sub .48-Z@O@sub 4@. Doped compositions show parallel increases or decreases in conductivity and thermopower magnitude unlike typical band-gap conducting materials. This is desirable for increasing the efficiency parameter called the power factor, S@super 2@@sigma@, for thermoelectric applications. While thermopower varies by as much as 30%, the conductivity changes by up to a factor of four in the compositions explored. Conduction is attributed to small polaron hopping between neighboring Mn ions. Thin films are

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

obtained through Metal Organic Decomposition processing. This is a low-temperature fabrication route that allows for the retention of meta-stable Mn@super 4+@ and Cu@super 1+@ ions that are essential to favorable electronic behavior. Compositional variations modify the Mn@super 3+@, Mn@super 4+@, Cu@super 1+@, and Cu@super 2+@ concentrations, and in turn change the conductivity and thermopower. Supplemental XPS work defines changes in Cu oxidation states and oxygen content, and thermopower data provides Mn oxidation state information. Using the Heikes and Nernst-Einstein transport models we explain the seemingly incongruent behavior in thermopower and conductivity and identify that the discrepancy occurs in the conductivity factor. The nature of the unusual conduction behavior will be discussed.

9:40am **EM-WeM5 Using Strain to Control Microwave Tunability and Loss in Barium Strontium Titanate Thin Films*, S.W. Kirchoefer,*** *W. Chang, J.A. Bellotti, J.M. Pond,* Naval Research Laboratory*; D.G. Schlom,* Pennsylvania State University **INVITED**

Barium strontium titanate thin films exhibit an electric field dependent dielectric constant which can be exploited for tunable microwave devices. This technology has been of limited applicability due to the relatively high dielectric losses that typically accompany high tuning. The control of dielectric loss is of critical technological importance. Manipulation of deposition conditions and film impurities have been investigated widely as means for achieving improved films. Engineered film strain is an additional material parameter that can be controlled toward these ends, and this talk will report on experiments that demonstrate the advantages of both strain minimization and strain enhancement on the microwave properties of barium strontium titanate and strontium titanate thin films. It will be shown that the structural distortion caused by film strain results in decreased dielectric constant and tuning for compressive strain and increased corresponding values for tensional strain at room temperature. These results can be understood by examining the effects of lattice distortion on Curie temperature. A model based on thermodynamics and strain-induced polarization will be presented. The effects of strain on dielectric losses and device quality factor will also be discussed. Results from substrate mismatch strain and film annealing studies will be presented. Ongoing efforts to measure effects of extrinsic strain induced by externally-applied pressure will be discussed.

10:20am **EM-WeM7 Displacive Phase Transition in SrTiO@sub 3@ Thin Films Grown on Si(001)*, F.S. Aguirre-Tostado,*** CINVESTAV-Querétaro, México, Mexico*; A. Herrera-Gómez,* CINVESTAV-Querétaro, México*; J.C. Woicik,* National Institute of Standards and Technology*; R. Droopad, Z. Yu,* Motorola*; D.G. Schlom,* Pennsylvania State University*; J. Karapetrova, P. Zschack,* University of Illinois and Argonne National Lab*; P. Pianetta,* Stanford Synchrotron Radiation Laboratory

Polarization dependent x-ray absorption fine structure and x-ray diffraction have been used to study the local structure in SrTiO@sub 3@ thin films grown epitaxially on Si(001). For films less than a critical thickness of ~ 80 Å, a splitting of the Ti-O distance perpendicular to the interface is observed: r@sub Ti-O@ = 1.87 ± 0.02 Å and r@sub Ti-O@ = 2.09 ± 0.06 Å, whereas only a single Ti-O distance is observed within the plane of the interface: r@sub Ti-O@ = 1.95 ± 0.01 Å. These findings indicate that the in-plane compressive strain imposed on the SrTiO@sub 3@ layer by the Si substrate results in a tetragonal plus displacive ferroelectric distortion of the SrTiO@sub 3@ cubic unit cell. This study therefore suggests the existence of a Curie "thickness" for strained-layer, epitaxial perovskite growth.

10:40am **EM-WeM8 Dielectric Response of Asymmetric KNbO@sub 3@/KTaO@sub 3@ Superlattices*, J. Sigman,*** *H.J. Bae, D.P. Norton,* University of Florida*; J.D. Budai, P.H. Fleming, L.A. Boatner,* Oak Ridge National Laboratory

The K(Ta,Nb)O@sub 3@ perovskite is an interesting paraelectric/ferroelectric system with tunability of the dielectric response with applied electric field. Pulsed laser deposition (PLD) has been used to achieve atomic layer-by-layer growth in KTaO@sub 3@/KNbO@sub 3@ superlattices. Previously, a symmetric 1 unit cell x 1 unit cell KTaO@sub 3@/KNbO@sub 3@ was grown on KTaO@sub 3@(100) and its dielectric response and structural properties were studied. Increasing capacitance with increasing applied dc bias for temperatures just below the structural transition was observed and suggested an anitiferroelectric response. We have investigated several asymmetric KTaO@sub 3@/KNbO@sub 3@ superlattices to provide further elucidation on this anomalous dielectric response. This positive tunability appears to be a function on the thickness the KNbO@sub 3@ layer. Above three unit cells of KNbO@sub 3@, the positive tunability disappears. Below three unit cells of KNbO@sub 3@, the positive tunability is seen in the same temperature region as the 1 x 1 superlattice, regardless of the Nb:Ta thickness ratio.

Homeland Security Topical Conference
Room 309 - Session HS-WeM

Plenary Session on Homeland Security

Moderators: R.J. Colton, Naval Research Laboratory, J.N. Russell, Naval Research Laboratory

9:00am **HS-WeM3 The DoD Chemical Biological Defense Program: Technical Base*, R.A. Mackay,*** SBCCOM **INVITED**

The DoD Chemical Biological Defense Program (CBDP) is a joint service program, with oversight and management through the Office of the Secretary of Defense for CB. The technical base portion of the CBDP, basic and applied research and concept development, is managed by the Defense Threat Reduction Agency (DTRA). Participants in the program include the services, industry and academia, and the projects are executed principally through the service laboratories. Each service is assigned responsibility by DTRA for monitoring supporting SBIR/STTR projects with industry, and DTRA is also responsible for ensuring coordination with other federal agencies and organizations. While the principal function of the CBDP is to support the warfighter, it also supports dual-use technology, which may be applied to homeland security. Some examples of relevant technology will be presented.

9:40am **HS-WeM5 Framework for Technology in Homeland Security*, S. Hallowell,*** Transportation Security Administration **INVITED**

As an element of the Border and Transportation Security (BTS) under the Department of Homeland Security (DHS), the Transportation Security Administration is responsible for providing security solutions for rail, maritime, transit, pipeline, aviation and highway modalities. The Office of Security Technologies will develop and implement the best security technology solutions to protect the nation's transportation systems, ensuring freedom of movement for people and commerce. The provision of security against the safety, privacy, and surface of the traveling public is a challenging balance. The Transportation Security Laboratory is responsible for research development, and test and evaluation of next generation security procedures, processes and equipment. Our current security R&D program is addressing measures that can be taken to protect people, cargo, conveyances, and facilities against explosives, weapons, unauthorized access, and chemical/biological/radiological/ and nuclear agents. Many novel technologies are being developed and assessed in our laboratory in order to meet these challenges, including walk-through portals that detect explosive residues, explosive detection systems (EDS), nuclear quadrupole resonance, X-ray diffraction, and neutron and gamma ray systems. Other areas of R&D include enabling technologies such as biometrics, vehicle tracking and intrusion surveillance. The scope of the need is large, and the threat is real, but layered elements of technology and procedures suggest a blueprint for future security.

10:20am **HS-WeM7 The Role of the Science and Technology Directorate in Homeland Security*, A. Fainberg,*** Department of Homeland Security **INVITED**

The Science and Technology (S&T) Directorate is one of four directorates in the newly formed Department of Homeland Security (DHS). Its Office of Research and Development includes National and Federal Labs, University programs, and activities focused on standards, test & evaluations, and bio-countermeasures. The Plans, Programs and Budget Office will determine broad lines of R&D that will be carried out by the Office of Research and Development and the Homeland Security Advanced Reaerch Projects Agency. While DHS is not fundamentally a basic research agency/funder, the S&T Directorate will engage in both applied research and rapid prototyping of near-ready products. Longer-term exploratory research will be conducted by University programs or through the Homeland Security Advanced Projects Agency, a new component of the S&T Directorate.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI-WeM

Current-Induced Magnetic Switching and Excitations

Moderator: S.E. Russek, National Institute of Standards and Technology

8:20am **MI-WeM1 Direct Measurements of Spin Momentum Transfer Induced Dynamics***, **W.H. Rippard**, M.R. Pufall, S. Kaka, S.E. Russek, T.J. Silva,* National Institute of Standards and Technology

Slonczewski and Berger first predicted that the angular momentum from a spin-polarized current can be transferred to a ferromagnetic film creating a torque on the film magnetization, the so-called spin momentum transfer (SMT) effect. Previous work has shown that for sufficiently high current densities and applied magnetic fields, there occurs an abrupt increase in the dc resistance of point contact junctions or nanopillar devices. In accordance with theoretical predictions, these steps have been attributed to the onset of coherent magnetization dynamics. We will discuss our recent results from studying these excitations directly in a number of different materials, sample geometries, and applied field geometries. In general we find that the excitations can be well described with the Kittel equation for magnetization dynamics. We commonly observe these excitations from frequencies below 5 GHz to greater the 25 GHz. We have found that these linewidths are often as narrow as 20 MHz and persist for fields from H = 200 Oe to ~1 T, although the specifics depend on the particular geometry and material of the device under study. We also compare these results to single-domain model simulations of SMT induced dynamics and find good agreement between the simulated and measured behavior.

8:40am **MI-WeM2 Dynamical Modes of Nanomagnets Driven by a Spin-Polarized Current***, S.I. Kiselev, **J.C. Sankey**, I.N. Krivorotov, N.C. Emley,* Cornell University*; S.E. Russek,* National Institute of Standards and Technology*; R.J. Schoelkopf,* Yale University*; R.A. Buhrman, D.C. Ralph,* Cornell University

A spin-polarized current can apply a torque directly to a ferromagnet through transfer of angular momentum. Here we report direct electrical measurements of microwave-frequency magnetic dynamics driven by DC spin-transfer currents in Co/Cu/Co nanopillar structures. We demonstrate that spin-transfer can produce several types of excitations, including small angle elliptical precession, more complicated large angle motions and high current static state. Microwave power emitted by magnetic multilayer devices may enable nanoscale oscillators and microwave sources generated by DC current.

9:00am **MI-WeM3 Current-Induced Precession at Ferromagnetic Interfaces***, **A. Zangwill**,* Georgia Institute of Technology **INVITED**

It is well established experimentally that the relative orientation of two ferromagnetic layers in a multilayer film can be switched by passing a sufficiently large current through the film. Often, this "converse GMR" effect is preceded by a precession-type instability of one or both ferromagnetic layers. The signature of this instabilty has also been seen during point contact current injection into a single ferromagnetic film. In this talk, I discuss the precessional phenomenon theoretically using a combination of phenomenological modelling, Boltzmann transport theory, and first-principles quantum mechanical calculations. The key ingredient is a "spin-transfer" torque associated with spin polarization of the electric current. Special emphasis is placed on the possibility of quantitative comparison with experiment.

9:40am **MI-WeM5 Spin-transfer Induced Magnetic Switching in Batch-fabricated sub-100 nm Spin-valves***, **J.Z. Sun**,* IBM T.J. Watson Research Center*; T.S. Kuan,* SUNY at Albany*; M.J. Rooks,* IBM T.J. Watson Research Center*; J.M.E. Harper,* IBM T.J. Watson Research Center and University of New Hampshire*; R.A. Carruthers, S.M. Rossnagel, R.H. Koch,* IBM T.J. Watson Research Center **INVITED**

A hard-mask stencil method is developed for the efficient fabrication of sub-100nm current-perpendicular spin-valve junctions with low contact resistance. The approach uses a trilayer template. The templated substrate is batch fabricated first with the junction features defined by a top stencil layer and an undercut in the insulator. The spin-valve thin film stack is deposited afterwards into the stencil, with the insulator undercut providing the necessary isolation of magnetic exchange coupling. By placing electron-beam lithography at the very beginning of the process before the deposition of the magnetic thin films, this approach improves the turnaround time for materials optimization in nanostructures. Using this approach, spin-transfer induced magnetic switching and magnetic excitation are observed for junctions down to 50nm x 100nm in size.

10:20am **MI-WeM7 Current-Driven Magnetization Reversal at High Magnetic Fields in Co/Cu/Co Nanopillars***, **B. Oezyilmaz**[1], A.D. Kent,* New York University*; D. Monsma,* Harvard University*; J.Z. Sun, M.J. Rooks, R.H. Koch,* IBM T.J. Watson Research Center

Recently there has been great interest in current induced angular momentum transfer in magnetic nanostructures. Its observation in point contact experiments on magnetic multilayers in the field perpendicular geometry has boosted efforts to understand the underlying mechanism.@footnote 1@ We have studied spin transfer torques in the same field perpendicular configuration in sub-micron size (~100 nm) Co/Cu/Co pillar devices at 4.2 K and 293 K. Pillars have been fabricated by means of a new nano-stencil mask process, which enables the production of large arrays of templates ideal for systematic variations of layer thicknesses and compositions. I(V) measurements in large magnetic fields (>1.5T) show an abrupt increase in device resistance at high current densities for one current polarity. The onset of this transition is marked by both a hysteretic step in the DC voltage and a hysteretic peak in dV/dI. The magnitude of the step in resistance is similar to the device in-plane GMR (~5 %) and is thus consistent with current-induced switching into a high resistance state of anti-parallel magnetization in large applied perpendicular magnetic fields. In contrast to experiments with point-contacts, our results suggest that the peak in dV/dI marks the end and not the onset of magnetization dynamics.@footnote 2@ High field hysteresis in MR measurements at fixed (positive) bias current is also observed which is consistent with this interpretation. Micromagnetic modeling that includes a spin-transfer torque is in qualitative agreement with these observations and provides an explanation for the basic features observed in the device I-V characteristics as a function of magnetic field. Further, to study the importance of the longitudinal spin-accumulation, pillars with only a single Co layer have been fabricated. Initial experiments with these Cu/Co/Cu sub-micron size pillar devices will be discussed. @FootnoteText@@footnote 1@M. Tsoi et al, Nature 406, 46 (2000). @footnote 2@B. Oezyilmaz et al., arXiv:cond-mat/0301324.

10:40am **MI-WeM8 Current-Triggered Domain Wall Motion in Focused Ion Beam Fabricated Magnetic Nanowires***, **C.T. Rettner**, M. Tsoi, L. Thomas, S. Parkin,* IBM Almaden Research Center

Focused ion beam techniques have been used to pattern NiFe and CoFe thin films into nano-wires to study magnetic domain wall motion triggered by an electric current. We have investigated a variety of shapes, including simple and notched straight lines as well as zigzags and semi-circular shapes. Our scheme begins with a large structure created by deposition of the magnetic material onto SiO2 through a shadow mask. This structure consists of 1 mm pads connected by a 0.1 mm line. The focused ion beam is first used to cut this line with a 11 nA beam leaving just 6 microns of film on the centerline. Next an 11 pA beam is used to roughly form the desired shape in this region, and a 4 pA with ~25 nm resolution is used to add details such as notches and to form the final dimensions. We will discuss our observations of current-triggered domain-wall motion in these structures, including results for motion in zero fields. These results include magneto-resistive measurements and MFM imaging. Finally, we will briefly discuss the results in terms of micro-magnetic simulations for these structures.

Microelectromechanical Systems (MEMS)
Room 320 - Session MM-WeM

New Frontiers in Microsystems: NEMS and BioMEMS

Moderator: R. Ghodssi, University of Maryland

8:20am **MM-WeM1 The Science and Technology of Nanomechanical Resonant Structures***, **L. Sekaric**,* Cornell University **INVITED**

The development of nanometer-scale mechanical structures into sensitive and integrated devices has enabled us to envision applications such as cell phones the size of a wrist watch, fast and sensitive pathogen detectors, and ultra-sensitive field and force gauges. An exact understanding of the physical phenomena affecting NEMS behavior should aid in the successful application of these systems. Several important achievements in this field will be described - from fabrication of ultra-small and ultra-high frequency resonant structures in a variety of materials to understanding their

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[1] **Falicov Student Award Finalist**

behavior and improving their performance. Some of the topics to be discussed include the time scales of nanoscale dynamics, the operation of NEMS in vacuum and in air, the sources of energy dissipation, and the effects of thin film mechanics in NEMS.@footnote 1@ @FootnoteText@ @footnote 1@In collaboration with: M. Zalalutdinov, K. Aubin, A. T. Zehder, J. M. Parpia, and H. G. Craighead, Cornell Center for Materials Research, and J. E. Butler, Naval Research Labs.

9:00am **MM-WeM3 Investigation of Nanostructuring by Use of Focused Ion Beam Fine Milling*, Y. Fu,*** Nanyang Technological University, Singapore

Micro-pillars with nano-sizes for application of molecular controlling were fabricated by use of focused ion beam (FIB) fine milling on substrate of silicon. The nano-pillars can realize cell/molecular adhesion, and movement control by its high-density contact dots and tiled cone angle of the pillars, which can be obtained by means of FIB directly fine milling with a stage in a certain tilted angle. The milling process was investigated under different beam current and the stage-tilting angle, which determines an aspect ratio and the tilted angle of the pillars. Chemical assistant etching (GAE) with chemical gas of XeF2 was used for the purpose of deviating the pillars with higher aspect ratio. With these features, the pillars can realize cell/molecular movement in only one direction and cannot be backward. It will be helpful for DNA and protein analysis, such as molecule separation and purification, molecular detection, and DNA hybridization, etc.

9:20am **MM-WeM4 Electron Interactions in Nanoscale Focused Electron Beam Processing*, P.D. Rack*,** *J. Kim, J.D. Fowlkes, S.J. Randolph, D.C. Joy,* University of Tennessee

Focused electron beam induced processing has recently been demonstrated to be a viable technique for selective nanoscale processing. The technique is similar in principle to focused ion beam processing, however, the electron-stimulated reactions have been shown to have a smaller effective beam width (~ 50nm) and do not suffer the collateral damage associated with gallium implantation. In this presentation, we will show our recent progress in electron beam stimulated deposition and etching. Particular attention will be given to the effects that secondary and backscattered electrons have on the deposited or etched structure. Electron-solid and electron-gas Monte Carlo simulations will be correlated to the observed deposition and etching profiles profiles. Beam energy and current density effects will also be shown and explained. Finally, application of the process to several nanoscale devices will be demonstrated.

9:40am **MM-WeM5 BioMEMS-Based Platforms for Drug Delivery: Implantable, Ingestible, and Beyond*, T.A. Desai,*** Boston University**INVITED**

Microfabrication techniques, which permit the creation of multifunctional platforms that possess a combination of structural, mechanical, and electronic features, may surmount several challenges associated with the conventional delivery of therapy. In this talk, in vivo delivery concepts are presented which capitalize on the strengths of micro and nanofabrication. Current work on micromachined nanoporous implantable biocapsules for the immunoisolation of pancreatic islet cells - as a possible treatment for diabetes -- will be described. In addition, asymmetrical, reservoir-containing microfabricated particles and arrays with specific biorecognition ligands will be discussed for improving the oral delivery of peptides and drugs. Such microengineered interfaces may be optimized for biomolecular selectivity and surface bioactivity. With the capability to design components spanning from the millimeter down to the nanometer range, few other engineering technologies can so closely parallel the multidimensional size scale of the living cells and tissues, with control and reproducibility, in the same fabrication process. Micro/Nanotechnology can add flexibility to current practices while becoming an enabling technology leading not just to new therapies and laboratory techniques, but to new models for delivering healthcare to the patient.

10:20am **MM-WeM7 Flexible, Polyimide-Based Microfluidic Devices for BioMEMS*, S. Metz*,** *A. Bertsch, Ph. Renaud,* Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland

We present flexible, polyimide-based microfluidic devices for a wide range of applications in the field of BioMEMS. Fluidic microchannels are manufactured by a modified lamination technique or a sacrificial layer method. For the lamination technique a layer of uncured polyimide is irreversibly bonded to open channel structures of semi-cured polyimide, which yields very high bond strengths. The sacrificial layer technique implies the use of a heat-depolymerizable polycarbonate sacrificial material. The material is embedded in two layers of polyimide and diffuses through the channel cover layer during the last fabrication step leaving empty microfluidic channel networks behind. The microchannels can be combined with metallization layers for the integration of microelectrodes inside the microchannels, which is a major requirement in the field of miniaturized bio-chemical analysis. The electrodes inside the channels can be used for fluid actuation or detection of substances. The embedded layers of metal can also be used as microelectrodes for the recording or stimulation of bio-electric activity. This results in devices, which are capable of selectively delivering fluids to cells and at the same time enable electrophysiological monitoring. Additionally, the channel walls can be made porous by ion track technology, which yields sub-micron, high aspect-ratio pores perpendicular to the fluidic structure with a pre-defined pore density. The pores can be generated in the top and/or bottom channel walls of the microfluidic device and the pore size is adjustable down to tens of nanometers. These devices can be used for the separation of particles by cross-flow filtration.

Manufacturing Science and Technology
Room 326 - Session MS-WeM
Sensors, Metrology, and Control

Moderator: A. Diebold, SEMATECH

8:20am **MS-WeM1 Critical Dimension and Remaining Film Thickness Within Wafer Uniformity Improvement by Advanced Process Control Based on Optical Integrated Metrology*, J. Luque*,** *G.P. Kota, V. Vahedi,* Lam Research Corporation

The first generation of advanced process control using integrated metrology in polysilicon etch processes has been focused on correcting wafer averaged critical dimension (CD). Schemes have ranged from feed-forward to feed-forward/feedback closed loop control. In all these cases the information from optical CD is used to obtain a target wafer averaged CD and minimize the lot-to-lot and within lot- variations of post-etch CD by correcting perturbations from lithography and etch steps. In the present work we explore some of the cases where improvement of isolated to dense loading, within wafer CD uniformity after gate etch or uniformity of the remaining films in recess etch applications is important. Because device performance is directly related to the CD, it is necessary to improve the uniformity of the CDs as much as is important to reach the specific target CD. Correction of the CD within wafer uniformity can be achieved by feedback of the CD information to the track/scanner cluster (litho step) or by feed-forward to the etch module. We show how non-uniformities generated in a concentric pattern by the litho step can be partially or completely eliminated during the etch step using a tunable temperature gradient in the chuck of a Lam Versys 2300 etching system. This approach to improve CD uniformity opens a path to more complex advanced process control that will deliver simultaneous CD and uniformity control. The results from this method should be better than those from schemes based on just averaged CD control. Similar approach is investigated in etch processes that can be characterized by simple thin film measurement instead of full optical profile characterization.

8:40am **MS-WeM2 Real-time In-situ Chemical Sensing in GaN MOCVD for Advanced Process Control*, S. Cho*,** *G.W. Rubloff,* University of Maryland*; M.E. Aumer, D.B. Thomson, D.P. Partlow,* Northrop Grumman Corporation

Gallium nitride is a strong candidate material for next generation semiconductor devices for high frequency, high power electronic applications. Despite the potential of this material, the industry has yet to realize a systematic methodology for reproducible manufacturing at the high performance levels envisioned. As a joint project between the University of Maryland and Northrop Grumman, we have addressed this challenge with the use of a real-time in-situ chemical sensing technique. Residual gas analysis downstream to the MOCVD process has enabled us to monitor in real-time the by-product species due to the deposition reaction as well as other background impurity species inherent to the process. A metric derived from the by-product signals provided us with a real-time means for accurately predicting the crystal quality of the material as determined by the post-process ex-situ XRD (X-ray Diffraction) with an average uncertainty of 5% or less. Background impurity levels in the gas-phase were also closely correlated to the post-process ex-situ PL (Photoluminesence) measurements for material quality. In addition, time-integration of the by-product signals during the deposition process generated metrology for predicting and controlling the thickness of the individual layers in the GaN-based HFET structure. This creates opportunities for advanced process control based on real-time in-situ sensing, with the promise of major benefit in reproducibility and cost reduction in GaN-based semiconductor manufacturing.

9:00am **MS-WeM3 Flexible Simulation Tools for Design, Control, and Optimzation of Semiconductor Processing Systems*, R.A. Adomaitis,*** University of Maryland **INVITED**

Physically based simulations are valuable tools for understanding the chemical and physical mechanisms responsible for spatial non-uniformities in films produced by chemical vapor deposition systems. In this talk, an alternative will be presented to the "traditional" (e.g., CFD-based) approaches to high-fidelity equipment simulation. This work was motivated by the need for flexible simulation tools that allow rapid evaluation of reactor design choices and that interface readily with available optimization, process control, and numerical analysis tools. An object-oriented framework was created to generate modular simulation elements corresponding to CVD reactor physical components, as well as simulator elements derived from the abstraction of boundary-value problem based model solution (global spectral) methods and the other numerical methods necessary to solve the nonlinear equation models. The role of information technology issues and distributed computing concepts in implementing this framework will be presented. Results of our simulation-based design and prototype testing of the Programmable Chemical Vapor Deposition reactor system, a highly-controllable CVD system under development at UMd, and our interaction in redesigning CVD systems with an industrial research partner will be discussed. It will be shown that the flexibility built in to the simulation methodology from the outset is critical to enabling a relatively rapid simulation/experimental-evaluation/redesign cycle in these CVD reactor design and construction projects.

9:40am **MS-WeM5 Spatial Uniformity as a Key Challenge in Semiconductor Process Control*, D.S. Boning,*** Massachusetts Institute of Technology **INVITED**

Semiconductor process control has advanced to address manufacturing needs -- primarily wafer to wafer uniformity of device and interconnect structures -- using improved metrology, real-time, and run-by-run control techniques. Here, the need for improved spatial uniformity is discussed, and the challenges for advanced process control in achieving these needs outlined. First, the impact of variation on integrated circuits of wafer to wafer, within wafer, and within die variation is considered, highlighting that yield and performance can depend at least as strongly on spatial uniformity as on wafer to wafer uniformity. Within die uniformity in particular pose difficult challenges; examples include uniformity in interconnect geometry (e.g. pattern dependent CMP and plating effects such as copper dishing and erosion), as well as device geometry and electrical properties (e.g. channel length variation due to lithography and plasma etch pattern dependencies). Finally, the resulting needs and challenges for process control are discussed: metrology must evolve to enable observation of within die variations, models are needed to relate control parameters to within die as well as across wafer results, and algorithms are needed that can address both spatial and temporal variation objectives.

10:20am **MS-WeM7 In-situ Defect Metrics Based on Real-Time Sensor Integration and Analysis*, J.A. Mucha,*** INFICON, Inc.

The concept of advanced metrology is not new to the semiconductor industry. However, the focus of attention always seems to be on increasing the capabilities of visual inspection for defects even though yield-affecting defects include non-visible electrical defects, parametric defects and electrical faults whose root cause is often difficult to determine. The "2001 SIA International Roadmap for Semiconductors: Yield Enhancement" notes that current Data Management Systems (DMS) have limited abilities to incorporate real-time in-situ sensor data that can be correlated with lot and wafer-based data. Further, current DMS are even more limited in their abilities to use the information in a yield-predictive way in spite of the fact that real-time analysis of such data would result in more rapid identification and prioritization of defect generating mechanisms to a broad sector of engineering group. In this presentation, the sensor-integration and analysis system, FabGuardÃ¢, is used to address these shortcomings by combining sensor output with logic and signal analysis to create real-time in-situ metrics for wafer health. These can then be used to track potential non-visible yield-loss defects in a way that can drive continuous product improvement with decreased emphasis on in-line and ex-situ metrology. The use of residual gas analysis in monitoring the degas operation in PVD cluster tools is shown to be a capable for generating metrics that sensitive to process variations exhibited by prior processing equipment such as etch, ash and CVD. Case studies of applying this metrology are presented that identify root causes of contamination-induced yield-limiting defect mechanisms.

10:40am **MS-WeM8 Prototype Development of Four-Point Probe with 100 µm Probe-Spacing for Resistivity Measurements*, M. Suzuki*,** *Y. Sato, T. Ogiwara,* NTT-AT, Japan*; S. Kiyota, K. Watanabe,* Kiyota Manufacturing Co., Japan*; N. Matsubayashi,* AIST, Japan*; S. Matsumoto,* Keio University, Japan

The four-point probe technique has been used commonly to measure the semiconductor resistivity. It is, however, difficult to detect changes in resistivities over distances smaller than 3 mm because of the standard probe-spacing of 1 mm. With the reduced dimension of devices, it is very significant to determine resistivity variations on a very small scale. Thus we have developed the prototype of the four-point probe with 100 µm probe-spacing and confirmed the adaptability for practical use. The four probes are made from 50-µm-diameter tungsten carbide wire, and their apexes are ground down to a radius of 20 µm. It is found that the tip apex is durable and is not contaminated after 1.5 x 10@super 5@ times probing onto the Si surface. The measurement system is constructed with mechanical driving parts, a commercial dc current source, and a digital voltage meter under the design concept same as the conventional four-point probe technique. We have demonstrated that it is possible to measure the resistivity radially across a Si wafer very near the wafer edge (about 0.5 mm), while conventional system with 1 mm probe-spacing was limited to measure the resistivity to the points of about 4 mm from the wafer edge. This 100-µm probe can also measure the resistivity in the phosphorus-doped poly-silicon film of 0.5 x 0.5 mm@super 2@ on an oxidized Si wafer. Our results suggest that the probe can measure a resistivity distribution on one LSI chip area, and that this system will be used as a monitoring tool for various fabrication processes. This project was performed with the financial support of Ministry of Economy, Trade, and Industry, Japan.

Nanometer Structures
Room 308 - Session NS-WeM

Nanomechanics

Moderator: N.A. Burnham, Worcester Polytechnic Institute

8:20am **NS-WeM1 Dissipation in Few Atom Systems*, J. Pethica,*** University of Oxford, UK **INVITED**

9:00am **NS-WeM3 Quantitative Imaging of Local Electromechanical Properties of Ferroelectric Surfaces by Piezoresponse Force Microscopy, *S.V. Kalinin,*** Oak Ridge National Laboratory*; J. Shin,* University of Tennessee*; A.P. Baddorf, J.F. Wendelken,* Oak Ridge National Laboratory*; M. Kachanov, E. Karapetian,* Tufts University

Piezoresponse Force Microscopy has become the primary tool for the characterization of ferroelectric materials at nanoscale dimensions. Application of a periodic bias to the AFM tip in contact with the surface results in surface oscillations due to an inverse piezoelectric effect. These are detected with a lock-in amplifier to produce PFM amplitude and phase images. Special attention has been attracted to the potential of this technique for local spectroscopic measurements, i.e. the local electromechanical hysteresis loop of the material. Application of a dc bias or force to the tip can switch the local polarization, opening possibilities of PFM as a nanolithographic tool. Despite extensive effort, a detailed understanding of PFM imaging, including tip induced mechanical and electrostatic phenomena inside the ferroelectric, has not previously been achieved. Here, the analytical solution of the coupled electromechanical problem for piezoelectric indentation is used to derive the electric field and strain distribution inside the ferroelectric material, providing a complete continuum mechanical description of the PFM imaging mechanism. These solutions are used to quantitatively interpret PFM spectroscopic measurements and bias- and stress-induced domain behavior. It is shown that the dielectric gap formation at the tip surface junction due to surface contamination significantly affects the PFM imaging mechanism. Preliminary results of PFM imaging under controlled atmosphere and UHV conditions are presented.

9:20am **NS-WeM4 Evaluating Nanocomposite Strength at Individual Nanotube-Polymer Interfaces*, S.R. Cohen*,** *A.H. Barber, C.A. Cooper, H.D. Wagner,* Weizmann Institute of Science, Israel

Nanocomposites formed from carbon nanotubes have been proposed as an ultra-high strength material. Although bulk measurements of the properties of such nanocomposites support these claims, until this work the only direct microscopic investigation of the nanotube/polymer interfacial strength has been by theoretical predictions. We have developed two novel SPM-based techniques which measure, for the first time, the direct pull-out forces of individual nanotubes in a polymer matrix.@footnote 1@ In one approach, the nanotubes are mixed into an epoxy resin using a procedure which results in a porous structure with nanotubes bridging the pores and embedded into the polymer matrix. The SPM tip is used to drag these nanotubes out of a film formed by microtoming this structure. The force exerted is extracted from the SPM measurement, whereas embedded length is measured with the aid of TEM. In the second approach, a nanotube attached to an SPM probe is pushed into a polymer melt, and pulled out from the hardened polymer after cooling. Here, the SPM measurement is used to evaluate both the forces and embedded length. Our results verify the predicted high nanotube-polymer interfacial strength, and reveal trends correlated to fiber diameter and embedded length. @FootnoteText@ @footnote 1@ (a) Carole A. Cooper, Sidney R. Cohen, Asa H. Barber, and H. Daniel Wagner Appl. Phys. Lett. 81, 3873-75 (2002); (b) Asa H. Barber, Sidney R. Cohen, and H. Daniel Wagner Appl. Phys. Lett. (June, 2003) .

9:40am **NS-WeM5 Mechanics at the Nanoscale***, T. Uchihashi, M. Higgins,* Trinity College, Ireland*; J.E. Sader,* E.T.S. Walton Visitor, Trinity College, Ireland, Australia*; **S.P. Jarvis,*** Trinity College, Ireland **INVITED**

Atomic force microscopy (AFM) evolved from the observation of the effects of mechanical contact in the scanning tunnelling microscope. Thus, even from its first inception, nanomechanics and atomic force microscopy have been inextricably linked. Whilst not all mechanical phenomena have been intentional or welcomed in AFM measurements there has also been a concerted effort to apply AFM to the investigation of mechanics at the nanoscale. Due to its highly localised measurement ability, the microscope can be applied to characterise the mechanical response of materials too laterally specific to be investigated by Surface Forces Apparatus or nano-indentation devices. For example, measuring mechanical responses with a probe of lateral dimensions comparable to that of a single molecule provides an invaluable insight into the processes controlling if and how a molecule approaches another molecule or a membrane and how mechanical property variations in any intervening fluid can modify that interaction. We introduce a significantly modified AFM which includes the ability to control the force sensor directly via a magnetic field in order to make sensitive dynamic measurements and direct stiffness measurements. In addition, to isolate the measured interaction to the tip apex we have used a multiwalled carbon nanotube attached to the tip. For the extension of the method to include lateral activation, and hence open up the possibility of measuring local viscosity, a new shape of cantilever has been used. To understand the mechanics of our new force sensors we have employed finite element analysis (FEA) to assess and improve the design and for calibration.

10:20am **NS-WeM7 Nanomechanics of Cytoskeletal Proteins***, **J.G. Forbes,*** NIAMS, NIH, DHHS*; K. Wang,* LMB, NIAMS, NIH, DHHS

Striated muscle is the primary source of biomechanical force in organisms from worms to man, and can be thought of as a composite material that is organized on several length scales. The motor protein in all muscles is myosin, which generates piconewtons force through its interaction with actin and the hydrolysis of ATP. The tiny force generated by a single myosin is amplified by aggregating large numbers of myosin heads into an ordered structure called the thick filaments. The thick and thin filaments are then assembled into the basic contractile machinery called the sarcomere that link serially from one end of the muscle cell to the other. Striated muscle shortens by the sliding of actin filaments as they are dragged towards the center of the myosin filaments. When muscle relaxes, its original length is restored elastically. An array of cytoskeletal proteins are required to regulate the size, assembly and function of the sarcomere, as well as transmit force and provide elasticity for restoring the structure. One such protein is the giant protein titin (3-4E6 g/mol), which spans half of the muscle sarcomere length. The passive elasticity of muscle at a physiological range of stretch arises primarily from the extension of titin. Nebulin serves as a ruler for the actin filaments and may alter their compliance and tensile strength. Other proteins such as dystrophin help transmit force out of the muscle and desmin forms intermediate filaments, which help to stabilize the sarcomere organization. We have studied the elastic properties of these motor and cytoskeletal proteins via force spectroscopy with the AFM. We have found that the elasticity of proteins can arise from mechanisms other than simple entropic elasticity. These mechanisms work at the nanoscale and may allow for their properties to be fine tuned to fit the need of muscle to work under a variety of conditions. These insights from biology may allow for the engineering of more effective elastic materials.

10:40am **NS-WeM8 Effect of the Ionic Strength on a Natural Lipid Bilayer Assembling and Stability: A Force Spectroscopy(nanomechanical) Study***, **S. Garcia-Manyes**, M.J. Kogan, F. Sanz,* University of Barcelona, Spain*; D. Ludevid,* CSIC, Spain*; E. Giralt,* University of Barcelona, Spain

Lipid bilayers have been widely studied on account of their biological interest regarding cell characterization, membrane protein transport, etc. In the last recent years many studies have been focused on the study of such membranes using Atomic Force Microscopy, since it gives chemical and topographic information in the nanometer scale. Some of these studies dealt with lipid deposition on flat substrates such as mica, silica or graphite either in the form of Langmuir-Blodget films or after bilayer self-assembling. Some of these lipid surfaces have been used to support proteins in order to study lipid-protein interaction or to test new drugs. Most of these studies used synthetized bilayers for the a priori sake of reproducibility and simplicity in their chemical composition. In these work we present novel results concerning the study of a natural plant bilayer membrane formation under physiological conditions. By using force spectroscopy we demonstrate that solution ionic strength is crucial in the self-assembling process and that small variations in ionic strength give rise to huge variations in bilayer compactness. There is a threshold ionic strength under which bilayers are not self-assembled, connected with the charge repulsion between the hydrophilic charged heads of the molecule. As the ionic strength is increased the charge repulsion seems screened out and the assembling process achieved, and this is reflected in a discrete jump in the force plot. The force at which this break takes place (the so-called yield point) is highly influenced by the own magnitude of the ionic strength, and ranges from ~ 1.5 nN at 10 mM to ~ 9 nN at 1 M. A nanomechanical study concerning the elasticity of the bilayer, as well as an evaluation of the forces that take place (double layer, hydration forces, Van der Waals, etc.) is also included.

Organic Films and Devices
Room 318/319 - Session OF+NS-WeM

Molecular Electronics

Moderator: D. Cahen, Weizmann Institute of Science, Israel

8:20am **OF+NS-WeM1 Electronics and Mechanics with Single Molecules***, **P.L. McEuen,*** Cornell University **INVITED**

It is now possible to make electronic and mechanical devices where an individual molecule is the active element. Examples include devices made from single-walled carbon nanotubes or single organic molecules. These molecular devices are proving to be wonderful systems for the study of the physics of materials at the nanometer scale. In this talk, I will review recent progress within our group on the electrical, electromechanical, and electrochemical properties of individual nanotubes and single molecules, as inferred from both transport and scanned probe measurements.

9:00am **OF+NS-WeM3 Understanding Charge Transport in Molelcular Electronics***, **J.G. Kushmerick**, R. Shashidhar,* Naval Research Laboratory

We use an experimentally simple crossed-wire tunnel junction to interrogate how factors such as metal-molecule coupling, molecular structure and the choice of metal electrode influence the current-voltage characteristics of a molecular junction. Results on junctions with symmetric and asymmetric metal-molecule contacts demonstrate that a specific molecular core can act either as a molecular wire or a molecular rectifier depending on its coupling to the metal electrodes. By tuning the coupling at the two metal-molecule interfaces-through the use of different attachment chemistries and metal electrodes-we are able to control the extent of current rectification. Experimental measurements and theoretical calculations demonstrate that the conductance of a molecular wire can be directly related to how well it's @pi@-conjugated backbone mimics an ideal one-dimensional metal. Finally, we will show that the conductance of a molecular junction scales with the number of molecules contacted, and that the @pi@-systems of molecular wires connected in parallel are not strongly coupled. Initial results demonstrating the utility of in situ vibrational spectroscopy to characterize the molecular junction will also be presented.

9:20am **OF+NS-WeM4 Observation of Negative Differential Resistance Measured through Individual Molecules on Silicon at Room Temperature***, **N.P. Guisinger**, R. Basu, A.S. Baluch, M.C. Hersam,* Northwestern University

In recent years, substantial progress has been made in the emerging field of molecular electronics. In particular, metal-molecule-metal junctions have been widely studied. In this paper, charge transport through molecule-semiconductor junctions is considered. The presence of the energy band gap in semiconductors provides opportunities for resonant tunneling through individual molecules, leading to interesting effects such as negative differential resistance (NDR). The ultra-high vacuum (UHV) scanning tunneling microscope (STM) allows individual molecules to be imaged, addressed, and manipulated on semiconducting surfaces with atomic resolution at room temperature. This paper considers two distinct chemistries on the Si(100) surface. Styrene reacts with Si(100) via a covalent silicon-carbon bond. On degenerately n-type Si(100), STM current-voltage characteristics on individual styrene molecules show clear NDR at negative sample biases of approximately -2.5 V and -4 V. However, at positive sample bias, the styrene is liberated from the surface via inelastic electron stimulated desorption (ESD). In an effort to minimize perturbation via ESD, individual 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) molecules were bound to degenerately n-type Si(100). The exceptional stability of the silicon-oxygen bond allows charge transport measurements on TEMPO at high biases up to ±5 volts without ESD. Similar to styrene, NDR is clearly observable at negative sample biases of approximately -3 V, -4 V, and -4.5 V. These effects will be explained by considering the energy band diagram of the semiconductor-molecule junction.

9:40am **OF+NS-WeM5 Molecular Materials and Devices***, **C.R. Kagan**, A. Afzali, R. Martel, P.M. Solomon, L.M. Gignac, A.G. Schrott, B. Ek, C. Lin,* IBM T.J. Watson Research Center **INVITED**

Efforts to fabricate devices based on active molecular components have been driven by both the fundamental interest in using chemistry to build function at the molecular level and the looming technological expectation of the end of Moore's law. In this talk, we describe the directed assembly of organic and metal-metal bonded supramolecular systems that are interesting materials for potential electronic and memory device applications. Molecules are chosen with head groups that bind to metal or oxide surfaces and tail groups that bind to metal electrodes or that template the growth of the particular molecular system. Optical spectroscopy, atomic force and scanning tunneling microscopy, electrochemistry, and electrical measurements are used to characterize the chemistry and physics of molecular assemblies and the behavior of devices. Self-assembled organic monolayers are used to fabricate reported field-effect transistor structures and to elucidate the important requirements necessary to successfully design two- and three-terminal molecular devices. We demonstrate the layer-by-layer assembly of metal-metal bonded supramolecules and utilize this approach to fabricate molecular devices.

10:20am **OF+NS-WeM7 Mediating Electronic Switching of Single Molecules Using Chemical Interactions***, **P.A. Lewis,*** The Pennsylvania State University*; C.E. Inman,* University of Oregon*; J.M. Tour,* Rice University*; J.E. Hutchison,* University of Oregon*; P.S. Weiss,* The Pennsylvania State University

We have studied conjugated phenylene-ethynylene oligomers inserted into amide-containing alkanethiolate self-assembled monolayers using scanning tunneling microscopy in order to determine their physical and electronic properties when surrounded by a hydrogen-bonded matrix. The phenylene-ethynylene oligomers show stability in two conductance states, an ON and an OFF state. We observe fewer switching events between the ON and OFF states than previously reported for n-alkanethiolate matrices and attribute this to the rigidity due to the hydrogen bonds of the amide groups in the matrix. Furthermore, we demonstrate bias-dependent switching as a result of hydrogen bonding between the substituents of the inserted oligophenylene-ethynylene and the matrix molecules. We demonstrate that the chemical and physical environment of proposed molecular devices is crucial to their function and can be exploited to impart tunable electronic properties.

10:40am **OF+NS-WeM8 Two-Photon Photoemission Studies of Molecular Affinity Levels in Oligo-Phenylene Ethynylene Self-Assembled Monolayers***, **C. Zangmeister**, S.W. Robey, R.D. van Zee,* National Institute of Standards and Technology

Two-photon photoemission has been used to study unoccupied electronic levels for a family of thiolated oligiomeric phenylene-ethynylene self-assembled monolayers. Self-assembled monolayers of a three phenyl ring oligomer (OPE) and the same oligomer with a nitro group substituted for one hydrogen on the center ring (NO@sub2@-OPE) were formed on polycrystalline Au/Si substrates as well as [111] oriented Au on mica. This class of compounds has received attention because of measured conduction characteristics and the reported negative-differential resistance behavior of these compounds in nanometer-sized pore structures. Single-color, two photon photoelectron spectroscopy measurements were performed in the ultraviolet using frequency-doubled, subpicosecond pulses from a Ti:Sapphire-pumped optical parametric amplifier. For the OPE monolayers we have, based on the excitation energy dependence, identified an unoccupied level ca. 1 eV above the vacuum level. Using previous two-photon photoemission and inverse photoemission of condensed benzene layers as a guide we tentatively identify this as the remnant of the e@sub2u@ unoccupied level for benzene localized on the carbon atoms of the phenyl ring. Results of studies on NO@sub2@-OPE layers will also be discussed.

Plasma Science and Technology
Room 314 - Session PS1-WeM

Plasma Processing of Nanostructures and Nanomaterials

Moderator: S. Samukawa, Tohoku University, Japan

8:20am **PS1-WeM1 The Study of Plasma Etching Limits Using Nanometer-Scale Self-Assembled Arrays***, **Y. Zhang**, T.J. Dalton,* IBM

Fine patterning of semiconductor nano-scale features at the sub-20nm region is a challenging task. Among the nanometer scale features of importance in microelectronics and bio-microelectronics applications are: (1) open standing nano-features, i.e., a Si gate, and (2) small nano holes, i.e., an array of vias with nanometer scale diameter. The rapid shrinking of conventional CMOS technology is quickly approaching a perceived scalability limit or "brick wall". Plasma etching of true nanometer scale features may also face its limits. For open standing nano-features, the main challenge (or soft limits) is CD control, e.g., line edge roughness (LER) control of sub-10nm Si gate lines. A LER tolerance of 10% for 10nm gates means controlling 1nm, which has about 1 layer of silicon atoms on each side of gates. For true nanometer scale via arrays, the diameter of the vias for sub-10nm sizes is approaching the sizes of reactive products, e.g., SiBr4, SiF4, and SiCl4. In this case, plasma etching may hit its ultimate limits ("hard" limits). In this study, self-assembled nanometer scale diblock copolymer arrays were used to generate large scale (across 200 mm wafers) sub-20 nanometer test structures. The nanometer hole arrays were used to tested plasma etching characteristics of different materials, i.e., silicon, silicon dioxide, and silicon nitride with different plasma chemistries, from fluorine, chlorine, to bromine to vary the sizes of reactive species, F, Cl, to Br, and etching byproducts, such as SiF4, SiCl4, to SiBr4, with the aim of finding the plasma etching limits. In this paper, we present our recent work on the challenges of pattering nano-features, e.g., decreasing patterning layer thickness, aspect ratio dependent etch (ARDE), selectivity, and limits for sub-10 nm scale holes. Underlying principle of the different etching chemistry and processing parameters and their advantage and drawback to etch nanometer scale features will be also discussed.

8:40am **PS1-WeM2 Insights into Nanoparticle Formation Processes in a Thermal Plasma Process***, **C.R. Perrey**, C.B. Carter, T. Renault, A. Gidwani, R. Mukherjee, X. Wang, J. Hafiz, W.M. Mook, W.W. Gerberich, P.H. McMurry, J.V.R. Heberlein, S. Girshick,* University of Minnesota

As nanoscale metal and ceramic particles are increasingly considered for industrial applications, a fundamental understanding of the effects of processing on particle morphology is required. The size, shape, structure, chemistry, and resulting properties of nanoparticles are all potentially functions of the formation method. This study examines the structure and chemistry of both nanoparticle films and individual nanoparticles produced by hypersonic particle plasma deposition. The process utilizes a thermal plasma to generate nanoparticles which are then rapidly assembled to form nanostructured films; the mechanical properties of both the particles and the films appear to differ significantly from the bulk material of the same composition. Observations made by electron microscopy are used to analyze the materials at each stage of the process. The presence of nanoparticles with atomically flat planar defects and a spherical shape imply a rapid condensation and crystallization from the gas phase. This paper will illustrate studies involving the production of Si, SiC, and Ti nanoparticles and nanostructured films, allowing comparisons for the different materials.

9:00am **PS1-WeM3 Reactive Gas Condensation of Aluminum Nitride Nanoparticles***, **C. Baker**, A. Ceylan, S.I. Shah,* University of Delaware

AlN nanoparticles were synthesized using Reactive Gas Condensation (RGC) technique in which a gas mixture of NH3 and N2 was used for the nitridation of aluminum vapors that were obtained by resistive evaporation of Al wire. NH3 served as the reactive gas while N2 served as both a carrier gas and a source for particle condensation. The process was carried out at a pressure range of 50 - 100 Torr in order to facilitate the condensation. X-ray diffraction (XRD) and X-ray photoelectron (XPS) analysis revealed that the samples deposited with more than 10% NH3 in N2 were composed entirely of hexagonal AlN nanoparticles. The particles were single crystal, as determined by electron diffraction in transmission electron microscopy. The particle size was controlled by varying the pressure of the gas mixture for high relative concentrations of NH3. AlN nanoparticles were dispersed in various liquids to enhance the fluid thermal conductivity. Results will be presented to show that the thermal conductivity of the liquid was considerably increased with the addition of minimal amount of AlN nanoparticles.

9:20am **PS1-WeM4 Properties of Carbon-based Nanofibers Grown by Low-pressure Plasma Enhanced Chemical Vapor Deposition***, **J.B.O. Caughman**, L. Zhang, D.W. Austin, M.A. Guillorn, A.V. Melechko, V.I. Merkulov,* Oak Ridge National Laboratory

The role of the plasma in the growth of carbon-based nanofibers is being determined by related plasma conditions to the physical and electrical properties of the nanofibers. Forests of nanofibers, as well as single isolated nanofibers have been grown using an inductively coupled plasma source operated from 50 to 200 mTorr. The plasma is composed of hydrogen and either acetylene or methane as the carbon source, with the addition of diborane and/or nitrogen to modify the composition of the nanofibers. The plasma conditions are determined by using mass spectroscopy and optical emission spectroscopy. The electrical properties of the nanofibers are found by using a four-point probe method, where electrodes are deposited on individual nanofibers. Processing results show that acetylene utilization increases with input power and reaches values of 70 to 80 percent as the discharge transitions to the inductively coupled regime, which results in well-formed cylindrical nanofibers. Excessive carbon in the plasma results in an increase in amorphous carbon deposition on the nanofiber sidewalls. Substrate bias plays an important role in controlling the physical etching component during deposition, where a transition is made from an amorphous thin film to a cylindrical nanofiber to a damaged structure as the bias increases. The electrical characteristics of the nanofibers grown with the low pressure method are compared to those grown with a conventional DC plasma-based method, where the resistivity has been found to be nearly the same as polycrystalline graphite. Details of the effect of plasma properties and the effect of nitrogen and boron addition on the electrical/physical properties of the nanofibers will be presented.

9:40am **PS1-WeM5 Growth of Vertically Aligned Carbon Nanotubes Using a High Density Plasma CVD Process***, **H.W. Wei**,* National Tsing Hua University, ROC*; K.C. Leou,* National Tsing Hua University, ROC, R.O.C*; M.T. Wei, K.J. Shen, C.H. Tsai, C. Lin,* National Tsing Hua University, ROC

Vertically aligned multiwall carbon nanotubes are grown on silicon substrates with Ni catalyst patterns using an inductively-coupled high density plasma chemical vapor deposition reactor. The plasma is produced by 13.56 MHz RF power and a feed gas of C@sub 2@H@sub 2@ and H@sub 2@ mixture at a pressure below 100 mtorr. A heated and DC biased subtrate stage is employed to allow low temperature and aligned growth of CNTs. Due to low pressure operation, the growth rate of the CNTs is relative low (50-200 nm/min.) while the diameter of the tubes ranges from 30 nm to 120 nm depending on growth conditions. Another feature of the patterned and aligned growth of the CNTs using this HDP-CVD process is that the density of CNTs is relatively low (10@super 8@ to 10@super 9@ 1/cm@super 2@) although the CNTs are directly grown on 5 µm x 5 µm catalyst patterns. This will result in a reduction of the shielding effect of electric field for field emission appication of the CNTs. Results from parametric study of CNTs properties based on Raman spectroscopy, TEM and field emission measurements with process conditions as well as measurements from a mass spectrometer and plasma emission actinometry (for H atom) will be presented. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

10:00am **PS1-WeM6 Correlation between Size of Clusters and Qualities of a-Si:H Films for SiH@sub 4@ High Frequency Discharges***, **K. Koga**, N. Kaguchi, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Previously, we have shown that a reduction of amount of particles below 10 nm in size (clusters) formed in SiH@sub 4@ high frequency discharges is the key to deposit hydrogenated amorphous silicon (a-Si:H) films of extremely small microstructure parameter R@alpha@ < 0.01. In this work, we have studied correlation between cluster size and a-Si:H film qualities by using the cluster suppressed plasma CVD method@footnote 1@ together with newly developed downstream cluster collection (DCC) method. The following results have been obtained in our experiment: 1) the DCC method offers a quite high sensitivity deduction of size and density of clusters above 1 nm in size and 10@super 4@ cm@super -3@ in the reactor; 2) An initial fill factor (FF@sub i@) of a n@super +@Si/a-Si:H/Ni Schottky solar cell gradually increases from 0.46 for mean cluster size d@sub c@= 9.0 nm to 0.48 for d@sub c@= 3.7 nm and significantly increases to 0.53 for d@sub c@= 1.6 nm. 3) The FF@sub i@ value increases with decreasing volume fraction of clusters. Experiments for studing correlation between amount of clusters of sub nm in size and film qualities is underway. @FootnoteText@ @footnote 1@M. Shiratani, K. Koga, M. Kai, and Y. Watanabe, Thin Solid Films 427, 1(2003).

10:20am **PS1-WeM7 Study of Plasma-Nanoporous Silica Surface Interactions in Fluorocarbon and O@sub2@ Discharges: Comparison with SiO@sub 2@ and Organosilicate Glass***, **X. Hua**, G.S. Oehrlein, R.M. Briber,* University of Maryland, College Park*; P. Lazzeri, N. Coghe, M. Anderle,* Center for Scientific and Technological Research, Italy

We have investigated plasma surface interactions of nanoporous silica (NPS) films with porosities of up to 50%, SiO@sub 2@ and organosilicate films in either C@sub 4@F@sub 8@/Ar discharges (used for plasma etching) or O@sub 2@ plasmas (used for resist mask removal). Surfaces of the various materials after the above plasma processes were studied by x-ray photoemission spectroscopy as a function of process conditions. In addition, time-of-flight secondary ion mass spectrometry (in static or dynamic mode) was used to obtain additional information on the compounds formed on the surfaces of these materials, or on variations of elemental densities as a function of depth. The plasma-surface interactions of NPS are strongly modified relative to conventional SiO@sub 2@ or OSG. Several depth scales of these alterations exist: The surface and near-surface region (down to ~10 nm), intermediate depth (~50 nm), and the complete NPS film thickness to the interface with the substrate. In the surface/near-surface region the porosity of the NPS material increases the plasma-surface interaction area, which during fluorocarbon etching leads to differences in surface fluorocarbon film coverage for NPS relative to SiO@sub 2@ and associated changes in etching behavior. The larger depth scales are especially relevant for O@sub 2@ cleaning which strongly decreases the residual carbon content of both OSG and NPS down to intermediate depths and for NPS materials of 30% and 50% porosity produces deep penetration of fluorine down to the substrate-interface.

10:40am **PS1-WeM8 High Flux and Low Energy Neutral Beam Formation Using a Low Angle Forward Reflected Neutral Beam System***, **D.H. Lee**, S.J. Jung,* Sungkyunkwan University, South Korea*; K.H. Baek,* Samsung Electronics, South Korea*; C.J. Kang,* Samsung Electronics, South Korea, Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon-based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particle such as positive ion and photons generated in the plasma. Charge-induced damage during the plasma etching is one of the serious problems that have to be solved for the deep submicron semiconductor devices as well as future nanoscale devices. To avoid the charge-related damage, several low-damage processes have been proposed and one of the techniques to avoid the problem is to use neutral beam etching. Among the techniques fabricating a neutral beam, a low angle reflection of the ion beam where ions extracted from the ion source are neutralized by a low angle reflection during the reflection has been investigated in this study. Previous studies showed that, by the reflection of the ion beam at 5 degree angle of incidence, most all of the ions could be neutralized and nearly vertical SiO2 etching could be obtained for various fluorine based gases. In this study, for the formation of high flux and low energy neutral beam, a modified neutral beam source was proposed, and Si and SiO2 etch properties such as etch rate, etch selectivity, and etch profiles with fluorine-based gases using this system have been investigated. Also, the surface damage of the etched Si surface was investigated using TEM.

Plasma Science and Technology
Room 315 - Session PS2-WeM

Etching Difficult Materials

Moderator: C.B. Labelle, Advanced Micro Devices

8:20am **PS2-WeM1 Ion-enhanced Etching of High-k Dielectric Films with Mass-analyzed Ion Beam Irradiation***, **K. Karahashi,** N. Yamagishi,* MIRAI-ASET, Japan*; T. Horikawa,* MIRAI-ASRC/AIST, Japan*; A. Toriumi,* MIRAI-ASRC/AIST and University of Tokyo, Japan

As advanced high-k gate dielectrics are being developed to replace SiO@sub2@ in future generations of microelectronics devices, understanding their etch characteristics becomes vital for introducing the materials into the manufacturing process. We report on the interactions of high-k dielectrics, such as HfO@sub2@, Al@sub2@O@sub3@, with ionic species contained in plasma etching environments. To clarify the ion induced reactions in the fluorocarbon plasma, we employed the mass-analyzed ion beam apparatus that can irradiate a single ionic species to sample surfaces under an ultra-high vacuum condition. CF@sub3@@super+@, ion is found to chemically etch HfO@sub2@ and Al@sub2@O@sub3@ films, and the etch yield scaled linearly with the square root of ion energy with a threshold energy between 20 - 40 eV. This indicates that the etching reaction is limited by the momentum transfer to the etched film. Etching yields decreased monotonically with decreasing fluorine atoms contained in incident fluorocarbon ions (CF@subX@@super+@, X=1-3). In the case of CF@super+@, ion irradiation, the etching stopped after slightly etching HfO@sub2@ films. Then an amorphous fluorinated carbon (a-C:F) film was continuously deposited on the HfO@sub2@ surface. Using x-ray photoelectron spectroscopy analysis, it was confirmed that carbon accumulates on the surface at the early stage as CF@super+@ ion dose increases, so that the transition to the a-C:F deposition is caused by surface modification with CF@super+@ ion irradiation. This work was supported by NEDO.

8:40am **PS2-WeM2 Etching Characteristics of High-k Dielectric HfO@sub 2@ Films in Inductively Coupled Fluorine-Containing Plasmas***, **K. Takahashi**, K. Ono, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. Regarding gate dielectrics, the technological challenge continues for growing ultrathin SiO@sub 2@ films of high quality; however, the ultimate solution relies on high dielectric constant (k) materials. In integrating high-k materials into device fabrication, an understanding of the etching characteristics of the materials is required for their removal and for contact etching. This paper presents the etch rates and possible etch mechanisms for HfO@sub 2@ thin films on Si substrate in inductively coupled plasmas containing mixtures of CF@sub 4@/Ar, C@sub 4@F@sub 8@/Ar, or SF@sub 6@/Ar, as a function of gas composition, rf bias power, and surface temperature. The discharge was established at a gas pressure of 20 mTorr and an rf source power of 300 W. As the concentration of F-containing gases was decreased, the etch rate of Si decreased owing to the decreased amount of F radicals, while the etch rate of HfO@sub 2@ remained almost unchanged, resulting in an increase in etch selectivity of HfO@sub 2@ over Si. Increasing the bias power increased the etch rates of both Si and HfO@sub 2@; however, the increase in etch rate was more significant for HfO@sub 2@ than for Si, also resulting in an increase in selectivity. These results imply that the etching of HfO@sub 2@ relies primarily on the sputtering by ion bombardment, and the etch rates were typically on the order of 20 nm/min with a selectivity > 1 at large Ar concentrations and high bias powers. A comparison is made with the results of plasma and surface diagnostics, to gain a better understanding of the physics and chemistry underlying the processing, and to achieve higher selectivities. @FootnoteText@ This wark was supported by NEDO/MIRAI Project.

9:00am **PS2-WeM3 Plasma Etching of High Dielectric Constant Materials on Silicon***, **L. Sha**, D.L. Ramirez, J.P. Chang,* University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as ZrO@sub 2@ and HfO@sub 2@, to enable their integration in sub-100 nm complementary metal oxide semiconductor (CMOS) devices. In the paper we discuss the study of the reaction kinetics of etching ZrO@sub 2@ and HfO@sub 2@ in chlorine and boron trichloride chemistry in an Electron Cyclotron Resonance (ECR) high-density plasma reactor. The BCl@sub 3@/Cl@sub 2@ plasma was characterized by Langmuir probe, optical emission spectroscopy (OES), and quadrupole mass spectroscopy (QMS). The etch rate of ZrO@sub 2@ and HfO@sub 2@ were determined to scale linearly with the square root of ion energy in Cl@sub 2@ plasma, indicating that the etching reactions are limited by the momentum transfer to the etched film. The etching products in Cl@sub 2@ plasma were determined to be highly chlorinated metal chlorides and chlorine oxides. The relative abundances of metal tetrachlorides were increased at higher ion energy due to the enhanced surface chlorination. Addition of BCl@sub 3@ reduced the ion densities, but significant enhanced the metal oxides etch rate, due to the enhanced removal of oxygen. Silicon etch rate was suppressed with formation of the passivation layer of B-Si, resulting in the improved metal oxide etching selectivity with respect to silicon. The etching threshold energy for ZrO@sub 2@ and Si in BCl@sub 3@ were determined to be 21 eV and 28 eV, respectively, providing a range of operating conditions with very high etching selectivity. Increasing the electron temperature and ion density in BCl@sub 3@ plasma could further increase the etching selectivity. Under the same operating conditions, the HfO@sub 2@ etch rate is lower than ZrO@sub 2@ etch rate, due to the stronger Hf-O bonds.

9:20am **PS2-WeM4 Investigation of Etching Properties of Hafnium Oxide Based High-K Materials Using Inductively Coupled Plasma***, **J. Chen,*** National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; S.H.D. Chan,* National University of Singapore

The HfO-based high dielectric constant (K) materials are being investigated as the most promising candidates to replace the conventional SiO-based dielectrics for CMOS device applications. Development of etching processes for these materials is challenging since their etch products are mostly non-volatile and therefore adversely affect device properties due to difficulties to control effective gate length and to reduce contact resistance and Si over-consumption. In this work, we investigated etching properties of HfO@sub 2@, HfO@sub x@N@sub y@, HfSi@sub x@O@sub y@, HfAl@sub x@O@sub y@ deposited by CVD and PVD, using ICP of Cl@sub 2@/HBr/CF@sub 4@/O@sub 2@. The results showed that the etch rates of the HfO-based high-K materials were only ~ 100Å/min in CF@sub 4@ plasmas but increased up to 1000Å/min in Cl@sub 2@/HBr plasmas. The etch rates increased rapidly with increasing inductive power, rf bias power, and/or the amount of Cl@sub 2@. It was interesting to find out that in Cl@sub 2@ plasmas, etch rates varied differently depending on the chemical components added to HfO. That is, etch rates increased with the addition of Si or N, but decreased with the addition of Al. The XPS analysis showed that, a significant amount of fluorides (F: 10%~16%) existed on surfaces of all the HfO-based materials after CF@sub 4@ plasma etching, whereas amounts of chloride and bromide were little (Cl: 1.0%~2.2% and Br: 0.6%~1.7%) after Cl@sub 2@/HBr plasma etching. We suggest that non-volatile etch products from the CF4 plasmas are responsible for the low etch rates, whereas more volatile etch products from Cl@sub 2@/HBr plasmas result in higher etch rates. Analyzing the etch rates and XPS results for various concentrations of O in the HfO-based materials, we also found that low-reactivity of the Hf-O bonds and low-volatility of etch by-products from HfO-based materials could be responsible for the low etch rates.

9:40am **PS2-WeM5 Selective Dry Etching of SrBi@sub 2@Ta@sub 2@O@sub 9@/CeO@sub 2@ in the High Density Inductively Coupled Plasma Reactive Ion Etching***, **S.I. Shim**,* Korea University*; Y.S. Kwon, S.I. Kim,* Korea Institute of Science and Technology*; Y.T. Kim,* Korea Institute of Science and Technology, Korea*; J.H. Park,* Korea University

The dry etching and etch stop of the ferroelectric film on the silicon surface without damage is the key process of the self-aligned gate structure for the fabrication of Single Transistor Type Ferroelectric Memory. The high vertical etching angle is also necessary for the high integration. In this paper, etching characteristics and selective dry etchings of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) film and CeO@sub 2@ film which is used for the buffer layer to improve the interface between SBT and silicon surface by using the Inductively Coupled Plasma Reactive Ion Etching (ICP-RIE) system with various Ar/Cl@sub 2@ gas mixtures were reported. The highest etching selectivity of SBT/CeO@sub 2@ was 6.8 and the vertical angle of SBT was 82°. The samples for etch were prepared by depositing CeO2 films with the thickness of 200 Å on Silicon substrates using rf sputtering of a Ce target in the reactive oxygen ambient. The SBT films with the thickness of 3000 Å were prepared on the CeO@sub 2@ film and Si substrate by MOD method. The capacitor-voltage (C-V) measurement shows there was no degradation of the ferroelectric characteristics after dry etching process. The SEM images and XPS data proved the etch stop was achieved successfully. For further investigation, N+/P diode junction and the metal ferroelectric insulator semiconductor filed effect transistor (MFISFET) with Pt/SBT/CeO@sub 2@/Si gate structure were fabricated.

The I-V characteristics of the N+/p junctions and the drain current-drain voltage (I@sub D@-V@sub D@) and drain current-gate voltage (I@sub D@-V@sub G@) characteristics of the fabricated MFISFET show the etch stop process by using ICP-RIE system was successfully achieved without damage of silicon surface and degradation of ferroelectric characteristics.

10:00am **PS2-WeM6 High Rate Etching of SiC in Ultrahigh Density Plasmas Excited by Electron Cyclotron Resonance***, **K. Nakamura**, M. Tuda, M. Taki, K. Shintani, H. Sumitani,* Mitsubishi Electric Corporation, Japan

Silicone carbide (SiC) is a promising substrate material for advanced high power devices, high frequency devices, and microelectoromechanical systems, because of good electrical, mechanical, and chemical properties. Fabrication for these devices, deep etching of SiC with a high rate and high selectivity to mask material is required. Etching of SiC is known to be difficult since its bonding energy is relatively larger than those for conventional Si and GaAs. Recently, fast SiC etching with an etch rate of ~1 µm/min has been reported,@footnote 1,2@ where high density ICP and Helicon Plasma sources were used. However, a much higher etch rate is needed for the bulk micromachining (typically, etched depth >100 µm) of SiC substrates. In this study, we have developed fast SiC etching processes using a ultrahigh density plasma source excited by electron cyclotron resonance (ECR); the plasma density measured for Ar was 10@super 12@-10@super 13@ cm@super -3@, and the ion current density onto a substrate stage was more than 100 mA/cm@super 2@. Etching of 4H-SiC was performed in SF@sub 6@/O@sub 2@ plasmas by varying gas pressure, flow rate, O@sub 2@ concentration, microwave power, and rf-bias power. With increasing microwave and rf-bias powers, the SiC etch rate increased up to ~8 µm/min. A high etch rate (>5 µm/min) and selectivity (>50 to Ni) was simultaneously obtained under optimized conditions. These results show that ultrahigh density ECR plasmas are desirable for SiC bulk micromachining. @FootnoteText@ @footnote 1@ F. A. Khan and I. Adesida, Appl. Phys. Lett. vol.75 2268 (1999)@footnote 2@ P. Chabert, N. Proust, J. Perrin, and R. W. Boswell, Appl. Phys. Lett. vol.76 2310(2000) .

10:20am **PS2-WeM7 Chemical Mechanisms of Metal Etching in High Density Plasmas***, **A.S. Orland**, R. Blumenthal,* Auburn University

Metals are found at the heart of many important current and developing device technologies, such as GMR read heads, MRAM and FeRAM. As the scale of these devices continues to be reduced, high performance etch technologies will become a necessary component of the fabrication of these devices. The chemical mechanisms of high-density plasma etching of Fe, Ni, Co and their alloys will be presented for a range of etch chemistries based upon CO@sub 2@/NH@sub 3@ etching and a new etch chemistry based on CO@sub 2@/H@sub 2@ gas mixtures. The chemical mechanisms of etching have been determined from measurements of the variation of chemical composition as a function of plasma conditions, using supersonic pulse, plasma sampling mass spectrometry. Finally, the mechanism of etching will be compared with the mechanisms of CO/NH@sub 3@ and CO/H@sub 2@ etching which have been previously shown to etch by the formation of volatile metal formates and metal acetates through a plasma-surface reaction. All of these etching chemistries are plagued by carbide deposition at high concentrations of CO@sub 2@ or CO, and an explanation of the deposition mechanism will be given as well.

10:40am **PS2-WeM8 Low Energy Electron Enhanced Etching (LE4) of HgCdTe and III-V Semiconductor Materials***, **J. Kim**, T.S. Koga, C. Miclaus, H.P. Gillis, M.S. Goorsky,* University of California, Los Angeles*; G.A. Garwood, D.R. Rhiger, S.M. Johnson,* Raytheon Infrared Operations

The high energy ion bombardment involved in the reactive ion etching (RIE) process creates damage sites in the HgCdTe material which cause type conversion, among other problems. The ion energy can be reduced by using electron cyclotron resonance (ECR) plasma etching; however, the etched surfaces are not reliably stoichiometric or smooth. We have been exploring a new dry etching technique called low energy electron enhanced etching (LE4) to achieve low-damage, smooth, stoichiometric etched surfaces with high-resolution pattern transfer.@footnote 1@ In the LE4 process, electrons at energies 1-15 eV and reactive species at thermal velocities arrive at the surface. The LE4 technique, because it completely eliminates ion bombardment and relies on low energy electrons to control the etching chemistry, holds promise for eliminating the damage while retaining the beneficial features of RIE. LE4 experiments were performed on non-patterned, or photoresist (PR) mesa patterned Hg1-xCdxTe (x~0.3) epitaxial layers grown by molecular beam epitaxy (MBE) on (211)-oriented Cd1-yZnyTe substrate or (211)-oriented CdTe/Si substrate. In LE4 of HgCdTe, the sample was placed between the cathode and anode in a dc plasma. Dc bias was applied to the backside of the sample to control the electron current density to the surface. A mixture of Ar-CH4-H2-N2 (AMHN) was used as the etching gas. We will summarize results from mechanistic study to optimize etch condition, and demonstrate how electron energy, CH4 concentration, and sample temperature influence the etch rate, surface stoichiometry, and surface roughness. In addition, we will show some results of our AMHN LE4 process for III-V semiconductor materials (GaAs and InP). @FootnoteText@ @footnote 1@ J. Kim, T.S. Koga, H.P. Gillis, M.S. Goorsky, G.A. Garwood, J.B. Varesi, D.R. Rhiger, and S.M. Johnson, Extended Abstracts the 2002 U.S. Workshop on Physics and Chemistry of II-VI Materials 173 (2002).

Surface Science
Room 328 - Session SS1-WeM

Adsorption on Semiconductor Surfaces

Moderator: E.D. Williams, University of Maryland at College Park

8:20am **SS1-WeM1 H Transfer and Ge/Si Site Exchange during Germane Adsorption at Si(001)***, **T. Murata**, M. Suemitsu,* Tohoku University, Japan

Germane adsorption at Si(001) is important as an initial elementary step for Ge/Si heteroepitaxy. It also provides an ideal platform to investigate Ge adsorption at Si sites, one of the elementary processes in SiGe epitaxy. Little is known, however, on its details. Among the remaining issues are whether H atoms from germane are transferred to Si atoms or they stay intact at Ge sites and whether a site exchange occurs between Si and Ge during adsorption. To tackle these problems, we have combined TPD and multiple-internal-reflection FTIR, and have investigated the Si(001) surface adsorbed with germane at room temperature. These two methods form a complementary pair since TPD backs up the quantitative aspect of the characterization while FTIR is most powerful in state-resolved analysis. The findings we present here are (1) that almost all the H atoms are transferred from germane to Si atoms and (2) that the site exchange does occur between Si and Ge even at room temperature. The finding (1) is supported by exhaustive dominance of both the SiH-related @beta@@sub 1@ desorption peak in TPD and the SiH-related stretching band in FTIR. Persistence of these SiH-related signatures up to ~1ML of hydrogen coverage is hardly understood without considering a site exchange between substrate Si and adsorbed Ge atoms, leading us to the conclusion (2). Recent ab-initio calculations suggest that the two findings originate from a single event: adatom diffusion. According to Jeong and Oshiyama,@footnote 1,2@ Si adatom diffusion on Si(001):H surface proceeds via release of the H atom from the adatom to a substrate Si atom, site exchange between the adatom and another substrate Si atom, and capture of the H atom by a "new" adatom. The larger Si-H bonding energy in excess of 30 meV/atom than that of Ge-H may stabilize the Si-H/Ge state once formed. @FootnoteText@ @footnote 1@ Jeong and Oshiyama: Phys. Rev. B58(1998)12958.@footnote 2@ Jeong and Oshiyama: Surface Science 436(1999)L666.

8:40am **SS1-WeM2 Surface Interaction of SiH@sub 3@ Radicals with Amorphous Silicon: Temperature Dependence of the SiH@sub 3@ Surface Reactivity and the Surface Hydride Composition***, **W.M.M. Kessels**, J.P.M. Hoefnagels, P.J. Van den Oever, Y. Barrell, A.H.M. Smets, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The growth of hydrogenated amorphous silicon (a-Si:H) thin films from SiH@sub 4@ plasmas is expected to be dominated by SiH@sub 3@ radicals created in the plasma. To obtain insight into the surface reactions of SiH@sub 3@ on the a-Si:H surface, the surface reaction probability of SiH@sub 3@ has been determined by time-resolved cavity ringdown spectroscopy. The experiments have been carried out under nearly pure SiH@sub 3@ conditions for substrate temperatures between 50-450 °C. It has been found that the surface reaction probability of SiH@sub 3@ is 0.30±0.03 independent of the substrate temperature. Information about the chemical state of the a-Si:H surface in terms of surface silicon hydrides has been determined by in situ attenuated total reflection infrared spectroscopy combined with Ar-ion induced desorption experiments. These experiments - carried out in the same temperature range - have revealed that the a-Si:H surface composition changes drastically with increasing substrate temperature from a -SiH@sub 3@ covered surface at low temperatures to a -SiH@sub 2@ and a -SiH covered surface at higher temperatures. From the combination of the experimental results and ab initio calculations and molecular dynamics simulations in the literature, it is concluded that a-Si:H film growth takes place by a two-step reaction mechanism of SiH@sub 3@ in which H abstraction from the surface by

SiH@sub 3@ in an Eley-Rideal reaction is the rate-limiting step. This abstraction reaction, which requires nearly zero activation energy, is unaffected by the changing surface silicon-hydride composition and leads to temperature independent growth site creation. SiH@sub 3@ radicals can subsequently stick on the dangling bonds created. Furthermore, some preliminary ideas on an (associated) surface diffusion mechanism will be discussed on the basis of the surface roughness evolution of a-Si:H at different temperatures.

9:00am **SS1-WeM3 Interface Structure of an Ultrathin SiO@sub 2@ Film Fabricated by Ozone on Si(100)***, **K. Nakamura**, S. Ichimura,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Highly concentrated ozone gas is one of the alternative oxidants to fabricate an ultrathin silicon oxide film at low temperature for the microelectronics technology. Our previous study using an HF etching rate of oxide films has implied that, in contrast to a thermally grown oxide film, the thickness of structural transition layers of an ozone-oxide film is so limited within a much thinner region.@footnote 1@ However, direct information on the structure of this interface has not been so far obtained. Thus, we investigated the structure of an ozone-oxide film at the interface on Si(100) by analyzing transverse optical (TO) and longitudinal optical (LO) phonon modes of Si-O-Si asymmetric stretching vibration with Fourier-transformed infrared spectroscopy (FT-IR). The Si-O-Si bond angle in the ozone-oxide film was found to be undistorted even in the region close to the interface. In the case of a thermally grown oxide film, both peaks are known to make a clear red-shift.@footnote 2,3@ However, the position of a TO phonon peak of an ozone-oxide film fabricated at 350 °C kept constant at 1065 cm@super -1@ within <2 nm thickness. Only the LO phonon peak made a red-shift from 1240 to 1200 cm@super -1@. Since the TO phonon frequency is a function of a Si-O-Si bond angle,@footnote 4@ the result shows that the Si-O-Si angle in the thermally grown oxide is distorted close at the interface, but that this bond angle in the ozone-oxide remains unchanged, thus reducing the thickness of structural transition layers compared to that of the thermal oxide. @FootnoteText@ @footnote 1@ K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, 17 (1999) 1275.@footnote 2@ S. Miyazaki, H. Nishimura, M. Fukuda, L. Ley, J. Ristein, Appl. Surf. Sci. 113/114 (1997) 585.@footnote 3@ K. T. Queeney, M. K. Weldon, J. P. Chang, Y. J. Chabal, A. B. Gurevich, J. Sapjeta, and R. L. Opila, J. Appl. Phys. 87 (2000) 1322.@footnote 4@ F. L. Galeener, Phys. Rev. B 19 (1979) 4292.

9:20am **SS1-WeM4 Application of MIR-FTIR to Multilayered Structures Built on Silicon Substrate: TiCN and Al Deposition and Effects of Hydrogen Diffusion***, S. Bocharov, **A.V. Teplyakov**,* University of Delaware

A combination of infrared spectroscopy, thermal desorption mass spectrometry, ToF-SIMS and AFM was used to analyze deposition of TiCN and Al from CVD precursors onto a Si(100)-2x1 surface. The TiCN films were easily deposited from tetrakis-(dimethylamino)-titanium (TDMAT) on a clean Si(100)-2x1 surface at slightly elevated temperatures and pressures of 2 microtorr and even lower. Monolayer chemistry does not lead to TiCN deposition. On the other hand, at 593K deposition of TiCN can be easily achieved. The onset of the deposition process coinsides with the thermal decomposition of surface species resulting from the monolayer reactions. The unusual application of MIR-FTIR to study multilayered structures was successfully performed for TiCN and Al deposition onto a TiCN-precovered Si(100). Interestingly, not only surface chemistry of the CVD precursors on TiCN, but also the transformation of the TiCN/Si interface can be followed by such an approach. Hydrogen diffusion from surface decomposition was shown to play a significant role in the formation of the multilayered structure. It was also observed that the diffusion of hydrogen atoms produced by hydrogen dissociation on a hot tungsten filament drives hydrogen towards TiCN/Si interface.

9:40am **SS1-WeM5 Indium Phosphide (001)-(2x1): Evidence for a Hydrogen-Stabilized Surface Reconstruction***, **G. Chen**, D. Cheng, D. Tobin, Y. Sun,* University of California, Los Angeles*; K. Raghavachari,* Indiana University*; R.F. Hicks,* University of California, Los Angeles

Metalorganic vapor-phase epitaxy (MOVPE) is widely used to produce InP-based optoelectronic devices. Deposition of InP (001) films occurs in a large excess of the group V precursors, resulting in the formation of a P-rich (2x1) reconstruction. Scanning tunneling microscopy indicates that the (2x1) is terminated with a complete layer of buckled phosphorus dimers. This structure has been the subject of debate, because it should violate the electron counting model and exhibit partially filled P dangling bonds. In this work, we report on a vibrational study of the (2x1) surface prepared in the MOVPE environment. Infrared spectra collected during deuterium titration reveals the presence of a single sharp P-H stretching mode at 2308 cm^-1. Based on theoretical cluster calculations using density functional theory, this mode results from a single hydrogen atom bonded to one end of the buckled phosphorus dimer. This structure does not violate the electron counting model. In addition, slab calculations by another research group indicate that hydrogen-termination of the P dimers should yield the most stable configuration for the (2x1). Therefore, it may be concluded that adsorbed hydrogen atoms stabilize the phosphorus-rich surface structure during indium phosphide film growth by MOVPE.

10:00am **SS1-WeM6 Chemically Resolved STM Imaging of Al on Al@sub 0.1@Ga@sub 0.9@As(001)-c(2x8)/(2x4)***, **M.J. Hale**, D.L. Winn, A.C. Kummel,* University of California, San Diego

It has been proposed that growing an oxide/AlGaAs/GaAs stack will prevent interface roughness from interfering with carrier mobility within the channel when attempting to create a GaAs-based MOSFET. Before attempting to grow an oxide/AlGaAs interface, one must first characterize the AlGaAs(001) surface. We will present STM images of the AlGaAs(001) surface in which Al and Ga can be distinguished. Al atoms in the second layer of Al@sub 0.1@Ga@sub 0.9@As(001)-c(2x8)/(2x4) cause the adjacent As atoms in layer one to be brighter than As atoms bonded to Ga atoms in STM images. Al is a stronger charge donor than Ga, which makes the As atoms in layer one bonded to Al atoms in layer two to have a greater charge density than As atoms bonded to Ga. This affect was only seen for p-type AlGaAs grown on a p-type GaAs substrate. Scanning tunneling spectroscopy (STS) measurements show that the excess charge transferred to the first layer As atoms from the second layer Al atoms causes electrical inversion to occur on the surface. For n-type Al@sub 0.1@Ga@sub 0.9@As(001)-c(2x8)/(2x4) grown on an n-type GaAs substrate, the ability to differentiate Al from Ga atoms in STM images is not possible. STS spectra show that the Fermi level resides near the conduction band, typical of a non-inverted n-type sample. This result is consistent with our model of a strong charge donation by Al since excess charge would not affect the position of the surface Fermi level in n-type material. The ability to differentiate between second layer Al and Ga atoms on p-type AlGaAs(001) with STM will enable further studies to understand the oxide/AlGaAs(001) interface.

10:20am **SS1-WeM7 Atomistic Mechanisms of Fermi-level Pinning at the Oxide-Semiconductor Interface***, **J.Z. Sexton**, M.J. Hale, D.L. Winn,* University of California, San Diego*; M. Passlack, A.A. Demkov,* Motorola Inc.*; A.C. Kummel,* University of California, San Diego

Understanding the mechanism of Fermi-level pinning is critical in the development of an electronically passive oxide - III/V semiconductor interface. This insulator-semiconductor interface is important in the development of a practical of III / V MOSFET technology. We have observed Fermi-level pinning and un-pinning in STM and STS at the GaAs(001)-2x4 surface in three cases, upon sub-monolayer a) deposition of oxygen atoms, b) vapor deposition of Ga@sub 2@O and c) vapor deposition of In@sub 2@O. We have seen that the oxide layer formed upon atomic oxygen exposure forms a pinned interface. However, when a vapor deposited gallium oxide layer is formed, the surface remains unpinned. When In@sub 2@O is vapor deposited on the GaAs-2x4 surface, several bonding structures are formed, ultimately leading to a pinned interface. We have identified the bonding structures using first-principles calculations and have identified the mechanism for Fermi-level pinning for all the cases listed above. The Fermi-level pinning in case a) is due to a deep-level state, caused by significant charge withdrawal from the gallium atoms by oxygen. The Fermi-level unpinning in case b) is due to the bonding configuration resulting in a geometrically favorable and charge balanced structure. The Fermi-level pinning in case c) is dependent on the specific structure observed in STM. We have done calculations to elucidate the bonding and electronic structure of the observed bonding configurations and have observed that some structures are pinned and some are unpinned. We have seen two types of Fermi-level pinning: 1) deep level pinning caused by a fixed interface atomic state in the band-gap region and 2) a dipole-like pinning that is distributed over the covalent bonding network which induces states on the valence and conduction band edges. In summary, the bonding structure at the interface determines the existence and type of Fermi-level pinning.

10:40am **SS1-WeM8 Coupling Reactions of Trifluoroethyl Iodide on GaAs(100)***, N.T. Kemp, N. Paris, **N.K. Singh**,* The University of New South Wales, Australia

Alkyl coupling reactions studied to date have been restricted to gold, silver and copper surfaces, where the only coupling product formed has always been the corresponding higher alkane. In this paper we report, the coupling reactions of trifluoroethyl iodide on GaAs(100) which forms, not only the higher alkane, but a higher alkene as well. In this respect the alkyl coupling reactions on the GaAs surface differ from those on transition metal surfaces. Additionally, the ability of a semiconductor surface to catalyse carbon-carbon bond formation has not been reported previously by other researchers. The techniques of X-ray photoelectron spectroscopy and thermal desorption spectroscopy have been used to study the surface reactions of 2-iodo-1,1,1-trifluoroethane (CF@sub3@CH@sub2@I) on GaAs(100). Our results show that coupling of surface CF@sub3@CH@sub2@ species, generated via the dissociative adsorption of CF@sub3@CH@sub2@I, yields both CF@sub3@CH@sub2@CH@sub2@CF@sub3@ and CF@sub3@CH@sub2@CH=CF@sub2@. The coupling pathway competes with the disproportionation reactions of CF@sub3@CH@sub2@, to form CF@sub2@=CH@sub2@ as the major product of this pathway. In addition, we observe the formation of volatile etch products IF@subx@, GaI, AsI, GaF, AsF and As@sub2@. This paper will discuss the mechanisms by which these products form from the adsorbed CF@sub3@CH@sub2@ and I species, and the role that the GaAs surface plays in the reaction pathways proposed.

Surface Science
Room 327 - Session SS2-WeM
Surface and Interface Structure: Metals

Moderator: R.J. Hamers, University of Wisconsin-Madison

8:20am **SS2-WeM1 Dislocation Mediated Interactions in Self-assembly: The S-induced Triangular Hole-array in Ag/Ru(0001)**, ***K. Thurmer***, *N.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

By depositing S onto a monolayer of Ag/Ru(0001) we are able to create very regular arrays of 2D-vacancy islands.@footnote 1@ Real-time STM measurements reveal the mechanisms of such adsorbate induced restructuring: Starting from a herringbone pattern of the clean Ag-film, the S transforms the film by a sequence of dislocation reactions that individually decrease the Ag density. Eventually all threading dislocations are eliminated and the film assumes a Moire-like structure, in which on-top Ag-atoms are replaced by holes filled with S. These holes form a strikingly regular triangular lattice with a nearest neighbor spacing of 5nm. The conventional assumption is that such pattern formation is caused by substrate-mediated long-range elastic interaction. To test this assumption, we have used STM to measure the thermal vibrations of the hole array as a function of temperature. Surprisingly, we find we can account for these observations without invoking substrate relaxations: By comparing the measured vibration amplitudes to 2D Frenkel-Kontorova simulations we find that the hole-array is stabilized by a pattern of partial dislocations connecting the holes. First principles electronic structure calculations of the 2D FK model parameters for Ag/Ru quantitatively reproduce the hole-hole interaction strength extracted from our measurements. @FootnoteText@ @footnote 1@K. Pohl et al. Nature 397 (1999) 238.

8:40am **SS2-WeM2 Molecule-Metal Surface Interactions Evidenced Quantum Mechanically via Tip-induced CS2 Interaction with Friedel Oscillations on Au{111}**, ***E.C.H. Sykes***, *P. Han, P.S. Weiss,* The Pennsylvania State University

Sub-monolayer coverages of CS2 adsorbed on Au{111} at 4 K were studied using scanning tunneling microscopy. The molecule forms well ordered islands on the terraces and molecular chains at the bottoms of the steps. The adsorption of the CS2 molecule at specific surface sites is explained in terms of the substrate electron density. Strong tip/molecule interactions are shown to be prevalent in this system at negative tip biases and yield images showing reversed corrugation. At low positive tip bias, the tip again perturbs the molecules, but in this regime the tip/molecule interaction is comparable to the molecule/surface interaction and higher residence times at certain surface sites are observed. This effect is explained fully in terms of the CS2 molecule having increased interactions with the areas of high electron density on the peaks of standing waves arising from electrons close to the Fermi energy. The importance of this result is discussed in terms of the fundamental surface physics of adsorbate/metal bonding.

9:00am **SS2-WeM3 Interactions Mediated by Surface States: Lines and Ordered Overlayers@footnote 1@**, *P. Hyldgaard,* Chalmers University of Technology and Göteborg University, Sweden*;* ***T.L. Einstein,*** University of Maryland, College Park

Since surface states on (111) noble metals are free-electron like, their propagators can be evaluated analytically.@footnote 2@ Since they are well-screened, one can use simple tight-binding formalism@footnote 3@ to study their effects.@footnote 4@ Applications to metallic surface states on semiconductors may also be fruitful. The needed phase shifts can be extracted from experiment.@footnote 2,4@ Hence, we can now make quantitative predictions of indirect interactions---at least the asymptotically dominant contribution from surface states.@footnote 2,4@ Here, we discuss the interactions of linear defects, relating them to the interactions of (n x 1) ordered overlayers and to the constituent pair and trio interactions. We discuss implications for step-step interactions (on vicinal surfaces), for extracting pair interactions from first-principles calculations of ordered overlayers or from experiments, and for atoms approaching large clusters. @FootnoteText@ @footnote 1@PH supported by ATOMICS, financed by the Swedish Foundation for Strategic research; TLE supported by NSF Grants EEC-0085604 and MRSEC DMR 00-80008. @footnote 2@ J. Repp et al., Phys. Rev. Lett. 85 (2000) 2981; P. Hyldgaard and M. Persson, J. Phys.: Condens. Matt. 12 (2000) L13.@footnote 3@ T.L. Einstein, in Handbook of Surface Science, vol. 1, ed. W.N. Unertl (Elsevier, Amsterdam, 1996), chap. 11.@footnote 4@ P. Hyldgaard and T.L. Einstein, Europhys. Lett. 59 (2002) 265; Surf. Sci., in press [doi:10.1016/S0039-6028(03)00173-0].

9:20am **SS2-WeM4 Structural Evolution of an Atomically Rough Surface: Faceting and Alloying of Re(12-31)**, ***A.S.Y. Chan,*** *H. Wang, W. Chen,* Rutgers University*; J.E. Rowe,* United States Army Research Office*; T.E. Madey,* Rutgers University

The thermal stability of ultrathin metal and oxide films on an atomically rough Re(12-31) surface has been studied using Low Energy Electron Diffraction (LEED) and High Resolution Soft X-ray Photoelectron Spectroscopy (HRSXPS) using synchrotron radiation. Re(12-31) is a morphologically unstable surface with 6 surface layers of atoms exposed. This highly corrugated surface exhibits a surface shift in the Re4f core levels of 0.17 eV towards higher binding energy, relative to the bulk peak. Adsorption of oxygen at room temperature leads to a disordered chemisorbed oxygen overlayer with a rich distribution of chemical binding states, while the surface retains a planar morphology. However, when the O-precovered surface is annealed to temperatures above 700 K, drastic restructuring of the surface occurs to form nanosized facets with a ridged "hill-and-valley" morphology. The facet planes are identified as (01-10) and (11-21) based on kinematic simulations of LEED patterns, and are consistent with Field Emission Microscopy results of our collaborators. By controlling the coverage of oxygen, different oxygen coordination sites on the Re facet planes can be selectively populated and identified by distinct chemical shifts (up to 0.73 eV) to higher binding energies in the Re4f core levels. In contrast, the Re substrate does not facet when precovered with a Pt or Pd overlayer and annealed. Ultrathin Pt films form a dilute alloy with the Re substrate at temperatures as low as 300 K; this surface alloy becomes increasingly Re-rich as the film is annealed.

9:40am **SS2-WeM5 Multilayer Thermal Expansion at Surfaces from Surface Core Level Shifts**, *A. Baraldi,* Sincrotrone Trieste S.C.p.A. and Universitá di Trieste, Italy*; S. Lizzit,* Sincrotrone Trieste S.C.p.A., Italy*;* ***K. Pohl,*** University of New Hampshire*; Ph. Hofmann,* University of Aarhus, Denmark*; S. de Gironcoli,* Scuola Internationale Superiore di Studi Avanzati (SISSA), Italy

Understanding the thermal properties of nanostructures is of great importance when it comes to making reliable predictions on their stability. By decreasing the size of nanoparticles the thermal behavior of the surface is going to dominate their properties. A basic manifestation of these anharmonic effects is thermal structural expansion. However, some open surfaces are violating our common sense by exhibiting significant negative thermal contraction while some close-packed surfaces show anomalously large thermal expansion. A theoretical understanding of the anharmonic effects at surfaces does not exist and state-of-the-art LDA calculations show large disagreements with experimental results. An especially puzzling case is the thermal expansion of Be(0001). A recent LEED investigation measured an anomalously large thermal surface expansion between 110 K and 700 K, 6 times larger than the bulk. This observation seems inconsistent with measurements reporting no anharmonicity in the out-of-plane surface phonon modes and with a subsequent LDA study within the quasiharmonic approach resulting in no significant thermal expansion. We will present a novel, independent, approach to determine the thermal expansion of Be(0001). We measured the binding energy of the surface state and the values of the surface core level shifts as a function of temperature and compared them to calculated DFT values for different geometries. Our results reveal that, in the temperature range from 300 to 700 K the 1st-to-2nd, 2nd-to-3rd and 3rd-to-4th interlayer coefficient of thermal expansion are 88±15, -10±15 and -6±20 x 10@super -6@ K@super -1@, respectively, to be compared with a bulk value of 12 x 10@super -6@ K@super -1@. Our results confirm the anomalously large thermal expansion of the surface and establish Be(0001) as a firm experimental standard for advances in our theoretical understanding of the thermal behavior of surfaces.

10:00am **SS2-WeM6 The Electronic and Geometrical Structures of Ultrathin Bimetallic Films of Pd and Cu on Ru(0001)***, **J. Onsgaard**, L. Bech,* Aalborg University, Denmark*; Z. Li,* University of Aarhus, Denmark*; T.H. Andersen,* University of Southern Denmark*; S.V. Hoffmann,* University of Aarhus, Denmark

Alloying conditions, low-dimensional effects and catalytical properties of ultrathin bimetallic films of Pd and Cu have been studied. Codeposition of the two metals on a relative inert substrate, Ru(0001), with overlayer thicknesses in the range 1 ML to 4 ML, were carried out. Deposition temperatures were either room temperature or 550 K and the thin films were characterized as a function of temperature. The information is based upon photoelectron spectroscopy based upon use of synchrotron radiation with high resolution core level studies of Pd 3d, Ru 3d, Cu 2p and valence band measurements. LEED was used to follow the order of the overlayers. Cu and Pd are distributed in one layer with temperature dependent mixing when the total coverage is one monolayer. The valence bands of the surface alloys are characterized by the Cu 3d band separated from the Pd 4d band at a temperature of 550 K. Heating causes hybridization of the Cu 3d and Pd 4d bands with formation of a new band between the individual metal bands. Surface alloying takes place at 660 K and above this temperature the structures of the overlayers are independent of the order of deposition. Cu 2p core-level binding energy shifts show two linear relationships with the composition of the film in 2-and 3 dimensions. An effect which is attributed to the different coordination numbers between Pd and Cu in 2- and 3 dimensions.

10:20am **SS2-WeM7 A Novel Local Free Energy Minimum on the Cu(001)-Surface***, **H. Wormeester**, M. Ovsyanko, G. Stoian, B. Poelsema,* University of Twente, The Netherlands

Glancing incidence Ar@super +@ ion bombardment of the Cu(001) surface leads to the formation of two atom layer deep nanogrooves parallel to the incident ion beam. High resolution LEED patterns show that sputtering along [110] and [100] leads to an intergroove distance that depends on temperature, ionfluence and -energy. Suprisingly, prolonged sputtering along [100] leads at various temperatures (175 to 235 K) to a persistent feature located at 1.0% BZ of the Brillouin Zone (BZ). Annealing at temperatures between 250 and 290 K of nanogrooves prepared after a much shorter sputtertime leads to an increase of their separation distance. Here too, the appearance of this persistent feature at 1.0% BZ is observed. These various preparation routes are indicative of a thermodynamic origin of this 1.0% feature, i.e. a local free energy minimum. Mild annealing above 400K transfers the surface to the global free energy minimum: It suffices to remove both the nanogroove structure and the feature at 1.0% BZ. The occurrence of the 1.0% BZ feature is attributed to the relieve of tensile strain, generally present at (001) fcc metal surfaces, leading to a contraction of the in-plane lattice constant of the (001) surface along the [010] azimuth. The energy balance between gain by stress relieve and cost due to lattice mismatch will be discussed. The presence of the nanogrooves along a azimuth turns out to be essential for the relieve of this strain.

10:40am **SS2-WeM8 Low Energy Electron Microscopy of the Quantum Electronic Structure and Stability of Ag Films on Fe(100)***, K.L. Man,* Hong Kong University of Science and Technology*; Z.Q. Qiu,* University of California at Berkeley*; **M.S. Altman**,* Hong Kong University of Science and Technology, Hong Kong

Laterally resolved measurements of the reflected electron intensity from Ag films on the Fe(100) surface have been made with low energy electron microscopy (LEEM). Intensity peaks are observed at very low energy that are associated with quantum well resonances in the Ag film above the vacuum level. The dispersion of the quantum well peaks with increasing film thickness is well accounted for by the phase accumulation model, which has been used widely to explain the occupied quantum well states that are observed with photoemission in this and other systems. The signature quantum well peaks that are observed in electron reflectivity are then used in combination with real-space LEEM measurements to monitor film stability during annealing. We find that uniform three monolayer (ML) thick films decompose directly into spatially separated two and five ML thick film regions, whereas uniform four ML thick films decompose initially into three and five ML thick regions and eventually into two and five ML thick regions. The greater stability of two and five ML thick films has been attributed to band structure features near the zone center, which are the source of long period magnetic oscillatory coupling through Ag films. The relative stability of three and four ML thick films may be evidence that band structure features related to the neck of the Fermi surface, which give rise to the short period oscillatory coupling, also play a role in film quantum electronic stability.

Thin Films

Room 329 - Session TF-WeM

Optical Thin Films and Photovoltaics I

Moderator: R. Sargent, OCLI

8:20am **TF-WeM1 Multilayer Optical Coatings Using Closed Field Magnetron Sputtering***, **J.M. Walls**, D.G. Gibson, J. Hampshire, D.G. Teer,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of multilayer optical coatings. The process operates at high energy producing dense, spectrally stable coatings. The sputtering process is also "cold", making it suitable for use on the widest range of substrates including polymers. This paper will describe a new process that allows high quality, multilayer metal-oxide thin films to be deposited at high rates using Closed Field magnetron sputtering together with pulsed dc power. The Closed Field process for optical coatings uses two or more different metal targets. The target is held in a partially oxidised state controlled using plasma emission monitoring and the oxidation occurs in the entire volume around the rotating substrate carrier. In addition to describing the new process, this paper will discuss the optical properties of individual layers and their application to a range of multilayer precision optical coatings. The ion current density and the low bias voltage provided by Closed Field magnetron sputtering produces films at a high rate with excellent optical properties. Machines based on the Closed Field are scaleable to meet a range of batch size requirements. Examples of multilayer coatings in the visible and infra-red spectra will be provided. Examples in the visible spectrum will include Anti-reflective and other coatings using fully oxidised SiO2, TiO2 ITO and other metal-oxide films. Applications in the infra-red will incorporate materials such as Si, Si3N4 and TiO2. Typically, thin film thickness control is accomplished simply using time although quartz crystal monitoring or optical monitoring are used for more demanding applications. Fine layer thickness control is also assisted with a specially designed rotating shutter mechanism.

8:40am **TF-WeM2 Smooth Optical Thin Film Formation by Oxygen Cluster Ion Beam Assisted Depositions***, **N. Toyoda**, I. Yamada,* Himeji Institute of Technology, Japan

Ta@sub 2@O@sub 5@/SiO@sub 2@ and Nb@sub 2@O@sub 5@/SiO@sub 2@ were deposited with oxygen gas cluster ion assisted deposition at low-temperature for optical filters. As one cluster ion has thousands of O@sub 2@ molecules, equivalently low-energy ion irradiations are realized at several keV of total acceleration energy. Due to the dense energy deposition of cluster ions, high-temperature and high-pressure conditions are realized at the impacted area, which enables to deposit high quality thin films without heating the substrate. Also, GCIB shows significant surface smoothing effects, which realizes very flat surface and interfaces for multi-layered structures. In this study, O@sub 2@-GCIB was applied to form high quality optical films. With gas cluster ion assisted deposition, high refractive index and very uniform amorphous structures were observed with cross-sectional SEM. The surface or interfaces of Ta@sub 2@O@sub 5@/SiO@sub 2@ films were also very flat by surface smoothing effect of cluster ion beams. Even though the deposited surface was rough (average roughness 1.5nm), the surface roughness of the deposited Ta@sub 2@O@sub 5@ film was improved to 0.7nm. As there is strong surface smoothing effect with O@sub 2@ cluster ion beam assisted deposition at low substrate temperature, it is appropriate to form multi-layered optical filters.

9:00am **TF-WeM3 Scandium and Vanadium Multilayer Mirrors: Working Towards High Reflectivity in the Extreme Ultraviolet***, G. Acosta,* ***D. Allred,*** *R. Davis,* Brigham Young University

Despite bulk reflectivities of materials in the EUV being typically less than 7%, it is possible to design a multilayer mirror using thin films to achieve reflectivities in the vicinity of 30-40%. Inspired by the 1998 Uspenski paper@footnote 1@ which theorized 72% reflectance of 42 nm light, we have been working on developing a design scheme that uses the rare earth metal scandium to achieve such high reflectivies. For the multilayer coating, we chose to pair scandium with vanadium to ensure distinct interfaces between the materials, since scandium and vanadium are immiscible. Our thin film samples (typically 1.5-10 nm thick) were characterized with Atomic Force Microscopy, Ellipsometry, and using an Extreme Ultraviolet Scanning Monochrometer for reflectivity measurements. In addition to preliminary EUV reflectivity predictions, optical constants were found experimentally over the 800-400nm range, as well as in the EUV. @FootnoteText@ @footnote 1@ Uspenski et al, Optics Letters, vol. 23, no. 10, 771.

9:20am **TF-WeM4 Improvement of Reproducibility in Deposition Rate of MgF@sub 2@ Film Prepared by an rf Sputtering Technique named Keep Molecular Sputtering Method***, K. Kawamata,* ***T. Deguchi,*** Olympus Optical Co., Ltd., Japan*; E. Kusano, A. Kinbara,* Kanazawa Institute of Technology, Japan

MgF@sub 2@ film is generally formed by electron-beam evaporation rather than sputtering, because sputtered MgF@sub 2@ film shows poor transparency, resulting from F deficiency. To solve this problem, we have proposed a Keep-Molecular-Sputtering (K-M-S) method. It involves keeping magnesium fluoride target at a high temperature, and providing the sputtering species as a form of molecules. However, deposition rate of the K-M-S method has a large dispersion. In this study, reproducibility of deposition rate of MgF@sub 2@ film in the K-M-S method has been improved by monitoring optical emission intensity ratio of MgF@super *@/O@super *@. A sputtering-up-type rf magnetron sputtering machine was used in the experiment. Sputter source is 1-2 mm granular MgF@sub 2@ put on a 100 mm diam. quartz plate backed with a Cu plate. The source-to-substrate distance was 75 mm. Discharge gas was O@sub 2@ with a flow rate of 80 sccm. MgF@sub 2@ films are deposited on glass substrate (BSL7) set to an aluminum holder rotating during film deposition. Pre-sputtering of the target started when H@sub 2@O partial pressure became constant. Rf power was controlled to a certain value in the range between 480 and 520 W to remain the optical emission intensity ratio of MgF@super *@/O@super *@ at a constant value. The reproducibility of the deposition rates has been improved to ±17%(115±24 nm/min.) by controlling rf power, compared with ±28%(111±31 nm/min.) obtained for a constant power of 550W. For all MgF@sub 2@ films, optical absorptance at a wavelength of 400 nm was less than 5%. We have also discussed mechanisms of the K-M-S process based on analysis using a quadrupole mass spectrometer.

9:40am **TF-WeM5 Optical Properties and Microstructure of Plasma Deposited Ta@sub 2@O@sub 5@ and Nb@sub 2@O@sub 5@ Optical Thin Films***, H. Szymanowski, J.-P. Masse,* ***O. Zabeida,*** *J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique of Montreal, Canada

Advanced optical filter applications require not only an appropriate control of the optical constants of the thin films but also a suitable control of other film properties such mechanical performance, thermal and environmental stability, absence of refractive index inhomogeneities and others. In this respect, plasma enhanced chemical vapor deposition (PECVD) allows one to fabricate films with low as well as with high refractive index, and it also offers a possibility for stress compensation, control of refractive index gradients, and high deposition rates at low substrate temperature. In the present work we study the characteristics of two high index optical materials, namely amorphous tantalum pentoxide (Ta@sub 2@O@sub 5@) and niobium pentoxide (Nb@sub 2@O@sub 5@) obtained by PECVD, respectively, from penta-ethoxy tantalum Ta@sub 2@(OC@sub 2@H@sub 5@)@sub 5@ and penta-ethoxy niobium, Nb@sub 2@(OC@sub 2@H@sub 5@)@sub 5@, precursors. We particularly investigated the effect of the energetic conditions on the film growth by using different modes of plasma excitation, namely radio frequency (RF), microwave (MW) and dual-mode microwave/radio frequency (MW/RF) discharges. Under sufficient ion bombardment, controlled by the RF-induced negative substrate bias, the dense Ta@sub 2@O@sub 5@ and Nb@sub 2@O@sub 5@ films exhibited a refractive index of 2.16 and 2.26 (at 500 nm), respectively, while the extinction coefficient was below 10@super -5@, as determined by spectroscopic ellipsometry, spectrophotometry and thermal deflection optical calorimetry. We found that increasing ion bombardment during the film growth leads to an appreciable increase of carbon concentration incorporated in the films, as indicated by a strong double peak at 1400 and 1500 cm-1 in the FTIR spectra. Elastic recoil detection (ERD) measurements reveal an atomic concentration of 2.5% and 5,5% of carbon in the bulk of the Ta@sub 2@O@sub 5@ and Nb@sub 2@O@sub 5@ films. The presence of carbon did not appear to negatively affect the film optical and mechanical performance and stability. We discuss the possible mechanism of carbon bonding in these films in a form of metal chelate and bridging groups.

10:00am **TF-WeM6 The Anneal Behavior of Reactively Sputtered HfN Films***,* ***J. Lannon Jr.****, C.C. Pace, S. Goodwin,* MCNC Research and Development Institute*; S. Solomon,* Acumen Consulting*; P. Bryant, J. Oleson,* Santa Barbara Infrared, Inc.

This article reports electrical, optical, structural and thermo-physical properties of reactively sputtered HfN films with respect to elevated-temperature annealing. All metal nitride films were sandwiched between sputtered Si3N4 films. The resulting reduction in electrical resistivity with anneal is explained by a combination of XPS, RBS and SIMS analyses, and the physical mechanisms responsible for the observed anneal behavior are discussed. The negative TCR is also explained. Infrared optical properties of these film stacks were investigated and found to show the expected correlation with electrical properties, while the anneal behavior was found to exhibit anomalies that were independent of the as-deposited properties.

Vacuum Technology
Room 323 - Session VT-WeM

Dynamic Vacuum Systems

Moderator: L.A. Smart, Brookhaven National Laboratory

8:40am **VT-WeM2 Is Mass 19 in the Residual Gas of Very High Vacuum just F@super +@?***,* ***C.R. Cole,*** *R.A. Outlaw, R.L. Champion, B.C. Holloway,* The College of William and Mary

Typically, the mass spectral peak observed at 19 amu in residual gas analyzers at very high vacuum has been solely attributed to fluorine. Using Fourier Transform Mass Spectrometry (FTMS), the presence of the hydronium ion, H@sub 3@O@super +@,has been fully resolved from F@super +@ and shown to be quite prevalent. Analysis is presented that shows that there is ample time for the formation of the hydronium ion through ion-molecule interactions and a direct correlation to the partial pressure of H@sub 2@O. The formation time and its correspondence to ionization, trap and resonance sequences have been characterized, as well as the gas collision formation mechanisms. Additionally, the generation of hydronium was further confirmed with D@sub 2@O experiments. Formation of D@sub 3@O@super +@ in a conventional quadrupole mass spectrometer has also been observed. Gas phase formation mechanisms of hydronium and deuteronium and other formation avenues, such as ESD, are discussed.

9:00am **VT-WeM3 Quartz Capillary Gas Flow Meters***,* ***R.F. Berg,*** National Institute of Standards and Technology **INVITED**

The flow rate of a gas through a laminar flow impedance can be inferred from the pressures at the entrance and exit of the impedance. If the hydrodynamic model of the meter is well understood, one calibration allows such a meter to be used over a wide range of pressures and flow rates and for a wide variety of gases. The calibration is required to determine the impedance's effective geometry. This talk describes measurements on five gases with a laminar flow meter whose impedances were constructed from quartz capillary manufactured for gas chromatography. The meter is presently used as a transfer standard for flows from 1 to 1000 micromol/s (about 1 to 1000 sccm). Two additional uses are discussed. The first use relies on the circularity and uniformity of the capillary's cross-section. A determination of the average capillary radius by weighing (sensitive to radius^2) will be close to the effective radius for flow (sensitive to radius^4). This would allow the meter to be used as a primary flow standard. The second use is for gas flow measurements for primary vacuum standards. This requires extending the model to handle exit pressures less than 100 Pa.

10:00am **VT-WeM6 Development of a Low Cost Cylindrical Magnetron for Coating Long Vacuum Vessels***, *P. He, H.C. Hseuh, M. Mapes,* ***R. Todd****, D. Weiss,* Brookhaven National Laboratory

The 2 MW US Spallation Neutron Source (SNS) includes a 248m accumulator ring that requires a 100 nm coating of TiN to reduce the secondary electron yield (SEY) of the vacuum chamber walls. Brookhaven National Laboratory (BNL) has developed a low cost cylindrical magnetron target capable of coating the wide variety of chamber geometries found in the SNS accumulator ring. Production chambers with lengths of 5m and diameters of 29cm have been successfully coated. This target is capable of reactive sputtering through the use of a gas introduction tube, and can easily be adapted for a wide variety of lengths. The magnetic field is such that primary electron trapping is longitudinally uniform, which results in excellent discharge characteristics. This method has also been used to successfully coat a Cu/TiN multilayer on production ceramic injection kicker pipes of SNS. Coating properties were analyzed with auger electron spectroscopy and scanning electron microscopy, and will be presented herein. Special emphasis will be given to the various coating configurations of production chambers and equipment used. *Work performed under Contract Number DE-AC05-00OR22725 with the auspicious of the U.S. Department of Energy.

10:20am **VT-WeM7 Advanced Closed Loop Control Method and Sensor for a Reactive Sputtering Drum Coater***,* ***M.A. George****, E.A. Craves,* Deposition Sciences, Inc.*; R. Shehab, K. Knox,* Ametek, Inc.

The reactive sputtering process is characterized by a hysteresis of reactive gas concentration and reactive gas flow.@footnote 1,2@ The precise control of the reactive sputtering process requires operating at a points on the hysteresis that ensures the desired high sputter flux and deposited thin film stoichiometry. The hysteresis is highly non-linear in these preferred operating regimes. The practical challenge of meeting this in the batch coating system requires a control system that can compensate for changes in reaction rate for various sputtered metals, system pumping speed changing with thermal variations and dynamic compensation of detrimental periodic cathode arcs. Closed loop control algorithms that rapidly bring the reactive sputtering system to the desired hysteresis steady state operating point are desired for multi-layer applications such as thin film interference filters that require many target starts (and stops). Conventional methods of starting the reactive sputtering process such as temporally ramping target power, voltage or current and target shutters are undesirable for precision thin film interference filters We will present control system hardware and closed loop control algorithms that permit the achievement of steady state operating points in less than 500 milliseconds on several different reactive sputtering drum coaters. The key feature of the hardware and control algorithms employed on these drum coaters is the determinism required for successful operation. We will discuss the reactive gas sensor and the algorithms employed for ensuring a temporally accurate signal of reactive gas concentration and the closed loop control method using this signal as an integral part of the loop. @FootnoteText@ @footnote 1@S. Schiller, U. Hesig, G. Beister, K. Steinfelder, J. Strumpfel, Chr. Kondorfer, and W. Sieber, Thin Solid Films, 118(1984), pp 255-270. @footnote 2@J. Affinito and R.R. Parsons, J. Vac. Sci. Technol. A, Vol. 2, No. 3, pp 1275-1284.

10:40am **VT-WeM8 The TRASCO-ADS Project Windowless Interface: Theoretical and Experimental Evaluation***,* ***P. Michelato****, D. Barni, D. Sertore,* INFN - Lab. LASA, Italy*; A. Colaiuda, P. Turroni,* ENEA Centro Ricerche di Bologna, Italy*; G. Bertacci,* ENEA Brasimone, Italy*; A. Bonucci, R. Giannantonio, M. Urbano,* SAES Getters, Italy*; L. Cinotti,* ANSALDO, Italy

TRASCO-ADS, the Italian acronym for Transmutation TRASmutazione) of nuclear Waste (SCOrie), is a national funded program in which INFN, ENEA and Italian industries work on the design of an accelerator-driven sub critical system (ADS) for nuclear waste transmutation. One of the most critical aspects of an ADS is the interface between the UHV environment of the accelerator and the pressurized system of the spallation target (400Â°C Pb-Bi eutectic or pure Pb at about 1 bar), due to thermomechanical issues and to radioprotection and safety constraints. Two interface concept designs have been evaluated. In a first case, a thin window physically separates the high pressure and the low pressure sides of the interface. In a second case (windowless), the linac and the spallation target are separated only by means of a suitable pumping system. This paper reports a description of the whole machine based on the windowless solution, an evaluation of the gas and vapour loads evolved from the hot interface region and the preliminary results drawn from numerical models developed to describe the flow of said vapours and gases inside the complex geometry of the interface. We here discuss about the experimental validation of the above models, carried out through suitably developed experimental devices. A first order design of the vacuum system is also proposed.

Applied Surface Science

Room Hall A-C - Session AS-WeP

Poster Session

AS-WeP1 A Simple Method Identifying the Influence of Photoperturbation Effect on Ultrashallow Junction Images Observed by Scanning Capacitance Microscope*, **M.-N. Chang,*** National Nano Device Laboratories, Taiwan, R.O.C.*; W.-W. Wan, J.-H. Lai,* National Tsing Hua University, Taiwan, R.O.C.*; C.-Y. Chen, F.-M. Pan,* National Nano Device Laboratories, Taiwan, R.O.C.*; J.-H. Liang,* National Tsing Hua University, Taiwan, R.O.C.

Scanning capacitance microscopy (SCM) with high sensitivity and high spatial resolution has attracted much interest in profiling two-dimensional carrier distribution and investigating ultrashallow junctions. Atomic force microscope (AFM), equipped with a SCM system, is a typical setup that synchronously provides SCM images and the corresponding topographic images for cross-sectional characterization. In this work, we have provided a simple method to investigate the influence of photoperturbation effect induced by AFM laser beam on ultrashallow junction images observed by SCM. The samples were ultrashallow p@super +@ junctions formed by BF@sub 2@@super +@ implantation at low energies. RTA processes were performed at 1050 °C for different anneal times from 5 to 30 seconds in N@sub 2@ ambient. The width and pitch of the designed grating pattern are 0.8 and 2 @micro@m, respectively. It is revealed that the photoperturbation effect induced by AFM laser beam leads to SCM image broadening and junction region narrowing. In other words, the photoperturbation effect not only significantly affects the dC/dV signals but also deteriorates the accuracy of junction characterization, in particular for ultrashallow junctions. The experimental results will be shown and discussed. The section analysis also reveals that there are distorted differential capacitance (dC/dV) profiles in the photoperturbed SCM images. Comparing dC/dV profiles of various photoperturbed SCM images, one can identify the area not affected by AFM laser beam. This simple method allows us to identify the influence of the photoperturbation effect on the pattern region. According to this study, the pattern edge region is more sensitive to the photoperturbation effect than the pattern central region.

AS-WeP2 Wettability Control of Polymer Surface through 126 nm Vacuum Ultraviolet Light Irradiation*, **Y. Nakanishi,*** Waseda University, Japan*; A. Hozumi, N. Shirahata,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan

The surface modification of polymeric materials through vacuum ultraviolet (VUV) light irradiation has attracted much attention due to its wide variety of applications, including improvement of the wettability, biocompatibility and coating adhesion of such surfaces. In this study, we report on the surface modification of poly (methyl methacrylate) (PMMA) using VUV light of 126 nm radiated from an Ar@sub 2@@super *@ excimer lamp. We have particularly focused on the effects of atmospheric pressure during VUV-irradiation on the surface wettability, chemical structure and morphology of the PMMA surfaces, since atmospheric oxygen plays a crucial role in the photocleavage of polymeric chains and subsequent photooxidation. Each of the samples was exposed to VUV light for 1~50 min under various pressures of 3x10@super -4@, 10, 10@super 3@ or 10@super 5@ Pa. Hydrophobic PMMA surface became hydrophilic during VUV irradiation conducted over the pressure range of 10~10@super 5@ Pa. However, the degree of hydrophilicity of the modified surface was primarily determined by the atmospheric pressure. The minimum water-contact angles of the samples treated at 10, 10@super 3@ and 10@super 5@ Pa were about 49, 31 and 64Â°, respectively. On the contrary, in the case of 3x10@super -4@ Pa, PMMA surface became highly hydrophobic with its contact angle changing from 80 to about 100Â°. As confirmed by X-ray photoelectron spectroscopy, at 3x10@super -4@ Pa the C concentration and the intensity of the C-C groups in the C1s spectra increased. This was probably due to crosslinking reactions including the formation of new C-C bonds. Since the oxidation reactions did not proceed efficiently under such high vacuum condition, the free radicals may have recombined and crosslinked with each other, resulting in the increase of C-C groups. These results indicate that surface wettability of the PMMA substrates might be controllable by selecting the atmospheric pressure during 126 nm VUV irradiation.

AS-WeP3 An XPS Comparison of ALD and PLD Grown Thin Al@sub 2@O@sub 3@ Layers*, A.I. Zinine, **J.M. Sturm**, R.G. Bankras, H. Wormeester, B. Poelsema,* University of Twente, The Netherlands

Atomic Layer Deposition (ALD) is regarded as a suitable deposition technique for high-K metal oxides. Pulsed Laser Deposition (PLD) is an attractive alternative for a fast identification of new materials. A comparative XPS study of thin Al@sub 2@O@sub 3@ films grown by ALD (5, 10 and 20 nm) and PLD (15 and 30 nm) was made. This analysis is possible without a sputterprofile and is thus not compromised by co-sputtering. Water and trimethylaluminum were used as precursors in the ALD process. Fully oxidized alumina films with good stoichiometry and a band gap of 6.8±0.1 eV were obtained in all cases. The Si 2p XPS peak of the ALD films grown on hydrogen terminated Si with 50 ALCVD cycles did not show the formation of SiO@sub 2@. Angle resolved measurements gave a thickness of 4.2 nm, while a film grown on silicon oxide was 5.0 nm thick as expected for 50 cycles for the recipe used. This indicates growth inhibition in the first case. We note that both films showed a negligible carbon contamination. Freshly prepared ALD samples showed an O 1s XPS peak, composed of oxygen bonded to aluminium and a 1.6 eV energy shifted feature. Angle dependent measurements showed that this shifted feature is limited to the two topmost layers and can be identified as an OH species. Prolonged air exposure introduced a third component, which is attributed to oxygen bonded with carbon. The PLD samples grown in oxygen or argon ambient pressures of 0.1 mbar showed both a significant carbon content. However, only samples prepared in oxygen ambient exhibited carbide contamination and oxidized interfacial silicon.

AS-WeP4 Plasma Etching of (Ba,Sr)TiO@sub 3@ Thin Films for DRAM Applications*, **G.H. Kim**, C.I. Kim, D.P. Kim, K.T. Kim,* Chung-Ang University, Korea

(Ba,Sr)TiO@sub 3@ (BST) thin film attracts a great interest as a new dielectric material in capacitors for the next generation ultralarge scale integrated dynamic random access memories, such as giga bit DRAM in the wide range of research institutes to semiconductor industries because of its large dielectric constant, low leakage current, low dielectric loss, lack of fatigue, and low Curie temperature. A lot of papers have been presented on BST film characteristics using growth methods, however, its patterning have been studied less. In order to realize the higher integration, it is important to minimize the dimension of storage capacitors, simplify the memory cell structure and maintain sufficient accumulated electric charge within a smaller capacitor. Although BST thin films are excellent capacitor dielectric materials for DRAMs, several problems such as fine pattern transfer and no plasma induced-damage etc. In order to solve these problems, the etch behavior of BST with Ar/Cl@sub 2@/CF@sub 4@ gas mixtures is investigated with inductively coupled plasma (ICP). In this study, ICP etching system was used for BST etching. The etching characteristics of BST thin films were investigated in terms of etch rates and selectivity as a function of Cl@sub 2@/Ar and additive CF@sub 4@ into Cl@sub 2@/Ar, rf power, dc bias voltage and chamber pressure. The Cl@sub 2@/Ar and additive CF@sub 4@ into Cl@sub 2@/Ar plasmas were characterized by optical emission spectroscopy and Langmuir probe analysis. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

AS-WeP5 Dielectric Properties of Epitaxial Growth (Pb, Sr)TiO@sub 3@ Thin Films on Al@sub 2@ O@sub 3@ (100) Substrate*, **K.T. Kim**, C.I. Kim,* Chung-Ang University, Korea

Electrical tunable dielectric devices rely on the variation of a ferroelectric materials dielectric constant with application of an electric field. The requirements of Ferroelectric materials are low dielectric constant, high tunability, low losses and low leakage current. The structure and morphology of the films were characterized using X-ray diffraction and scanning electron microscopy. We investigated on the structural, electrical properties of (Pb@sub 0.5@,Sr@sub 0.5@)TiO@sub 3@ thin films on the Al@sub 2@ O@sub 3@ (100) substrate prepared using MOD method. From the XRD analysis, the peak in the XRD pattern of PST thin films on the Al@sub 2@ O@sub 3@ substrate was shown epitaxial growth. The low loss (~0.001) and high tunability (~60%) were obtained for (Pb,Sr)TiO@sub 3@ thin films on the LaNiO@sub 3@ substrate measured at 1 GHz. @FootnoteText@ This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

AS-WeP6 Ferroelectric Properties of Bi @sub 3.25@La @sub 0.75@Ti@sub 3@O@sub 12@ Thin Films on (117)-oriented LaNiO@sub 3@ Electrodes*, C.I. Kim,* ***K.T. Kim,*** Chung-Ang University, Korea

The BLT thin films were prepared by using metal organic decomposition method. The structure and morphology of the films were analyzed by x-ray diffraction (XRD), atomic force microscope (AFM), and Scanning electron micrograph (SEM). SEM and AFM showed uniform surface of the films. The LNO thin films annealed at temperature as high as 600@super Â°@C exhibit the (100)-oriented structure. The BLT thin films were found to crystallize preferably with (117)-oriented grains on LNO bottom electrode annealed at 600@super Â°@C for 1h. However, the BLT thin films were grown using a Pt bottom electrode showed a polycrystalline phase. The BLT thin films grown on LNO thin films showed excellent ferroelectricity and higher remanent polarization than BLT thin film using a Pt electrode. The remanent polarization Pr and coercive field is 22.5 mC/cm@super 2@ and 120 kV/cm. The BLT thin films on LNO bottom electrode exhibited no significant degradation of switching charge at least up to 5x10@super 9@ switching cycles at a frequency of 50 kHz below cycling fields of 5 V. It was shown experimentally that there was no data loss after 3x10@super 4@ s of memory retention at room temperature.

AS-WeP7 Distinguishing the Dependence of the Apparent Local Barrier Height on Measurement Conditions*,* ***S. Yagyu,*** *M. Yoshitake,* National Institute for Materials Science, Japan*; Y. Mizuno, R.E. Kirby,* Stanford Linear Accelerator Center

Work function is an important and fundamental property of materials related to the electron emission and reaction of molecules on the surface. As functional materials of reduced dimension become increase, the measurement of the local work function becomes important. The apparent local barrier height (LBH) related to the local work function has been measured by STM. The LBH is not the local work function of a sample material but multi-parameters value correctly, because the LBH based on the STM technique depends on the tip parameters (material, shape), the measurement parameters (tunnel current (I), bias voltage (V) and tip-sample separation (s)) and certainly the local work function of the sample material. Since each LBH obtained on same material surface with various measurement parameters is extremely different, we should know relation between the measurement parameters and the LBH. In STM/LBH measurement a I is proportional to a V and a s. For example, if we fix a I and change a V, a s is changed automatically. We measured dependence of the LBH on the I, V, and s precisely on the reconstructed Au (111) surface with an Au tip. The results under three different conditions, a constant s, I, and V were compared in the low bias voltage range (-50mV to -5mV) where I-V curve shows linear (ohmic). Under a constant s, the LBH does not change with the V, indicating that the LBH is independent of the V. Under a constant I, the LBH increases with the increased V. Under a constant V, the LBH increases with the increased s. The three results indicate that LBH depends exclusively on the s in our experimental conditions.

AS-WeP8 The Systematic Study of Ga TOF SIMS High Mass Molecular Ion Registration, Composition and Fragmentation of Selected Peptide Hormones on Silver Substrate*, H Chen,* College of William and Mary and Incogen, Inc.*;* ***A. Wilkerson,*** College of William and Mary*; D. Malyarenko,* College of William and Mary and Incogen, Inc.*; E. Tracy,* Applied Research Center and College of William and Mary*; D. Manos,* Applied Research Center and College of William and Mary.

This paper reports the use of Ga+ SIMS to provide imaging simultaneously with high sensitivity and specificity for peptide hormone registration. Although this technique is developed for high molecular weight organic polymers on silver and gold, no similar systematic quantitative studies are reported for biopolymers. We report high resolution spectra obtained by ToF-SIMS for molecular ions of Vasopressin II, Human Angiotensin and Somatostatin adsorbed on silver substrate. Characteristic positive high-mass parent peaks and adducts have been identified. The mass resolution exceeds 2000 for all three peptides. The dependence of the yield for the parent peak on solution concentration has been studied for Angiotensin. Parent peak intensities comprise from 1 to 15 % of the intensity for identifiable fragments. Images confirm that the fragmentation is associated with multi-layer formation. Parent peak adducts reproducibly display the anticipated quantitative isotope ratios and are skewed toward high masses. Sodium contamination adducts are registered as well. The images of surface coverage are reported at the parent masses. Unlike MALDI, no multiply charged species, ladder fragmentation or dimers are observed in the intermediate mass range. The low molecular weight peaks (below 200 Da) have characteristic signatures of the amino acid content for the peptides.

AS-WeP9 Analysis of Silane Coupling Compound Monomolecular layer on Sapphire Glass used by TRXPS*, T. Tazawa,* JEOL Ltd., Japan*; C. Mochizuki, M. Shibata,* University of Yamanashi, Japan*;* ***Y. Iijima,*** JEOL Ltd., Japan

Recently, the material which spreads silane coupling compound is actively researched. This material is usually applied to the fabrication of chip level interconnects, ohmic contacts, and printed circuit boards, and plating. Moreover, the application to life sciences is expected as for this compound However, the thickness of silane coupling compound is very thin. In general, silane coupling compound is used by one or two molecular layers.Therefore, the analysis of interface between silane coupling compound and the base material surface becomes important. The interface and surface for this material is useful analyzed with XPS, because silane coupling compounds are organic compounds. It is difficult to measure interface information accurately in a normal XPS analysis, because the thickness of silane coupling compound is thin. There is total x-ray reflection photoelectron spectroscopy (TRXPS) as a method of solving this problem. The use of x-ray total reflection has become noteworthy in photoelectron spectroscopy. The angular dependence of photoelectron peak intensities corresponds to the position change in the standing wave was caused by change in the x-ray glancing angle. Especially, at the measurement of multi-layer film and/or monomolecular layer formed on glass or Si wafer, because the belly and the paragraph position of standing wave of x-ray can be adjusted in such a way that they coincide with the respective layer position by changing the glancing angle. In this work, we examined silane coupling compounds monomolecular formed on sapphire glass measured by TRXPS. The profile of photoelectron intensity was observed to grazing incidence x-ray with C and Si. As the result, it is observed that the island structure of silane coupling compounds formed on the glass surface.

AS-WeP10 Electronic Structure of Carbon Nanotube Filled with Cs*, Y.J. Song,* ***H. Kim,*** Seoul National University, Korea*; G.-H Jeong, R. Hatakeyama,* Tohoku University, Japan*; Y. Kuk,* Seoul National University, Korea

As one of the most promising candidate materials for nanoelectronic devices,a carbon nanotube (CNT) has attracted much interest for its ideal electrical properties. The properties of a pristine CNTs are now well understood after studies with scanning probe microscope, transmission electron microscope, raman spectroscopy and transport measurements. CNTs can be semiconducting or metallic, but their electronic properties cannot be controlled since they are determined by uncontrollable chirality. Recently it has been suggested that the local modification of their electronic properties can be done by inserting or adsorbing various molecules into or on the side wall of CNTs. The modification of the local density of states can be utilized to produce nanometer-scale electronic devices. Filling metals into CNTs produce local metallic nanotubes. We have chosen to fill CNTs with Cs. We studied the geometric and electronic structures of these CNTs. The local change in the geometric structure implies the modification of CNT with Cs metal filling. That was confirmed by measuring the shift of the van Hove Singularities in scanning tunelling spectroscopy. Partially filled Cs metal chains in CNT seems to work as carrier dopants.

AS-WeP11 Investigation of Secondary Cluster Ion Emission from Self-Assembled Monolayers of Alkanethiols on Gold with TOF-SIMS*, S. Sohn, M. Schröder,* ***H.F. Arlinghaus,*** Westfälische Wilhelms-Universität, Germany

Self-assembled monolayers (SAMs) of alkanethiols on gold are ideal model systems for studying the emission processes of secondary ions from thin organic layers on metal substrates under keV ion bombardment. In this experimental study, we focus on the emission processes of gold-alkanethiolate cluster ions, which are not well understood yet. For this purpose we carried out time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements on SAMs of different alkanethiols CH@sub 3@(CH@sub 2@)@sub n@SH with various alkyl chain lengths (1 @<=@ n @<=@ 17) on gold substrates. The gold-alkanethiolate cluster ions Au@sub x@M@sub y@@super -@ with M = CH@sub 3@(CH@sub 2@)@sub n@S, 1 @<=@ x @<=@ 7 and x-3 @<=@ y @<=@ x+1 show intense peaks in negative mass spectra of all investigated alkanethiol SAMs under 10 keV Ar@super +@ bombardment. Around the corresponding peaks, a characteristic peak pattern of additional ions is observed. We analysed the contribution of different cluster ions formed by an attachment or a loss of up to five hydrogen atoms and their isotopy to the individual peaks of the peak pattern. We found two different types of gold-alkanethiolate cluster ions. The first type has only one parent ion, which has no hydrogen atom attached. The second type has two parent ions, one with no attachment of additional hydrogen atoms and another with one additional hydrogen atom. Moreover, we found a universally valid sum formula, which predicts the most intense peak in the peak pattern of gold-alkanethiolate cluster ions of all investigated alkanethiol SAMs.

AS-WeP12 Multivariate Statistical Analysis of Time of Flight Secondary Ion Mass Spectrometry Images, Looking beyond the Obvious*, V.S. Smentkowski,* General Electric Global Research Center*; J.A. Ohlhausen, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Analytical instrumentation such as Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provides a tremendous quantity of data since an entire mass spectrum is saved at each pixel in an ion image. The analyst often selects only a few species for detailed analysis; the majority of the data are not utilized. Researchers at Sandia National Laboratory (SNL) have developed a powerful Multivariate Statistical Analysis (MVSA) tool kit named AXSIA (Automated eXpert Spectrum Image Analysis) that looks for trends in complete data sets (eg. analyzes the entire mass spectrum at each pixel). A unique feature of the AXSIA tool kit is the generation of intuitive results (eg. negative peaks are not allowed in the spectral response). The robust statistical process is able to unambiguously identify all of the spectral features uniquely associated with each distinct component throughout the data set. GE and Sandia used AXSIA to analyze raw data files generated on an Ion Tof IV ToF-SIMS instrument. Select examples will be shown. The MVSA toolkit positively identified metallic contaminants within a defect in a polymer sample. These metallic contaminants were not identifiable using standard data analysis protocol. We will also demonstrate that the MVSA toolkit is able to analyze images collected using the burst pulsing mode. This work was funded in part under CRADA SC00/01609 PTS 1609.02 Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-WeP13 Surface Composition of Polyurethane Foams with Accelerated Aging*, J. Manzerova,* *D. Parsons,* University of Nevada, Las Vegas*; S.W. Yu,* Lawrence Berkeley National Laboratory*; D.W. Lindle, A.L. Johnson,* University of Nevada, Las Vegas

Polyurethane foams find broad application as structural and insulating (shock, electrical, etc.) materials. The long term stability of these materials are of particular interest. We have studied ReCrete and TDI types of polyurethane foams by means of the near edge x-ray absorption fine structure (NEXAFS) spectroscopy and the x-ray photoelectron spectroscopy (XPS). The foams were subjected to accelerated aging studies (60C and 80C under atmospheric conditions) for times up to 2 years. Systematic shifts in composition of the surface of the samples were found. Spectral assignments will be given and issues having to do with the variability of the surface of the polyurethane with temparature and environmental exposure will be addressed.

AS-WeP14 Field Emission Electron Spectroscopy of Clean and Oxidized Mo Single Tips*, X. Zhao,* *R.A. Outlaw, R.L. Champion, D. Manos, B.C. Holloway,* The College of William and Mary

We have constructed a multi-functional apparatus to characterize surfaces by ARAES, ARXPS, EELS and TDS both prior to and after, measurement of field emission spectra. The fine structure of field emission energy distributions, in concert with these adjunct surface analyses, provides information of both bulk band structure and localized electronic structure as a function of adsorbate uptake. This paper reports measurements of field emission spectra taken on a 10 nm radius Mo tip under UHV (~10@super -10@ torr), and as a function of exposure to controlled doses of CO and O@super 2@ . Effective work functions are extracted from Fowler-Nordheim plots and show variation over the range of gas dosage. Field emission theory with total energy representation (TED) is used to further interpret the spectra and to elucidate the effects of oxygen bearing adsorbates.

AS-WeP15 Optical, Structural and Electrical Characteristics of High Dielectric Constant Zirconium Oxide Thin Films Deposited by Spray Pyrolysis*, M.A. Aguilar,* CICATA-IPN, Mexico, Spain*; G. Reyna,* UAM-I, Mexico*; M. Garcia, J. Guzman,* IIM-UNAM, Mexico*; C. Falcony,* CINVESTAV-IPN, Mexico

High dielectric constant zirconium oxide thin films have been deposited on silicon substrates at temperatures from 400 to 600°C, using the spray pyrolysis technique. The films were deposited from two spraying solutions (0.033 and 0.066M) of zirconium acetylacetonate dissolved in N,N-Dimethylformamide. The as deposited films were stoichiometric, transparent and with a very low surface roughness (5-40Å). The films present a dielectric constant in the range from 12.5 to 17.5, depending on the experimental conditions. The films deposited at 500°C and with the 0.066M spraying solution can stand electric fields up to 3 MV/cm, without observing destructive dielectric breakdown. X ray diffraction as well as transmission electron microscopy measurements indicate that the films are polycrystalline. Infrared spectroscopy show the existence of silicon dioxide (SiO@sub 2@) in the films. Spectroscopic ellipsometry indicates that SiO@sub 2@ as well as ZrO@sub 2@ and c-Si comform a roughness layer located at the ZrO@sub 2@/Si interface. The presence of this interface layer, as well as the overall optical and structural characteristics of the films prepared, are probably responsible for the good dielectric characteristics observed on them.

AS-WeP16 Using MEMS Microarrays and Neural Networks to Identify Preferred Surface Chemistry in Application-Specific Gas Sensing*, Z. Boger,* *R.E. Cavicchi, D.C. Meier, C.B. Montgomery, S. Semancik,* National Institute of Standards and Technology

Surface chemical interactions between target analytes and sensing films are of primary importance in determining gas sensor performance. However, selecting the most appropriate sensing materials and conditions to detect certain analytes in different gas monitoring applications is very difficult. We present a novel approach for identifying well-suited thin film and surface compositions, preferred microstructures, and operating temperatures for conductometric gas sensing. It employs response databases measured from multi-element MEMS microarrays as well as artificial neural networks (ANN) signal processing. The array elements are microsensor platforms that contain varied sensing film types (TiO@sub 2@ and pure and surface-modified SnO@sub 2@), and can be programmed to operate individually at a variety of temperatures (20 °C to 500 °C), while the composition of test gases is changed. Recursive ANN pruning and re-training techniques are used to identify the more relevant inputs (materials, temperatures) for recognizing and quantifying a specific analyte in a given background. We describe several example cases involving pure and metal-dosed oxide films for: 1) recognition of 6 gases (H@sub 2@, ethanol and varied VOCs); 2) estimation of concentrations for binary mixtures of H@sub 2@, methanol and acetone in the 5-200 ppm (micromole/mole) range; 3) concentration estimation of chemical warfare agents (sarin, tabun, sulfur mustard) and simulants in the range of several ppb (nanomole/mole) to several ppm. Greatly reduced subsets of materials and temperatures, in the range of 3-15 out of a possible 80-1260 combinations, have been shown to carry the most effective analytical information. These selected interfaces and operating conditions provide a basis from which to understand, and then predict, the adsorption, desorption and reaction behavior that are critical to solid state transduction processes for varied classes of gaseous compounds.

AS-WeP17 Nitrogen Doped Carbon Nanoflake Field Emitter Synthesized by RFI PECVD on Patterned Nickel Catalyst Layer*, M. Zhu,* *J. Wang, R.A. Outlaw, X. Zhao, N.D. Theodore,* College of William and Mary*; V.P. Mammana,* International Technology Center*; B.C. Holloway, D. Manos,* College of William and Mary

This paper reports the synthesis of a novel morphological form of carbon, which we call carbon nanoflake (CNF), using high-density RF inductively coupled plasma enhanced chemical vapor deposition. We observe that CNF grows rapidly in contact with a Ni catalyst which has been created using a self-assembling nano-sphere lithographic method. Experiments were performed using mixtures of hydrocarbon feedstock (methane or acetylene) diluted in hydrogen to deposit CNF onto the Ni catalyst pattern lying either on a doped-Si wafer, or lying on 300 nm of SiO@sub 2@. The gas composition was varied systematically from 10% to 100 % hydrocarbon. Pressure and temperature were varied over a small range in the vicinity of p = 10@super -1@ Torr and T = 680°C. We have also performed CNF deposition under conditions to produce nitrogen-doped CNF. SEM images show that the carbon nanoflake has edges less than 10nm wide and that the surface morphology changes with gas composition. CNF structures appear to be robust and well-suited for potential applications in field-emission devices. Kelvin Probe measurements show that the contact potential (work function) of CNF is close to that of graphite. Raman spectra show that the ratio of D to G peaks is a function of the gas composition. The paper also reports field emission tunneling parameters extracted from Fowler-Nordheim I-V curves and field emission spectra (FES).

AS-WeP18 Microsensor Technique for Analyte Surface Coverage vs. Sensor Response Correlation*, A.G. Shirke,* *R.H. Jackson, B.G. Frederick,* The University of Maine*; R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology*; M.C. Wheeler,* The University of Maine

This paper presents results based on the combined use of a single microsensor platform (as a Temperature Programmed Desorption [TPD] device) with a sensitive, calibrated mass spectrometer that has a minimum detection limit of 10@super 10@ molecules/s. Desorption kinetics of model systems have been investigated as part of an effort to develop a technique for correlating the relative surface coverages of gas analytes to the electrical responses of chemical sensors. The pulsed-TPD technique takes advantage of the rapid heating characteristics of micromachined sensor platforms (called microhotplates) which are layered structures developed at NIST. Microhotplate sensors include a sensing film, electrodes, and a polysilicon heater all separated by insulator layers. Previous microheater desorption experiments utilized arrays with large numbers of devices to provide enough desorption flux for detection while maintaining the rapid heating rate (over 10@super 6@ K/sec) of the individual devices. Unlike the current experiments that use single microsensors, the large array studies did not explore conductance changes of sensing films. The model system described in this work, condensed benzoic acid on the microsensor surface, is used to evaluate the challenges involved in extension of the technique to actual sensor systems. The experiments were conducted at a base pressure of 5x10@super -10@ Torr, using a constant, directed-dosing arrangement for benzoic acid (vapor pressure: 7x10@super -3@ Torr at 300 K). A voltage pulse of 500 ms duration was used to heat the polysilicon heater to temperatures up to 700 K within approximately 3 ms while the isothermal desorption flux was monitored by the differentially-pumped mass spectrometer. Limitations and modifications in the data acquisition, sample mounting, and minimum detectable desorption flux are discussed along with the presentation of the desorption isotherms.

AS-WeP19 High Spatial Resolution XPS Analysis of Si Samples Prepared using the FIB Lift-out Technique*, J. Fenton,* *J.E. Fulghum,* University of New Mexico*; L.A. Giannuzzi,* FEI Company*; F.A. Stevie,* North Carolina State University

The FIB lift-out technique is increasingly utilized to prepare a wide variety of samples for SEM and TEM analysis, although there have been few studies of sample preparation-related changes in surface chemistry. The goal of this project is to assess the impact of Ga@super +@ contamination resulting from FIB lift-out preparation of Si. X-ray photoelectron spectroscopy (XPS) has become an increasingly useful characterization technique for such samples due to recent advances in imaging and small area analysis. The Ga distribution on the Si surface, and the impact of sample preparation on surface oxidation, were evaluated using high spatial resolution XPS. The SiO@sub 2@ thickness and uniformity were compared with Si from a control sample, which was not exposed to the FIB Ga@super +@ source. Both quantitative, high spatial resolution imaging and spectra-from-images methods were used to characterize Ga and SiO@sub 2@ distributions. These methods are required for accurate characterization of the FIB samples, as the samples are generally smaller than the areas analyzed using small area spectroscopy methods.

AS-WeP20 Ion Beam Alignment of Liquid Crystals on Polymer Substrates*, S. Pylypenko,* *K. Artyushkova, J.E. Fulghum,* University of New Mexico*; L. Su, L. West,* Kent State University*; Y. Reznikov,* Ukraine Academy of Science

Liquid crystal alignment is generally obtained through rubbing methods that require direct contact with the alignment surface. Non-contact methods could solve many of the problems that result from rubbing. One of the latest non-contact techniques for alignment of liquid crystals, ion beam alignment, has become a promising substitute for the conventional method based on mechanical rubbing. Although LCD prototypes have been fabricated using the ion beam alignment technique, there is incomplete understanding of both the macroscopic and microscopic alignment mechanisms. Organic and inorganic alignment layers were studied using X-ray Photoelectron Spectroscopy (XPS) and Polarized Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) to characterize chemical changes and surface anisotropy to the alignment substrate. The surface analytical characterization results have been correlated with measurements of liquid crystal alignment and pre-tilt angle measurement to enhance our understanding of non-contact alignment.

AS-WeP21 Relation between RF Breakdown and Particles Contamination on RF-Processed X-band Structures*, F. Le Pimpec, S. Harvey,* *R.E. Kirby, F. Marcelja,* SLAC

X-band accelerator structures meeting the Next Linear Collider(NLC) design requirements have been found to suffer damage due to Radio Frequency (RF) breakdown when processed to high gradients. Improved understanding of these breakdown events is desirable for the development of structure designs, fabrication procedures, and processing techniques that minimize structure damage. RF reflected wave analysis and acoustic sensor pickup have provided breakdowns localization in RF structures. Particles contaminant, after the clean autopsy of 3 RF-processed travelling wave structures, have been catalogued and analyzed. Their influence on RF breakdown will be discussed.

Biomaterial Interfaces
Room Hall A-C - Session BI-WeP
Poster Session

BI-WeP1 Locally Addressable Electrochemical Patterning Technology (LAEPT) using Poly(L-lysine)-g-Poly(ethylene glycol), PLL-g-PEG, *C.S Tang,* Swiss Federal Laboratories for Materials Testing and Research, Switzerland

Protein-resistant polyelectrolyte, poly(L-lysine)-g-poly(ethylene glycol) PLL-g-PEG adsorbs spontaneously onto a substrate with surface contrast constituting of conductive titanium and non-conductive silicon-oxide. An applied potential between -0.4 and +1.7V removes the PLL-g-PEG from titanium but simultaneously, there was insignificant polyelectrolyte loss on the silicon-oxide. X-ray photoelectron spectroscopy confirmed the reduction of PLL-g-PEG on the titanium surface and it also indicated that approximately similar amount of PLL-g-PEG remained on the titanium oxide when low corresponding positive and negative voltages of up to 400mV were applied. At 1.7V, time-of-flight secondary ions mass spectroscopy and fluorescence microscopy distinctly demonstrated the intensity contrast between the retention of PLL-g-PEG on the silicon-oxide and PLL-PEG removal from titanium. It is believed that the native oxide layer of titanium undergoes morphological changes with ascending potential and this affects the adhesion stability of PLL-g-PEG on the titanium oxide surface. Electrochemical impedance spectroscopy monitored the voltage-induced changes in the oxide layer whose measured impedance and resistance were found to decrease dramatically with increasing voltage. Further investigations hinted that diffusional-controlled processes within the oxide caused complex morphological changes, eventuating in an unstable adhesion platform for weak PLL-g-PEG electrostatic binding. The difference in the response of an applied potential on the titanium/silicon region under electrochemical conditions permits the exploitation and regeneration of various immobilization techniques on titanium while maintaining a protein resistant background on the non-conductive region. This reliable method offers prospects in selective electrochemical patterning for the biomedical as well as semiconductor industries. It will be termed here as locally addressable electrochemical patterning technology, LAEPT.

BI-WeP2 Simple Fabrication of Polymer Thin Films with Lithographic Bas-relief Micro-pattern and Self-organized Micro-porous Structure*, T.A. Ohzono,* *T. Nishikawa, M.A. Shimomura,* RIKEN, Japan

The cost of making micro scale components through conventional lithographic techniques increases depending on the degree of design complexity. Whereas, non-lithographic approaches have also been investigated extensively to reduce or replace the complicated process involved in those lithographic techniques. Therefore, it seems necessary to combine the good aspects of the self-organization process and of the conventional lithography toward the optimum productivity for fabrication of micro scale textures for some practical applications . Adopting such approach, here we show a very simple method for fabrication of a patterned polymer thin film with a hierarchical structure. The structure consists of a bas-relief pattern at tens of microns and the ordered array of pores with diameters of 4-5 µm. The former pattern is originally fabricated through conventional photolithography. The latter emerges from self-organized process, where micrometer-size water droplets condensed on the surface of evaporating solutions are spontaneously arranged. The film is self-supporting. It is possible to control by the polymer concentration whether the film is bottomless, partially bottomless, or not. The bio-compatible polymer of the lactic-acid can be used as the material. The film with the novel structure will enable us to do patterning of functional particles, of cells, and of bio-sensing elements toward new bio-coupled devices.

**BI-WeP3 Adsorption Kinetics of Alkanethiol Self-Assembly on Hydrogenated Ge(111)*, M.R. Kosuri,* *R. Cone, Q. Li, S.M. Han,* University of New Mexico*; C.B. Bunker, T.M. Mayer,* Sandia National Laboratories

We have investigated in situ and in real-time the liquid-phase self-assembly of 1-alkanethiols on hydrogenated Ge(111), using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The water contact angle measurements on thiolated Ge demonstrate that the final packing density is a function of both alkanethiol concentration in 2-propanol and the chain length of thiolate molecules. The absolute saturation coverage of 1-hexadecanethiol is approximately 4.2x10@sup 14@ cm@sup -2@ based on the IR absorbance of C-H stretching vibrational modes near 2900 cm@sup -1@. We also report the adsorption rate constant of 0.1 M 1-hexadecanethiol on hydrogenated Ge(111) at room temperature. The rate constant is 2.1 ± 0.6 cm@sup 3@/mol-sec, based on a Langmuir isotherm.

**BI-WeP4 Deposition of Lipid DPPC Monolayer on SiO@sub 2@ Surface using OTS Self-assembled Monolayer Islands as Anchor Molecules*, M. Takizawa,* *Y.H. Kim,* The Graduate University for Advanced Studies, Japan*; T. Urisu,* The Graduate University for Advanced Studies and Institute for Molecular Science, Japan

Bilayer lipid membranes (BLMs) supported on the gold surface are active research target from the viewpoint of application to the biosensors. It is reported that the stability of the membrane can be extended significantly by using the "anchor molecules", i.e. the synthesized thiolipid which is chemically anchored to the gold surface. In this work, we have examined for the first time the deposition of DPPC (dipalmitoyl phoshatidylcholine) monolayer on SiO@sub 2@ surface using OTS (n-octadecyltrichlorosilane) self-assembled monolayer (SAM) islands as anchor molecules. OTS SAMs have been deposited by dipping the Si (111) substrates with thermally oxidized SiO@sub 2@ surface layer into ~10 % toluene solution (containing small amount of water) at a room temperature. After deposition of OTS SAM island, the DPPC monolayer was transferred to the substrates by Langmuir-Brodgett method at the surface pressure of 35 mN/m. The height of the OTS SAM island measured by AFM was ~2 nm, which is consistent with a previous report. The surface morphology measurements by AFM after the DPPC transfer shows that the flat DPPC monolayer is deposited almost completely filling the (hydrophilic) SiO@sub 2@ surface area-selectively. On the (hydrophobic) OTS SAM island surface, on the other hand, DPPC monolayer deposition was not observed. Instead, small lumps of condensed DPPC molecules were observed on the surfaces and the edges of the OTS islands. The surface of the DPPC monolayer on the SiO@sub 2@ area was almost the same height as the OTS island surface. These results indicate that the OTS SAM island has a potential of effective anchor molecules in DPPC BLM depositions on SiO@sub 2@ surfaces.

**BI-WeP5 Characterization and Durability of Organosilane Self-assembled Monolayers on the Native Titanium Oxide Surface*, R.M. Lennen,* *R.A. Brizzolara,* NSWC, Carderock Division

Titanium is a common material of heat exchangers and seawater piping systems on U.S. Naval vessels, as well as a key biomedical implant material. Several different organosiloxane self-assembled monolayers (SAMs) have been prepared on cleaned and hydroxylated titanium surfaces and characterized with x-ray photoelectron spectroscopy (XPS), angle-resolved XPS, and contact angle measurements. Precursors include trichlorosilanes and trialkoxysilanes with a wide array of terminal functional groups. Perfluorinated SAMs and multilayers were tested for their durability in natural filtered seawater from Port Everglades, FL; artificial seawater; artificial seawater inoculated with the biofilm forming bacterium Deleya marina; and flowing seawater at Port Everglades under two flow velocities. The thermal stability of coatings formed from alkyltrialkoxysilane precursors on titanium was also investigated in ultrahigh vacuum. In the future, these self-assembled monolayers will be used to investigate biofilm adhesion as a function of critical surface tension. This will lead to the development of ultra-thin antifouling coatings for shipboard titanium heat exchanger tubes with seawater intake. This work was funded by the NSWC Carderock Division In-House Laboratory Independent Research program and the Office of Naval Research.

**BI-WeP6 Amine-Reactive Mixed Monolayers on Scribed Silicon with Controlled Levels of Functionality: The Reaction of Scribed Silicon with Epoxides*, M.R. Linford,* *Y.-Y. Lua,* Brigham Young University

Epoxides are important in industry and in bioconjugate chemistry because of their reactivity with amines, sulfhydryls, and other nucleophiles. Here we report a significant advance in the preparation of patterned and functionalized silicon surfaces by showing that epoxides readily react with scribed silicon to yield monolayers with even greater efficiency that was reported for 1-alkenes,@footnote 1@ 1-alkynes,@footnote 1@ 1-haloalkanes,@footnote 2@ and alcohols.@footnote 3@ Mixed monolayers were prepared from solutions of 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane to control the number of free epoxide groups at the surface. The amine reactivity of these surfaces increases as the fraction of 1,2,7,8-diepoxyoctane in the monolayers increases. The formation of monolayers occurrs by wetting a dry, oxide-coated or hydrogen-terminated silicon surface with a liquid epoxide or Î±,Ï‰-diepoxide and by scribing in the air with a diamond-tipped instrument or tungsten carbide ball. In addition to this fundamental work, we plan to discuss i) the formation of biotinylated surfaces through a reaction of epoxide surfaces with biocytin (a lysine-biotin complex) and DNA-containing surfaces (through a reaction with amine-terminated oligonucleotides), and ii) patterning of silicon with these coatings using an AFM tip.@footnote 4@ @FootnoteText@ @footnote 1@ Niederhauser, T.L.; Jiang, G.; Lua, Y.-Y.; Dorff, M.; Woolley, A.T.; Asplund, M.C.; Berges, D.A.; Linford, M.R. Langmuir 2001, 17, 5889-5900.@footnote 2@ Niederhauser, T.L.; Lua, Y.-Y.; Sun, Y.; Jiang, G.; Strossman, G.S.; Pianetta, P.; Linford, M.R. Chemistry of Materials 2002, 14, 27-29.@footnote 3@ Niederhauser, T.L.; Lua, Y.-Y.; Jiang, G.; Davis, S.D.; Matheson, R.; Hess, D.A.; Mowat, I.A.; Linford, M.R. Angew. Chem. Int. Ed. 2002, 41(13), 2353-2356.@footnote 4@ Wacaser, B.A.; Maughan, M.J.; Mowat, I.A.; Niederhauser, T.L.; Linford, M.R.; Davis, R.C. Applied Physics Letters 2003, 82(5), 808-810.

BI-WeP7 Molecular Engineering of Surfaces for Sensing and Detection*, C.L. Boozer, J. Ladd, A. Taylor,* ***Q. Yu****, J. Homola, S. Jiang,* University of Washington

There is an urgent demand for developing sensors capable of quantitative and simultaneous detection, identification, and monitoring of multiple analytes in complex media for various applications ranging from homeland security and medical diagnostics to food and environmental monitoring. Immunological detection with antibodies is perhaps the only technology that has been successfully employed for the detection of bacteria, viruses, proteins, and low-molecular-weight compounds. In this talk, we will discuss our recent effort on molecular engineering of surfaces for sensing and detection. First of all, control of antibody orientation is achieved on charged surface assembled monolayers (SAMs). Antigen is used to probe antibody orientation measured by surface plasmon resonance (SPR) biosensor while direct evidence of preferred antibody orientation is provided by the time-of-flight secondary ion mass spectrometry. Second, it was shown in our previous work that the behavior of protein adsorption depended on nano-scale structures of a surface with which proteins interact. Polyethylene glycol (PEG) SAMs are used as a model surface to study surface resistance to protein adsorption. Atomic force microscopy/scanning tunneling microscopy (AFM/STM), SPR and molecular dynamics simulation techniques are used in such studies. Results show light on molecular-level understanding of non-fouling mechanism. Third, a new DNA-based protein immobilization method has been developed for use with SPR biosensors. This DNA-based immobilization method provides a convenient and versatile for multi-channel biosensors. We will demonstrate the quantitative and simultaneous detection of various analytes ranging from larger-sized to small-molecular weight analytes (e.g., E. coli, SEB, and simazine) in complex matrices (e.g., milk and ground beef) based on this new platform. Finally, we achieved single-molecular detection of immunoreactions using an AFM-based sensor.

**BI-WeP9 Multilayers of Functionalized Liposomes for Improved SPR Analysis of Transmembrane Proteins*, A. Granéli,* *F. Höök,* Chalmers University of Technology, Sweden

The cell membrane consists of a large fraction of transmembrane proteins, which mediates and performs a large number of reactions taking place in the cell membrane or at the cell membrane surface. All transmembrane proteins consist of a hydrophobic part that transverse the bilayer, which make most of them insoluble in water and therefore difficult to study. Accordingly, functional studies of individual transmembrane proteins generally require dissolving or reconstituting procedures, such as the use of detergents or incorporation in lipid assemblies such as proteoliposomes. In biosensing applications, including drug screening and medical diagnostics, as well as for fundamental studies of transmembrane proteins, surface-based techniques have turned out to be important analytical tools. Application of such techniques require that the proteins are immobilized on a solid surface, which often tends to have a negative influence on the protein activity. The necessity of having the transmembrane proteins residing in lipid membranes complicates immobilization of sufficient amounts of protein. To allow the use of surface analytical tools for studies of transmembrane proteins, protocols that enhance the amount of immobilized protein, thus the signal, are required. For that purpose, we have developed a strategy where multilayers of proteoliposomes are immobilized on Au or SiO@sub 2@ surfaces, proven versatile for studies of ligand-interaction kinetics using the quartz crystal microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR) techniques. This was achieved by utilizing a DNA-modified surface, to which proteoliposomes modified with complementary DNA was immobilized; a process that was possible to repeat up to at least 6 layers, thus allowing the use of the full sensing depth of QCM-D and SPR. Signal-amplification using the liposome multilayer approach was proven via dissociation or binding from/to the transmembrane protein transhydrogenase.

BI-WeP10 Surface Physico-Chemical Studies of Immobilised Oligonucleotides*, P-C.T. Nguyen*, *S. Kumar,* University of South Australia, Australia*; M. DeNichilo,* TGR BioSciences, Australia*; N. Voelcker,* Flinders University of South Australia, Australia*; H.J. Griesser,* University of South Australia, Australia

Single-stranded oligonucleotides can bind nucleic acid targets as well as other targets such as small molecules, peptides, proteins and cells. Compared to antibodies, the selectivity, specificity and affinity of oligonucleotides are equal and often superior. Thus, surface-immobilised oligonucleotides have become attractive choices as recognition elements in microarrays for high throughput, parallel and multidimensional analysis in biomedical diagnostics, and aptamers are increasingly replacing antibodies as molecular recognition elements. So far, most of the research involving oligonucleotide probes has focussed on end applications for the life sciences, with some work on fundamental aspects of surface immobilisation and target binding to immobilised oligonucleotides. In order to harness the apparent power of such arrays, a more detailed physical and chemical understanding is required, in addition to optimising the immobilisation process. Contributing factors include substrate, oligonucleotide structure, immobilisation chemistry and surface density of immobilised oligonucleotides. Our focus is to characterise and optimise the density of immobilised oligonucleotides, and measure hybridisation efficiency for a specific choice of substrate, oligonucleotide, and immobilisation chemistry. Glass and silicon are the most commonly used substrates but we are extending immobilisation to polymeric carriers. XPS, ToF SIMS and AFM are used to surface characterise the substrate and attached oligonucleotides. Using principles of surface science we study molecular interactions between oligonucleotide chains, and the effects that the structure and packing density of the oligonucleotide coating have on hybridisation, assessed by MALDI-ToF-MS. It is expected that oligonucleotide density will have a direct bearing on activity and steric availability for hybridisation.

BI-WeP11 Characterization of DNA Microarrays*, D. Barbash*, *J.E. Fulghum, Y. Wu, G.P. Lopez,* University of New Mexico

DNA microarrays are widely used for gene expression studies. Production of DNA microarrays includes attachment of single stranded DNA or oligonucleotides onto a variety of different substrata. Methods that are used include directed synthesis of oligonucleotides by photolithography and printing pre-existing cDNA using precision robots. Substrates available for immobilization are gold, modified glasses (aminosilane or polylisine) and filter membranes. There are multiple functional groups in DNA that are capable of attachment the surface to the substrate. The purpose of our study is to reveal the chemistry behind DNA attachment to surfaces. We are using the ATMS(p-aminophenyl trimethoxy silane)/diazotization method to spot oligonucleotides on a microscope glass surface.(Dolan, P.L. et al. Nucleic Acids Research 2001, 29, 21e107). This method include immersion of cleaned microscope glass into the ATMS solution, its activation by NaCl and HCl and spotting DNA onto it. The method results in robust covalent attachment of the DNA in a manner that is compatible with subsequent hybridization.The methods for studying attached nucleotides include X-ray Photoelectron Spectroscopy (XPS) and Attenuated Total Reflection Spectroscopy (ATR-FTIR). XPS allow us characterize the surface composition from less than 10nm depth while ATR-FTIR technique provides chemical information from up to 1mm of the surface.

BI-WeP12 DNA-Based Protein Immobilization vs. Biotin/Streptavidin Bridges*, C.L. Boozer*, *J. Ladd, Q. Yu, S. Chen,* University of Washington*; J. Homola,* Institute of Radio Engineering and Electronics, Czech Republic*; S. Jiang,* University of Washington

A new DNA-based protein immobilization method has been developed for use with SPR biosensors. This DNA-based immobilization method provides a convenient and versatile alternative to the commonly used biotin/streptavidin platform, with comparable, if not better, sensitivity. This work presents a comparison of these two platforms, focusing on the detection of hCG as a model system. Our results show that the DNA-based method allows for detection of lower hCG concentrations. Extensive control experiments have been performed to check both sensor platforms for non-specific binding and cross reactivity. In addition to the increased sensitivity, the DNA-based protein immobilization offers many other advantages crucial to biosensor development that the biotin/streptavidin platform does not have. While both the biotin/streptavidin complex and the DNA-based approach are robust and highly specific, the DNA based approach is much more versatile.

BI-WeP13 Molecular Simulation of Mixed SAMs Including Thiolated DNAs on Gold (111) Surfaces*, J.P. Sullivan*, *S. Jiang,* University of Washington

The ability to tether DNAs to a solid support has yielded a variety of practical technologies including DNA microarrays and DNA based biosensors. Yet in spite of the rapid advances of surface tethered DNAs in biotechnological applications, improvements to these technologies are made through a painstaking combinatorial process that suffers from a lack of mechanistic understanding. It has been shown that the hybridization of ssDNA SAMs can be affected by the introduction of a non-DNA terminated thiol as a diluent. Experimentalists in our group, for example, are using oligo-ethylene glycol (OEG) terminated thiols along with thiolated ssDNA to form mixed SAMs on gold (111). Speculation has been unable to yield a predictive tool for which diluent length and density will have the best impact on a given DNA probe. Accordingly, we turned to simulation to provide atomic resolution images of these mixed SAMs, revealing information that could not be intuited. All simulations were carried out in explicit solvent with Na+ to balance charge, and NaCl to control ionic strength. The CHARMM27 all-atom potential force field was used to model the DNAs, while the TIP3P potential was used for water interactions. The OEGs were treated using a SJY force field with demonstrated accuracy for OEG-thiols. We present results for the packing of pure DNA SAMs (both single and double stranded, of varying sequence lengths and compositions, and at different ionic strengths). The pure SAM packing results were then used to set up simulations of DNA SAMs mixed with oligo-ethylene glycol at varying diluent lengths (number of repeat units) and densities, for which results are also reported. These results will be instrumental in developing theory-based methods for selecting diluents and diluent densities. This will reduce or eliminate the trial and error process involved in determining diluent properties for the countless possible DNA probes that do not already have optimized diluents.

BI-WeP14 Vacuum-Based Diagnostics of Aqueous Microenvironments Using Evaporative Micro-Orifice Technique*, T.M. Valentine*, *J.J. Park, G.W. Rubloff,* University of Maryland

While gas and surface chemical analysis techniques can be applied to aqueous systems (e.g., electrospray mass spectrometry), the high surface/volume ratio of bioMEMS environments places a premium on biochemical characterization directly at or within the microfluidic system. We are exploring the direct sampling of the aqueous microenvironment via a micron-scale evaporative orifice which couples the microfluidic system to vacuum-based chemical analytical tools. Considering a variety of coupling designs, simulations indicate the possibility to observe volatile species (dissolved gases such as O@sub 2@, CO@sub 2@, and VOC's), metabolic activity of microorganisms, and nonvolatile species ejected as a consequence of microfluid dynamics at the sampling orifice. For orifice sizes up to 30 µm, differential pumping by the vacuum system will maintain sufficiently low pressures for operation of the vacuum analysis instruments. Considering the large water background and typical mass spectrometry sensitivity (200 ppb), simulations indicate that signals should be measurable from bacterial CO@sub 2@ and VOC evolution. Given flow rates 1-100nL/min at the orifice, ejection and measurement of nonvolatile organic species (proteins, biopolymers) should be possible at concentrations of biological interest. An experimental testbed has been developed to integrate aqueous environments with appropriate vacuum sensing equipment. Results of testing the experimental setup under various conditions, confirming and calibrating the simulation, and expanding the evaporative-orifice concept to integrate microfluidic devices being developed in parallel will be discussed. This effort was undertaken as a senior thesis project with the assistance of a 2003 AVS Undergraduate Research Award.

**BI-WeP15 Effects of Surface Treatment and Curing Conditions on Poly(Dimethylsiloxane) Metallization for Retinal Prosthesis*, M. Maghribi,* *C. Evans, K.J. Wu, A.J. Nelson,* Lawrence Livermore National Laboratory

Surface properties have a critical impact on the general performance of polymers and elastomers. Surface contamination, such as siloxane surfactants, can alter the surface properties of the material thus affecting the fabrication processes. Inadequately cured poly(dimethylsiloxane) (PDMS) is highly mobile and can cause adhesion failures. In this work we explore how surface treatments and PDMS cure time impacts process development for hybrid retinal implants. For example, oxygen plasma treatment is used to promote wetting of the PDMS surface as well as promoting adhesion. To photolithographically pattern metal traces on PDMS is not a trivial task and fundamental material characteristics must be examined to develop reliable and repeatable fabrication processes. Time of flight secondary ion mass spectrometry (ToF-SIMS) and high resolution X-ray photoemission spectroscopy (XPS) were utilized to reveal the surface chemistry attributed to different surface treatments and curing conditions. ToF SIMS results indicate that the basic molecular and chemical structure of poly(dimethylsiloxane) is altered under O@sub 2@ treatment. Specifically, a strong oxidation reaction to the dimethlysiloxane group occurs, replacing methyl with silanol groups; which is ultimately responsible for the success in metallization. XPS quantitative analysis revealed an oxygen rich surface with significantly increased Si-O bonding. In addition, high-resolution C 1s, O 1s and Si 2p core-level spectra revealed additional C-O and O-Si-O bonding following O@sub 2@ plasma treatment. We conclude from these results that the explanation for the affinity of metals to adhere to the PDMS following O@sub 2@ plasma treatment is due to the reactive Si-O group formed on the surface. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

BI-WeP16 Bioactivity of Titanium Coatings Prepared by Reactive Plasma Spraying*, M. Inagaki,* *Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

A simple treatment method using radio-frequency reactive plasma spraying (rf-RPS) was studied to induce bioactivity of titanium (Ti) coatings. Ti coatings were deposited on Ti substrates by a rf-RPS method using a thermal plasma of Ar gas containing 1-6% N@sub 2@ and/or O@sub 2@ at a input power of 16 kW. Ti powders impregnated with calcium were also sprayed. Composition change of coating's surface during soaked in a simulated body fluid (SBF)@footnote 1@ was examined by micro Fourier transform infrared spectroscopy and thin film X-ray diffraction. Ti coatings prepared with Ar-O@sub 2@ and Ar-N@sub 2@-O@sub 2@ plasma formed apatite after 3 days of soaking in 40 ml SBF. This indicates that such coatings have the ability to form a biologically active bone-like apatite layer on the surface. In the XRD patterns for both Ti coatings, minute peaks ascribable to TiO@sub 2@ (anatase and rutile phase) were commonly observed. On the other hand, composition change of coating's surface cannot be observed for Ti coating sprayed with pure Ar and Ar-N@sub 2@ plasma after 7 days of soaking in SBF. The 0.05-0.2 mol% impregnated Ti coatings prepared with Ar-O@sub 2@ and Ar-N@sub 2@-O@sub 2@ plasma formed apatite after 7 days of soaking in SBF. Thus it seems that calcium impregnation into Ti powders somewhat inhibited to form apatite at surface of coatings. Ti coatings with Ar-N@sub 2@-O@sub 2@ plasma gave excellent adhesion to substrate, whereas Ti coatings with Ar-O@sub 2@ plasma gave poor adhesion. Therefore, surface modification of Ti splat by Ar-N@sub 2@-O@sub 2@ plasma is an effective method to provide excellent adhesion and bioactivity for plasma sprayed Ti coatings. @FootnoteText@ @footnote 1@HM Kim, F. Miyaji, T Kokubo, T Nakamura, J. Biomed. Mater. Res 45, (1999)100-107.

BI-WeP17 RF Plasma Deposition of Acrylic Acid Thin Films: Relationship between Plasma Charaterisation and Films Physicochemical Properties*, N. Rossini, A. Valsesia, G. Ceccone, P. Colpo,* ***F. Rossi,*** Joint Research Centre, Italy

Acrylic acid thin films have been deposited by continuous and pulsed RF capacitive discharge. In situ diagnostics (Langmuir probe, Mass spectrometry and Self Excited Electron Resonance Spectroscopy) are used for the different plasma conditions to analyse the framentation processes and identify the species contributing to the growth of the film. The composition and physico chemical properties of the films are analysed with FTIR, XPS, contact angle and Quartz Crystal Microbalance with Dispersive mode. Relationship with plasma characterisation is established. Experimental conditions leading to high concentration of COOH functionalities as well as films stability are determined.

Homeland Security Topical Conference
Room Hall A-C - Session HS-WeP

Poster Session on Science & Technology for Homeland Security

HS-WeP1 Testing Air Jets as Trace Explosive Particle Removers*, R.A. Fletcher,* *J.G. Gillen, E.S. Windsor, G.A. Klouda,* National Institute of Standards and Technology

Detection of trace explosive particles is vital to airport security. One of the key steps in detecting explosive particles is the removal of the particles from the surface that they reside. This can be accomplished by swiping the surface or by energetic disruption such as an air jet that will provide enough force to overcome the particle attachment due to van der Waals forces. Our initial experiments are following the experiments of Phares et al.@footnote 1@ and Smedley et al.@footnote 2@ for polystyrene latex spheres on smooth surfaces. We are utilizing fluorescence tagged spheres of various diameters that we can image through an optical fluorescence microscope. Images of fluorescent particles are captured and recorded before an air jet interrogates the sample. Particle removal is seen in live time; the particles that are not removed from the surface are captured in a subsequent image. Image processing allows us to quickly determine the size distribution the particles that have been removed and the ones that remain. By using polydisperse spheres, we can detect the particle release threshold for a given jet condition in terms of particle diameter. A second study is under way to examine the efficiency of removal for actual high explosives from characteristic surfaces like clothing and luggage. A test substrate is mounted in a small vertically oriented laminar flow wind tunnel. The airflow in the tunnel is hepa filtered to remove all particles greater than 0.3 um diameter. An air jet is used to remove particles from the test surface. The size distribution of the removed particles is determined in real time using a particle detector mounted down stream that works on the basis of measuring particle impact energy. Results from both experiments will be presented.@FootnoteText@@footnote 1@Phares, D.J. et al. J. Forensic Sci. 2000:45;(4) 774-784. 2. Smedley, G.T. et al. Exper. In Fluids 1999:26, 324-334.

HS-WeP2 Temperature-Dependent micro-Raman Study of Some High Explosives*, E.S. Etz,* *S.V. Roberson, G. Gillen,* National Institute of Standards and Technology

In collaboration with the Transportation Security Agency, NIST has initiated a chemical metrology program that will support the nationwide operational deployment and utilization of trace explosives detection devices. The project critically examines the analytical methodology whereby collections of micrometer-sized high explosives (HE) particles undergo thermal vaporization at the front-end of an ion-mobility spectrometer (IMS), leading to sample detection and identification. We have started to examine this front-end process in detail with a focus on particle transport and HE thermalization-vaporization for the IMS detection system. Of interest here is the temperature behavior and the thermochemistry of the analyte HEs in the temperature regime leading to the melting point, and beyond to the vapor phase. To understand the fragmentation and decomposition of HEs, we are using Raman microspectroscopy to study the particle spectra of relevant HEs heated to their melting temperature, and beyond, on a microscope hot-stage. The spectra are examined for (i) shifts in the peak frequency of Raman bands, (ii) temperature-induced changes in the spectral halfwidth and asymmetry of bands, (iii) changes in the relative intensities of bands and (iv) the presence of decomposition products. The spectra are acquired with a commercial Raman microprobe utilizing 514.5, 532, and 785 nm excitation. Discussed are the results obtained for the explosives TNT (m.p. 80.7 °C), PETN (m.p. 141.3 °C), RDX (m.p. 204 °C), and the plastic binary composites Semtex and C-4. The spectra show considerable changes as the sample is ramped up to the higher temperatures. These changes take on various forms, including substantial peak shifts to lower frequencies, band broadening with lowering of symmetry, and pronounced relative intensity changes. These spectral manifestations are correlated with the structural and compositional changes of these organic samples.

HS-WeP4 Vapor Preconcentration during Explosive Detection: Study of Variables in a NIST Standard Test System*, R.M. Verkouteren,* National Institute of Standards and Technology

The reliable detection of ever-decreasing levels of explosives constantly challenges the public safety and analytical communities. The total absence of false negative responses is required while minimizing the rate of false positive responses. While much progress has been achieved, further significant improvements in methods may be enabled by the systematic study of the total measurement process, especially near the limits of detection. Fundamental data from such studies are needed by system designers, instrument manufacturers, and public safety officials in improving the sensitivity and specificity of portal screening systems, while balancing the human dimensions that include ease of use, speed of analysis, detection risk tolerance, personal invasiveness, and profiling decisions. Described will be a NIST standard test system and preliminary flash desorption experiments, designed to investigate variables affecting the efficiency of one segment of explosive detection: the preconcentration stage. The standard test system was built to enable robust monitoring and control over static and dynamic temperature regimes and gas flow, and was designed to allow modifications in the configuration of components. We intend that this system be used to compare reliably the relative performances of materials, configurations, and methods, and to provide a benchmarking reference to enable measured improvements to technology. In the NIST system, a known quantity of sample is introduced onto a metal felt collector, which is then desorbed into a gas stream by resistive heating and monitored by IR thermography. The vapors released are then trapped on a second metal felt collector, the temperature of which is controlled by a thermoelectric cooler. The amount of trapped sample is determined by off-line quantitative methods. Factorial experimental design will be discussed as an effective tool to investigate a large number of variables in a limited number of experimental runs.

HS-WeP5 Chemical-Biological Nanosensors*, N.L. Jarvis,* Edgewood Chemical Biological Center*; A.W. Snow,* Naval Research Laboratory*; H. Wohltjen,* Microsensor Systems, Inc.*; **R.R. Smardzewski,*** Edgewood Chemical Biological Center

A new class of nanometer-scale, low power, solid-state devices is being investigated for the detection of hazardous vapors. These chemical vapor sensors are comprised of nanometer-sized gold particles encapsulated by monomolecular layers of alkanethiol surfactant deposited as thin films on interdigitated microelectrodes. These new, alkylthiol-stabilized, gold nanocluster materials are appropriately categorized as metal-insulator-metal ensembles (MIME). When chemical (agent, hazmat) vapors reversibly absorb into these thin MIME films, a large modulation of the electrical conductivity of the film is observed. The measured tunneling current between gold clusters is extremely sensitive to very small amounts of monolayer swelling or dielectric alteration caused by absorption of vapor molecules. For chemical agent simulants, a large dynamic range (5-logs) of sensitivities is observed and extends down to well below sub-ppm vapor concentrations. Tailored selectivities of the sensors are accomplished by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. Current research efforts are focused on examining the molecular mechanism(s) of conduction and mapping the selectivity and sensitivity of sensor elements. Targeted applications include: low-cost, low-power CB agent sensors, filter residual life indicators and orthogonal detector applications.

HS-WeP6 A Portable GC with a Nanosensor Array Detector*, **A.W. Snow,*** Naval Research Laboratory*; H. Wohltjen,* Microsensor Systems, Inc.*; N.L. Jarvis,* U.S. Army Edgewood Chemical and Biological Center

Development of portable rapid-screening analytical methods/instrumentation for the detection of chemicals identified by the Chemical Weapons Convention (CWC) as associated with the production and use of agents is an activity of interest to homeland security as well as to CWC inspection capabilities. The instrument described in this presentation consists of a temperature programmable gas chromatograph combined with a novel detector array based on gold nanocluster chemresistors.@footnote 1,2@ In this configuration peaks eluting from the GC are "fingerprinted" by the detector array using an on-board pattern recognition computer and an on-board library look-up. The thermoelectrically cooled array detector is very compact, works with any carrier gas, and uses minimal power. The array detector consists of four interdigital microelectrodes coated with different gold nanocluster materials. This device structure is called a "MIME" device (a pneumonic for Metal-Insulator-Metal Ensemble which reflects the electron transport through the organic monolayer shells encapsulating the metal cores of adjacent nanoclusters). Absorption of vapors into the insulating ligand shell surrounding the core produces a change in conductivity that is interpreted as a GC detector signal. The vapor sensitivity, selectivity and response time of each MIME device in the array are dependent on the composition, molecular structure and thickness of the ligand shell resulting in the array detector having a unique pattern for a particular analyte or interferent. Numerous candidate materials were evaluated for their effectiveness in the detection of organophosphorus compounds and other chemicals associated with the production of chemical weapons. @FootnoteText@ @footnote 1@ H. Wohltjen and A.W. Snow, "Colloidal Metal-Insulator-Metal Ensemble Chemiresistor Sensor", Anal. Chem. 1998, 70, 2856.@footnote 2@ A.W. Snow, H. Wohltjen, N.L. Jarvis, "MIME Chemical Vapor Microsensors", NRL Review, 2002, 45.

HS-WeP7 A Rapid Optical Assay for the Detection of Bioterriorism Agents Using Thin-Film Technology*, **S.C. Francesconi,*** Nova Research, Inc.*; A.M. Churilla,* Naval Research Laboratory

Rapid, field analysis of environmental samples for the presence of biological agents is important in both military and civilian law enforcement and public health applications. Development of assay formats, useful in these settings must be easy to operate and interpret. Additionally, the assay must be highly sensitive yet yield a low rate of false positive results. To this end, we have modified a commercially available, thin-film format to develop an assay capable of detecting multiple biological agents, simultaneously. The current assay is capable of simultaneously detecting ricin, botulinum toxin and anthrax, plus negative and positive controls, simultaneously in less than 30 minutes. The assay is performed on disposable silicon nitride wafers spotted with capture antibody specific to target agents. Samples, mixed with enzyme-coupled detector antibody are exposed to the capture antibody-spotted wafers. Exposure of the wafer to enzyme substrate results in a thin-film. Final detection of agents, therefore, is creation of a change in refractive properties of the wafer spots yielding a visible color change proportional to the amount of antigen originally present in the sample. The assays perform well using a number of sample matrixes including tap water, sea water or oily water. Further, the assay can be expanded to include additional target agent detection capability.

HS-WeP8 Detection of Nucleic Acid Hybridization by Infrared Absorption Spectroscopy*, **K. Miyamoto**, Y. Kimura, H. Ishii, M. Niwano,* Tohoku University, Japan

Biotechnology and medical diagnostics are currently in need of devices able to quickly and selectively detect biological molecules. DNA chip technology has gained considerable interest because of its importance to disease diagnostics, mutation detection, gene discovery, and so on. DNA chips facilitate the detection of specific DNA fragments (target DNA) by hybridization with a complementary strand (probe DNA). In conventional DNA chips, probe DNA that is immobilized on a solid substrate such as glass, are hybridized with fluorescently-labeled target probes, and the hybridization is measured with a laser scanner. However, if hybridization were in-situ monitored by spectroscopic tools, fluorescent label would be unnecessary. We propose an alternative method of monitoring hybridization of nucleic acids using infrared absorption spectroscopy in the multiple internal reflection geometry (MIR-IRAS). Since hydrogen bonding plays an important role in the hybridization of nucleic acids, we have investigated how hybridization induces spectral changes in the C=O and N-H stretching vibration regions of DNA. Results of ab-initio calculations demonstrate that changes in vibration frequency of the C=O stretching and N-H scissors modes are induced due to the base pairing of Guanine and Cytosine. We show the possibility of high-sensitive detection of DNA hybridization using MIR-IRAS.

Magnetic Interfaces and Nanostructures
Room Hall A-C - Session MI-WeP

Poster Session

MI-WeP4 Magnetic and Structural Properties of Fe@sub 3@Pt/Fe Thin Films*, **M.A.I. Nahid**, T. Suzuki,* Toyota Technological Institute, Japan

Recently hcp phase of Fe@sub 3@Pt is stabilized by e-beam evaporation which shows 6-fold in-plane magnetic anisotropy (K@sub in@) of the order of 2x10@super 5@erg/cc.@footnote 1@ However it does not show significant perpendicular magnetic anisotropy (K@sub per@).Theoretical calculation by A. Sakuma predicts that uniaxial anisotropy is expected in a Fe@sub 3@Pt/Fe system.@footnote 2@ Therefore it is investigated the magnetic properties of Fe@sub 3@Pt/Fe system in conjunction with structure. The thickness of Fe underlayer(d) was varied from 0-300Å. The hcp phase of Fe@sub 3@Pt thin films has been synthesized onto Al@sub 2@O@sub 3@(00.1) substrate using Fe underlayer by e-beam evaporation at deposition temperature 400°C. The epitaxial relationship is found as Al@sub 2@O@sub 3@(00.1)[10.0]||Fe(110)[1-10]||Fe@sub 3@Pt(00.1)[11.0]. The superlattice peak (00.1) intensity of Fe@sub 3@Pt changes with Fe underlayer thickness and becomes maximum at the 100Å. The 6-fold symmetry of Fe@sub 3@Pt was observed in the so called @PHI@-scan measurement when the X-ray is irradiated at the grazing angle. From the perpendicular hysteresis loop of Fe@sub 3@Pt measured by MO polar kerr instrument, the coercivity and remanence is found to increase with Fe thickness and becomes constant after d=200Å. This suggests that a perpendicular magnetic anisotropy (K@sub per@) exists in the Fe@sub 3@Pt thin films by using Fe underlayer. The maximum K@sub per@ is about 3x10@super 6@erg/cc at d=100-150Å. Besides the K@sub per@, the Fe@sub 3@Pt films possess the 6-fold in-plane magnetic anisotropy (K@sub in@) which increase with increasing d and become constant after 200Å. The maximum K@sub in@ of Fe@sub 3@Pt is obtained about 3.2x10@super 5@erg/cc which is much larger than that of Co.@footnote 3@ @FootnoteText@ @footnote 1@M.A.I. Nahid and T.Suzuki: Accepted for publication in the IEEE trans. on Magn. Sep,2003. @footnote 2@A.Sakuma: J. Phy. Soc. Japan. 64,4317(1995). @footnote 3@Y. Kadena: J.Sci. Hiroshima Univ.31,21(1967). .

MI-WeP5 Ultrafast Laser Measurements of Electron and Spin Dynamics in Half-metallic CrO@sub 2@ Thin Films*, **H. Huang**, K. Seu, A.C. Reilly,* College of William and Mary*; W.F. Egelhoff, Y. Kadmon,* National Institute of Standards and Technology

Half-metallic ferromagnets are an important class of materials in which one spin state is conducting while the other has a semiconductor-like gap. While evidence of half-metallic behavior has been found, there are still many questions regarding the bandstructure and dynamics in these materials. Ultrafast laser pump-probe techniques have shown great promise for elucidating such information in a variety of materials. Recently, such pump-probe techniques have been applied to study spin dynamics@footnote 1@ in Sr@sub 2@FeMoO@sub 6@ and coherent magnetization rotation@footnote 2@ in CrO@sub 2@. We will present measurements of charge and spin dynamics in half-metallic CrO@sub 2@ thin films by ultrafast laser pump-probe reflection, transmission and MOKE experiments as a function of temperature and energy (wavelength). We find that the pump-probe reflection and transmission consist of components simlar to those seen in the other half-metallic systems such as LCMO and Sr@sub 2@FeMoO@sub 6@: An initial fast peak which decays within ~ 1 ps, and a longer component with a rise of ~ 10 ps and a decay time of ~ 500 ps. This may indicate similar mechanisms for these systems. We attempt to correlate the temperature dependence with the two-order-of-magnitude increase in resistivity with temperature that is taken as a signature of the half-metallic behavior. The wavelength dependence is used to explore the bandstructure. For example, we observe different electron and spin dynamics for excitation energies of 1.5 eV and 3 eV, corresponding to the energies of excitation within the conducting spin-up band and across the gap for the spin-down state. @FootnoteText@ @footnote 1@T. Kise et al., Phys. Rev. Lett., 85, 1986 (2000). @footnote 2@Qiang Zhang et al., Phys. Rev. Lett., 89, 177402 (2002).

MI-WeP7 Spin-polarized Scanning Tunneling Microscopy Study of Ferromagnetic Arrays Fabricated by In-situ Alumina Shadow Mask*, **J.H. Choi**, T.-H. Kim, S.H. Kim, Y. Kuk,* CSNS and Seoul National University, Korea

Spin-polarized scanning tunneling microscopy(SPSTM) can detect the local electron spin density of the sample surface in atomic resolution, so it has been used to study magnetic properties of ferromagnetic materials. However, SPSTM study of patterned nanomagnetic arrays has not been done because all the fabrication process of nanomagnetic arrays must be done in-situ in UHV chamber to avoid contamination problems. We fabricated a shadow mask for in-situ SPSTM study of nanomagnetic arrays on Si wafer. 500nm thick aluminum was thermally evaporated on Si wafer and indented by SiC mold to produce an ordered pore of porous alumina. The sample was electrochemically anodized in oxalic acid. After pore widening and removing barrier layer, we opened 5x5mm@super 2@ window on backside Si substrate by photolithography and etched Si wafer completely using deep silicon etch process until the aluminum layer was appeared. Fabricated shadow mask was mounted in front of Si substrate in UHV chamber. Fe was evaporated on a Si wafer through shadow mask, forming nanomagnetic arrays of 30-80nm dia. The magnetic properties of ferromagnetic arrays studied by SPSTM will be discussed.

MI-WeP8 Properties of Self-assembled Nanowires Fabricated using Glancing Angle Deposition*, **H. Alouach**, G.J. Mankey,* University of Alabama

The spin-dependent transport in nanoscale spin electronic devices, such as Current Perpendicular to the Plane Giant Magnetoresistive (CPP-GMR) devices, is closely dependent on the spin arrangement and physical properties of single wires. Self-assembled Cu and permalloy nanowires were deposited using glancing angle electron beam evaporation technique with and without substrate rotation. Wire texture and crystallographic orientation of such features are known to be strongly dependent on the deposition parameters. We report an unprecedented and efficient method allowing determination of the crystal orientation independent of the geometrical wire and grain orientation. For Cu wires deposited without substrate rotation, the (111) crystal orientation, which corresponds to the close packed low energy surface of Cu, coincides with the geometrical wire orientation. Whereas, for Cu wires deposited with azimuthal rotation of the substrate, the (111)-crystal direction and the wire orientation are different depending on the rotation speed. We compared the validity of the empirical tangent rule@footnote 1@ and the geometrical Tait rule@footnote 2@ which are different equations which describe the relationship between the incident flux angle and the resulting wire orientation. Applications in nanowire circuits will also be discussed. @FootnoteText@ @footnote 1@ J.M. Nieuwenhuizen and H.B Hannstra., Philips Tech. Rev. 27, 87 (1966)@footnote 2@ R.N. Tait, T. Smy and M.J. Brett, Thin Solid Films 226, 196 (1993) .

MI-WeP9 Characterization and Room-temperature Ferromagnetic Properties Of Ti@sub 1-x@Co@sub x@O@sub 2@ Films Prepared by Cobalt Implantation*, K.H. Cheng, K.W. Lo, C.F. Chow, Y.W. LAI, W.M. Tsang, N. Ke, W.Y. Cheung,* Chinese University of Hong Kong*; **S.P. Wong**,* Chinese University of Hong Kong, Hong Kong

In this work, TiO@sub 2@ thin films were prepared by RF sputtering onto thermally grown oxide layers on Si substrates. Cobalt implantation was performed using a metal vapor vacuum arc (MEVVA) ion source at an extraction voltage of 65 kV to doses ranging from 1.4x10@super 16@ cm@super -2@ to 1.4x10@super 17@ cm@super -2@. Annealing was performed in vacuum at 600@super o@C for 2h. The cobalt composition and distribution in these implanted Ti@sub 1-x@Co@sub x@O@sub 2@ films was studied using Rutherford backscattering spectrometry. The crystal structures were studied using x-ray diffraction. The optical properties were studied using spectroscopic ellipsometry in the wavelength range from 350 to 700 nm. The magnetic properties were measured by vibrating sample magnetometry. We observed clear room-temperature ferromagnetic properties for all the as-implanted and annealed samples prepared under the above conditions. The measured M@sub S@ values ranged from 0.5 µ@sub B@/Co atom to 2.1 µ@sub B@/Co atom and the coercivity values ranged from 200 Oe to 500 Oe, depending on the Co dose and annealing conditions. The correlation between the optical properties, the magnetic properties and their structures will be discussed. This work is supported in part by the Research Grants Council of Hong Kong SAR (Ref. number: CUHK4216/00E and CUHK4221/00E).

MI-WeP10 Characterization of Transition Metal Doped CVD-grown ZnO Films*, D. Hill, J. Quinn, L. Wielunski, **R.A. Bartynski**, P. Wu, Y. Lu, G. Popov, M. Greenblatt,* Rutgers University

A crucial element for the success of spintronics is finding a material that combines the desirable properties of ferromagnets and semiconductors. Diluted magnetic semiconductors (DMS) are intriguing materials that offer the possibility of studying magnetic phenomena in crystals with a simple band structure and excellent magneto-optical and transport properties. ZnO, a wide bandgap (~3.3 eV) semiconductor that has received increasing attention due to its broad applications and its many desirable material properties, has recently has been identified as a promising DMS candidate for room temperature spintronics. We have characterized the chemical, compositional, and magnetic properties of TM-doped ZnO films grown by MOCVD. Doping using V, Mn, Fe, Co, and Ni has been investigated. X-ray photoelectron spectroscopy indicates that the TM dopant is in the 2+ oxidation state and thus may be substitutional for Zn. Squid magnetometry measurement show that the Mn- and Fe-doped films exhibit ferromagnetic behavior, with Mn-doped films having a Curie temperature of ~ 45K. For Fe-doped films, the Curie temperature is above room temperature. Both Rutherford backscattering spectrometry and XPS depth profiling indicate that Mn and Ni show extensive diffusion while Fe and Co exhibit more penetration into the ZnO film.

MI-WeP11 Epitaxial Growth, Structural, and Magnetic Properties of a Chalcopyrite Magnetic Semiconductor: MnGeN2*, S. Hardcastle, **L. Li**,* University of Wisconsin, Milwaukee

Epitaxial thin films of MnGeN2 were grown on Al2O3(0001), 6H-SiC(0001), and MgO(111) substrates using ECR plasma assisted MBE at 500 C. In situ RHEED studies indicated that the growth was 3D, consistent with ex situ AFM investigations. X-ray diffraction studies revealed that the films are single-phased material. Hysteresis loop with a coercive field of 100 Oe was observed at 300 K using a SQUID magnetometer, indicating ferromagnetic ordering at room temperature.

MI-WeP12 Ferromagnetism in Epitaxial Mn:Ge Films*, A.P. Li,* Oak Ridge National Laboratory*; C. Zeng,* The University of Tennessee*; Z. Gai, J.F. Wendelken,* Oak Ridge National Laboratory*; H.H. Weitering,* The University of Tennessee and Oak Ridge National Laboratory*; J. Shen,* Oak Ridge National Laboratory

We report on the magnetic properties of Mn-doped homo-epitaxial Ge films. Two different approaches are used to fabricate ferromagnetic Ge films. In the first approach, Mn-doped Ge films were grown on (2x1) reconstructed Ge(100) using molecular beam epitaxy (MBE) as was reported by Y.D. Park et al (Science 295, 651 (2002)). The Mn-concentration was varied between 1% and 5%. The Ge films show ferromagnetic ordering with Curie temperatures ranging from 25 K to 295 K, which have been determined from the remnant magnetization measured with a SQUID magnetometer. The magnetic response appears to consist of two different contributions, namely the ferromagnetic response from the dilute magnetic semiconductor (DMS) and the response from ferromagnetic alloy precipitates. X-ray diffraction (XRD), Rutherford Backscattering, and ion-channeling experiments were used to characterize the stoichiometry, homogeneity, and epitaxial quality of the films. In the second approach, a 40 nm Mn film is deposited onto Ge(111) and annealed to 150 °C for several minutes. Scanning Tunneling Microscope and XRD measurements show a high-quality epitaxial Mn@sub 5@Ge@sub 3@ alloy film with Mn@sub 5@Ge@sub 3@(001)//Ge(111). The Curie temperature of this ferromagnetic alloy film is 295 K, which is similar to that of bulk Mn@sub 5@Ge@sub 3@. The identical Tc of the epitaxial alloy film and Mn-doped Ge(100) films strongly suggests that the DMS film contains bulk Mn@sub 5@Ge@sub 3@ precipitates. These precipitates are below the detection limit of XRD. This thin film ferromagnetic system has good potential for spin-injection studies in silicon-compatible semiconductors. This research was sponsored by the LDRD Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

MI-WeP13 Increase of Conductance and Magnetoconductance with Oxygen Exposure During Deposition of Spinvalves*, A.T. McCallum*, *S.E. Russek,* National Institute of Standards and Technology

It has been found that the magnetoconductance and conductance of spinvalves increase when a small partial pressure of oxygen(1 x 10@super -9@ - 5 x 10@super -9@ torr)is present during deposition. Conductance measurements made during the sputter deposition of spin valves show directly that the conductance increases are occurring in the active layers of the spin valve flims. The Ne`el coupling between the free layer and the pinned layer is also reduced suggesting that the oxygen is leading to smoother growth. Eventually a high enough partial pressure of oxygen will lead to oxidation of the deposited metal and a drop in giant magnetoresistance. A series of conductance measurements at different gas flows show the onset of oxidation beginning with the NiFe and Cu layers. Relatively thick layers of material also have a higher conductance when grown in the presence of oxygen. The in-situ conductance measurement for NiFe layers reveal that the increase in conductance is starts at 1 nm and ends at 5 nm. After this the differential conductivity is the same for samples grown with and without oxygen. This is consistent with the samples grown in oxygen having a smoother surface but essentially the same microstructure.

MI-WeP14 Exploring Spintronic Materials and Structures with Interatomic Potentials*, D.A. Murdick*, *X.W. Zhou, H.N.G. Wadley,* University of Virginia*; D.G. Pettifor, D. Nguyen-Manh,* University of Oxford

The use of interatomic potentials in atomistic simulations has become a powerful approach for studying the atomic structures of materials. Molecular dynamic atomic simulations allow assembly phenomena encountered during the synthesis of spintronic devices to be analyzed in detail and allow the optimization of process conditions for desired spintronic structures and compounds. This approach has been successfully applied in metal/metal oxide multilayer systems to identify the deposition conditions for creating atomically smooth interfaces with minimized interlayer mixing. The extension of such an approach into semiconductors is very promising. The key to this is the availability of a high fidelity interatomic potential that can accurately describe covalent bonding in doped compound semiconductors and can be used for simulation of vapor deposition to reveal the time-dependent atomic structure as a function of processing conditions. We demonstrate that the existing literature multi-component interatomic potentials are too limited for spintronic applications. We describe a new class of bond-order potentials that overcome these limitations. The bond order potential has been successfully applied for GaAs systems and is being extended to (Ga,Mn)As/GaAs heterostructures and other doped semiconductors of group IV and III-V semiconductors.

MI-WeP15 The Isomer Dependent Semiconductors of Boroncarbide*, A.N. Caruso,* University of Nebraska*; L. Bernard,* Ecole Polytechnique Federale de Lausanne*; B. Doudin, P.A. Dowben,* University of Nebraska

We demonstrate that boroncarbide, grown by chemical vapor deposition, is an effective dielectric barrier layer for magnetic tunnel junctions. Decomposition of the insulator closo-1,2 dicarbadodecaborane or orthocarborane (C@sub 2@B@sub 10@H@sub 12@) has been shown to form p-type semiconducting boron carbide (C@sub 2@B@sub 10@).@footnote 1-4@ We present recent photoemission results which indicate that closo-1,7 dicarbadodecaborane or metacarborane (C@sub 2@B@sub 10@H@sub 12@) forms an n-type semiconducting boroncarbide (C@sub 2@B@sub 10@) upon decomposition. Bonding, orientation, and electronic structure of the two materials in both associative and decomposed configurations are compared as adsorbates. The electronic structure of orthocarborane and metacarborane are calculated to be very similar, but there are significant differences in the experimental binding energies for each isomer as an adsorbed species. Metacarborane adsorbs on both Co and Au with the Fermi Level (chemical potential) placed closer to the lowest unoccupied molecular orbital than is observed with orthocarborane adsorbed on Co and Cu. @FootnoteText@@footnote 1@ S. Lee and P.A. Dowben, Appl. Phys. A 58 (1994) 223. @footnote 2@ Dongjin Byun, Seong-don Hwang, Jiandi Zhang, Hong Zeng, F. Keith Perkins, G. Vidali and P.A. Dowben, Jap. Journ. Appl. Phys. Lett. 34 (1995) L941-L944@footnote 3@ D.N. McIlroy, C. Waldfried, T. McAvoy, Jaewu Choi, P.A. Dowben and D. Heskett, Chem. Phys. Lett. 264 (1997) 168-173@footnote 4@ Seong-Don Hwang, Ken Yang, P.A. Dowben, Ahmad A. Ahmad, N.J. Ianno, J.Z. Li, J.Y. Lin, H.X. Jiang and D.N. McIlroy, Appl. Phys. Lett. 70 (1997) 1028-1030 .

MI-WeP16 Extraordinary Hall Effect in Mn Ion-implanted p@super +@GaAs:C*, *J.D. Lim,* *S.B. Shim, K.S. Suh, Y.D. Park,* Seoul National University, Korea*; C.R. Abernathy, S.J. Pearton,* University of Florida*; R.G. Wilson,* Consultant

Gas source molecular beam epitaxy (GSMBE) prepared p@super +@GaAs:C (p = 3 x 10@super 20@cm@super -3@) on SI GaAs substrate was ion-implanted with Mn at 250 keV (at 350° C) with dose ranging from 1 - 5 x 10@super 16@ cm@super -2@. AC-magnetotransport measurements were conducted in Van der Pauw geometry using indium soldered contacts on as-implanted samples (I@sub ac@ = 100@mu@A @@ 17.1 Hz). Resistivity as function of temperature (@rho@ vs. T) for various applied fields showed anomalies consistent with magnetic properties. For various applied fields (up to 9 Tesla) for the temperature range considered (5 K - 400 K), the magnetoresistance (MR) was found to be positive, as oppose to nanometer-sized ferromagnetic clusters embedded in semiconductor matrix systems, which generally show a cross-over in sign of MR.@footnote 1@ Hall Effect measurement show a positive response consistent with overall p-character of the implanted samples. Sheet resistance increased with dose due to the expected implantation damage, and sheet carrier concentration as measured at 300 K increased with dose. Determination of the exact carrier concentration was made difficult with the onset of extraordinary Hall Effect (EHE) below 280 K (where @rho@@sub H@=R@sub o@B + R@sub S@H), again consistent with magnetic properties. For specific temperature range, the dominant EHE mechanism was found to be skew scattering (R@sub s@ ~ c@rho@). An apparent mobility enhancement was not observed as reported in inhomogeneous systems.@footnote 2@ Along with detailed magnetotransport measurements, effects of temperature of sample during implantation process and post-implantation anneal processes will be discussed. @FootnoteText@@footnote *@ partially supported by Samsung Electronics Endowment and KOSEF through CSCMR.@footnote 1@ H. Akinaga et al., Appl. Phys. Lett. 72, 3368 (1998); D.R. Schmidt et al., Phys. Rev. Lett. 82, 823 (1999).@footnote 2@ Sh.U. Yuldashev et al., J. Appl. Phys. 90, 3004 (2001).

Nanotubes
Room Hall A-C - Session NT-WeP
Poster Session

NT-WeP1 Reactor Design Considerations in the Hot Filament/DC Plasma Synthesis of Carbon Nanotubes/Nanofibers*, **B.A. Cruden**, A.M. Cassell, Q. Ye,* Eloret Corporation/NASA Ames Research Center*; M. Meyyappan,* NASA Ames Research Center

A combined hot filament/DC plasma approach to chemical vapor deposition (CVD) of carbon nanofibers (CNFs) has been explored. As a part of the study, the impact of filament usage and substrate holder design has been examined by SEM imaging of deposition products and monitoring of downstream products by residual gas analysis (RGA). It is demonstrated that the filament wire is important only in the pre-treatment of the substrate, where ammonia is dissociated and reacts with the substrate surface, improving CNF growth quality. However, the filament has no apparent impact when combined with the DC plasma, as demonstrated by RGA analysis of the plasma chemistry and the resultant films. The substrate holder is modified by introducing a graphite spacer into the electrode. By varying the size of the spacer, the effective surface.

NT-WeP2 Large-Area Growth of Aligned Carbon Nanotubes by Hot-Filament Assisted DC Plasma CVD*, **K. Ueda**, T. Negishi, Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

Hot-filament assisted dc plasma chemical vapor deposition (HF/DC-PCVD),@footnote 1@ in which a plasma is generated between the anode of hot-filaments and the cathode of a substrate, was developed to grow carbon nanotubes in a large-scale. Carbon nanotubes are expected to be used for the field emitters of a field emission display (FED) because their high aspect ratio and small radius of curvature lead to large electric-field enhancement at their tips resulting in low operating voltage for electron emission. However the method of large area growth of vertically aligned carbon nanotubes should be developed to be applied to field emitters of FED. We have succeeded to grow well-aligned carbon nanotubes on an iron substrate of 5 X 5 cm@super 2@ in a CH@sub 4@/H@sub 2@ DC plasma at 2.7KPa (20Torr) by HF/DC-PCVD. In this process, the plasma sheath plays an important role for the growth of vertically aligned carbon nanotubes. The sheath was formed all over the substrate with uniform thickness, i.e., uniform electric field strength, when three hot-filaments spaced 5mm were stretched parallel to the substrate. In order to grow well-aligned carbon nanotubes on a larger substrate, we generated plasma above a substrate of 10 X 10 cm@super 2@ at 1.35KPa (10Torr) using three hot-filaments spaced 15mm. Therefore the large-area growth of well aligned carbon nanotubes on a 10 X 10 cm@super 2@ substrate is expected. @FootnoteText@ @footnote 1@Y.Hayashi, T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19(2001) 1796.

NT-WeP3 Carbon Nitride Nanostructures Prepared by Surface Treatments*, **J.H. Hong**, S.H. Kim, S. Lee, Y.B. Hahn,* Chonbuk National University, Korea

Nano-dots and nano-stripes of carbon nitride (CNX) were fabricated by surface treatment. Amorphous CNX thin films grown on Si (100) wafer by plasma enhanced chemical vapor deposition at room temperature were first treated by H2 plasma and then annealed at 200-300@degree@. The effects of surface treatments on chemical and structural properties of the films were investigated by Auger electron spectroscopy (AES), Fourier transform infrared sprectra(FT-IR). Well-defined nano-dots and nano-stripes were formed depending on temperature and treatment time. This was attributed to recombination of adatoms and rearrangement of film structure caused by surface energy change between the film and the substrate. The AES showed that the composition of the film is 90 at.% C and 9 at.% N. The FT-IR spectra showed the presence of C-N peak at 1260 cm-1 and C=N peak at 1640-1670 cm-1, respectively.

NT-WeP5 Preparation of Self-Assembled Carbon Nano-Ropes and Carbon Nanotubes Using Microwave Plasma-Enhanced Chemical Vapor Deposition@footnote 1@*, **M. Taniguchi**, M. Hiramatsu, Y. Ando,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan

Carbon nano-structures such as carbon nanotubes, nanofibers and nanocrystalline diamond films are of tremendous interest from both a fundamental and an applied prospective. From the point of view of their wide applications, it is desirable to control properties such as the size, shape, and growth direction of surface structures during the growth. Carbon nano-structures with different structure and morphology can now be fabricated using several techniques. Among various techniques used for the growth of carbon nano-structures, plasma-enhanced chemical vapor deposition (PCVD) has gained considerable importance for the industrial application due to its feasibility and potentiality for large-area production with reasonable growth rates. In this work, aligned carbon nano-structures were grown using a conventional microwave plasma-enhanced chemical vapor deposition (MWPCVD) with a 1.5-kW microwave generator. A mixture of acetylene and hydrogen was used as a carbon source gas. The applied microwave power and the pressure during the growth were 400-1200 W and 25-80 Torr, respectively. The growth experiments were carried out for 1-15 min at substrate temperatures ranging from 500 to 800 °C. The morphologies of the grown carbon nano-structures depended strongly on the growth temperature. Vertically aligned, self-assembled, stranded carbon nano-fibers (carbon nano-ropes) were grown at relatively low temperature of about 500 °C. On the other hand, carbon nanotubes were grown on the catalyzed Si substrate at the temperature of about 800 °C. The field emission characteristics for the aligned carbon nano-structures were investigated. @FootnoteText@ @footnote 1@This work was supported by 21st century COE program, Nano Factory.

NT-WeP6 Synthesis of Multi-walled Carbon Nanotubes by CVD using Methane and Acetylene*, **S.A. Moshkalyov**,* UNICAMP, Brazil*; C. Reyes-Betanzo,* INAOE, Mexico*; A.C.S. Ramos, J.L. Gonçalves, J.W. Swart,* UNICAMP, Brazil

For the CNTs growth, a number of methods was developed, including different versions of chemical vapor deposition (CVD). CVD methods have certain advantages over other ones as they provide a way for controlled, directional growth of both single-walled and multi-walled CNTs. Here, results of CNTs synthesis using two different catalytic CVD techniques (plasma-enhanced low-pressure CVD and atmospheric-pressure thermal CVD) are presented. Thin Ni films (1-40 nm thick) were used as a catalyst material. For the film deposition, electron-beam thermal deposition was employed. Then, the films were thermally treated (~700 C) in a nitrogen atmosphere to provide formation of separate catalyst nanoparticles. As substrates, Si wafers were used previously covered by thin (50 nm) oxide films. CTNs synthesis was realized in two different reactors. The first one uses a low-pressure microwave plasma source, with low-pressure (~1Torr) nitrogen-acetylene gas mixtures. Samples are heated up to 700 C by a halogen lamp heater. In the second reactor, the flowing gas mixture and samples are heated in a resistive heating furnace to temperatures up to 900 C. Atmospheric pressure methane-hydrogen based mixtures were used in this case. After synthesis, the samples were examined using high-resolution scanning electron microscopes. The first results obtained here have shown fast CNT growth in both reactors. The process appears to depends critically on the catalyst thickness. For thin catalyst films, it was possible to grow long (randomly oriented), and small diameter (smaller than 10 nm) CNTs. In most cases, small catalyst particles were detected at the tip of the tubes. This suggests that the tip growth mechanism is responsible for the CNTs synthesis under the present conditions. The future work will focus on comparison of the two techniques and optimization of the processes, in particular, in order to achieve directional CNTs growth.

NT-WeP7 Growth of Cone-shaped Carbon Nanotubes by Arc Discharge in Anode*, **S.-C. Kung**,* Industrial Technology Research Institute,Taiwan*; C.-M. Hsu,* Industrial Technology Research Institute,Taiwan, Taiwan*; B.-J. Li, H.-J. Lai,* Industrial Technology Research Institute,Taiwan

Various synthetic methods are developed and the main method for the production of high quality CNTs (carbon nanotubes) is the DC (direct current) arc discharge between two graphite electrodes in a buffer atmosphere which is usually is helium, leading to the formation of nanotube-containing deposit on the end of the cathode. Many factors such as the velocity distribution of carbon ions, the density of carbon vapor, and the growth temperature have been suggested to affect the growth of CNTs. The pressure of carrier gas in the evaporation chamber is generally considered as the most important factor. Here, we report the production of CNTs without catalytic metals by DC arc discharge between two graphitic rods of the same diameter at the low pressure ambiance (ca. 10@super -2@ torr) and higher pressure helium atmosphere (ca. 900 torr). After the arcing was carried out, CNTs were discovered in the deposit on the anode instead of the cathode in low pressure working ambiance. The morphologies of CNTs on the anode deposit are specifically cone-shaped, 15 nm in diameter. The difference of nanometirc graphitic structures synthesized under the noble and higher vacuum atmosphere were discussed and characterized by FESEM, HRTEM, RAMAN spectrometer, TGA, and field emission properties measurement.

NT-WeP8 Growth of Carbon with Vertically Aligned Nano-scale Flake Structure by rf Sputtering, ***E. Kusano***, *H. Zhang,* Kanazawa Institute of Technology, Japan*; T. Kogure,* University of Tokyo, Japan*; I. Yoshimura, K. Yamamoto, A. Kinbara,* Kanazawa Institute of Technology, Japan

Carbon nanoflake has been deposited by rf sputtering using the mixture of Ar and CH@sub 4@ with a total pressure of 14.5Pa as a discharge gas and a graphite disk as a target. A Si (110) wafer was used as a substrate on which carbon nanoflakes was grown at 670°C. The rf (13.56MHz) discharge power was kept 100W for all deposition. Deposition time was changed from 15 min to 3 hours. Microstructure of deposited carbon was investigated by Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscope (HRTEM). Under the present conditions, high-density vertically aligned carbon nanoflakes with a thickness of about 30 nm were obtained. High intensity and symmetry of electron diffraction pattern indicated that carbon nanoflakes deposited by rf sputtering had the three dimensionally perfect crystallinity with an interlayer spacing of 335pm. In particular, there was no disorder in stacking of layer structure. It was further found that the thickness of the flakes was independent of deposition time while the length of the flakes increased to about 600-800 nm with increasing deposition time to 3 hours. Width of the carbon nanoflake was about 300 nm after 3-hour deposition. The results suggest that a critical thickness of carbon nanoflake exists, possibly depending on deposition conditions such as substrate temperature and discharge pressure. This critical thickness was almost equal to the layer number of about 90. Some potential applications of the carbon nanoflake film are being considered in vacuum electronic devices, chemical catalyst, frictional abrasion resistance, etc.

NT-WeP9 Synthesis of Aluminosilicate Nanotube "Imogolite" in the Presence of Polymer Solution*, **K. Yamamoto**, H. Otsuka, S.-I. Wada, A. Takahara,* Kyushu University, Japan

Inorganic nanotube "Imogolite" is a hydrous aluminosilicate polymer with an external diameter of ca. 2.5 nm and lengths from several hundreds nanometer to a micrometer. The authors introduce a novel method for the preparation of polymer nanohybrid through in situ synthesis of imogolite in the aqueous solution of water-soluble polymer. A polymer nanohybrid prepared by this method can be expected to improve the dispersion of imogolite in the polymer matrix compared with that prepared by conventional blending.@footnote 1@ The aqueous dilute solution of aluminum chloride and tetraethoxysilane was stirred and refluxed at 369 K for several days and freeze-drying of the solution gave white powder of synthetic imogolite. The polymer nanohybrid was also prepared through in situ synthesis of imogolite in the presence of poly(vinylalcohol)(PVA) in solution and this reaction was carried out at various concentration of PVA. The formation of synthetic imogoltie was confirmed by IR, WAXD measurement, and AFM observation. The content of imogolite in the each polymer hybrid sample was evaluated by TGA measurement. WAXD profiles of PVA-imogolite nanohybrid showed the sharp diffraction peak of PVA and the diffractions corresponding to the parallel orientation of the bundle of imogolite nanotubes. It was confirmed that synthetic imogolite formed nanoscale fibrous network structure in PVA matrix by the above mentioned procedure. Furthermore, high transparency of synthetic imogolite/PVA hybrid film prepared by this method was attained because of the high dispersibility of synthetic imogolite in PVA solution. @FootnoteText@ @footnote 1@K. Yamamoto, H. Otsuka, S. -I. Wada, A. Takahara, J. Adhesion, 78, 591 (2002).

NT-WeP11 A Novel Field Emission Triode Configuration Based on a Cylinder/Plane Geometry and Carbon Nanotubes*, **V.P. Mammana**, O. Shenderova, G.E. McGuire,* International Technology Center

Field emission devices are an excellent alternative for a myriad of applications requiring highly efficient and compact electron sources, such as flat panel displays, microwave tubes and plasma thrusters. Although field emission devices with several different triode configurations have been developed, there is still a need for devices with increased robustness, lower gate voltage and lower gate parasitic current that are easy to manufacture. In this work we propose a new configuration based on a cylinder/plane geometry, in which the cylinder plays the role of cathode and the plane performs as the gate. In the proposed configuration, an insulating dielectric is used between the cathode and the gate, in a way that the gate current is significantly reduced while the overall robustness is increased. Manufacturing this structure is straightforward, since it does not require patterning of the dielectric. The complexity is further reduced if no pixel addressing is needed (for non-display applications), since the dielectric may be blanket deposited or grown. We present electrostatic field calculations made in order to optimize the geometrical parameters of the device, and these calculations demonstrate that emission takes place at gate potentials of a few tens of volts, if carbon nanotubes are included into the structure in order to enhance the local electrostatic field. In this paper we address the dependence of the electrostatic field on the gate voltage, type of dielectric, cylinder/plane distance and cylinder cross-section. Some focusing issues are preliminarily addressed too. A process flow for the manufacture of the device is also proposed.

NT-WeP12 Field Emission Properties of Carbon Nanotubes Relative to Buffer Layer*, **C.-M. Hsu**, S.-C. Kung, B.-J. Li, H.-J. Lai,* Industrial Technology Research Institute, Taiwan

Effect of field emission and growth of carbon nanotubes use various buffer layers Carbon nanotubes (CNTs) were synthesized with various buffer layers by electron cyclotron resonance chemical vapor deposition (ECR-CVD) and microwave plasma chemical vapor deposition (MPCVD) system. Growth was performed in a flowing mixture of H@sub2@, CH@sub4@ and N@sub2@ as precursors at temperature 600°C and -200 V substrate bias, sputter Co as catalysts material. The preliminary results indicate that well-aligned carbon nanotubes show significant emission current. Field emission property of carbon nanotubes and buffer layers relationship will be compared. Field emission scanning electron microscopy (FESEM) shows that the CNTs are well aligned with high aspect ratio and growth direction vertical to the substrate. The field emission properties of CNTs and buffer layers relationship will be characterized by I-V measurement, XRD, TEM, and RAMAN.

NT-WeP14 Modification of Contact Resistance by Nano-bonding and Thermal Treatment*, S. Lee, H.J. Chung,* CSNS and Seoul National University, Korea*; J.-Y. Park,* Cornell University*; Y.S. Cho, **Y.D. Park**, J.H. Choi, Y. Kuk,* CSNS and Seoul National University, Korea

When we connect a nano-structure with conducting wires, we face difficulty fabricating them around ultra-fine and dense nanostructures. In order to use nanotubes or nanowires as interconnection materials, the contact resistance should be controllable because it may become main noise and dissipation sources with this low electrical current signal. In this study, the variation of the contact resistance in the carbon nanotubes (2-8 nm) on Au electrodes was investigated. The contact resistance between a nanotube and a electrode was changed the nanometer sized dots of Au and Ni formed by the field evaporation of the metals coated cantilever using atomic force microscopy (AFM) combined with a thermal treatment of 400-500 °C by a rapid thermal annealing (RTA). By using this method, the contact resistance of ~100 k@ohm@ is routinely produced despite of the geometry of nanotubes. This method can be used to other transport experiments to be required to modify the contact resistance.

NT-WeP15 Fabrication and Characterization of Active Nanoscale Electronic Devices Based on Vertically Aligned Carbon Nanofibers (VACNF)*, M.L. Simpson,* Oak Ridge National Laboratory*; **X. Yang**,* University of Tennessee*; M.A. Guillorn,* Oak Ridge National Laboratory*; D.W. Austin,* University of Tennessee*; V.I. Merkulov, A.V. Melechko, D.H. Lowndes,* Oak Ridge National Laboratory

Arrays of deterministically grown VACNFs were synthesized in a high-density Plasma-Enhanced Chemical Vapor Deposition (PECVD) process that provides a high degree of control of the growth conditions and, consequently, the resultant electronic properties. After inspection of fiber morphology and composition using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis, a layer of SiO2 was deposited conformally onto the fibers by a silane-based RF PECVD process. Following planarization of the substrates by chemical mechanical polishing, the tips of the fibers were uncoverd by reactive ion etching of the SiO2 layer. Electrodes were patterned on the substrate surface to make contact to individual fiber tips within the array. Current versus voltage (I-V) curves indicate the presence of a metal-semiconductor (Schottky) junction and display a rectifying behavior. I-V measurements made with respect to temperature reveal an average barrier height of 300 mV. Additional experiments indicate that the junction occurs at the nanofiber/silicon interface. An empirical model of the material system will be presented along with an explanation of the experimentally observed charge transport behavior.

NT-WeP16 Fabrication of Top gated Single-Walled Carbon Nanotube Field Effect Transistor Utilizing Scanning Probe Lithography*, **S.H. Choi**, J. Heo,* SungKyunKwan University, Korea*; W.B. Choi,* Samsung Advanced Institute of Technology, Korea*; I.S. Chung,* SungKyunKwan University, Korea

We attempted to fabricate top gated single wall carbon nanotube field effect transistor(SWNT FET) utilizing scanning probe lithography(SPL) method. In SPL, electrons induce chemical reactions at the desired position during scanning. Thus, gate electrode as well as source/drain formation would be done using lift-off method without using e-beam lithography. N type or p type FET can be formed according whether the oxygen annealing process is given or not. Thus, we can easily form an inverter based on top gate structure. In this study, SWNTs were dispersed on pre-patterned substrate prior to deposit top gate oxide. Our device shows excellent electric characteristics by thinner gate oxide.

NT-WeP17 Large Paramagnetic Susceptibility and Field Induced Persistent Current for Carbon Nanotube Tori*, **R. Tamura,*** Shizuoka University, Japan*; M. Tsukada,* University of Tokyo, Japan

Magnetic susceptibilities have been calculated for a number of Carbon nanotube (CNT) tori with the tight binding model. We found large paramagnetic susceptibility which cannot be expected when the system size is larger than the order of the nanoscale. The CNT torus with six-fold rotational symmetry is composed of six unit cells. The unit cell is an armchair nanotube with two pentagonal defects and two heptagonal defects. Direction of the tube axis is changed by sixty degrees by the defects. When this unit cell is repeated periodically, on the other hand, the helical CNT is formed.@footnote 1@ The energy levels of the CNT torus can be obtained from the dispersion relation of the helical CNT, E(k), by choosing only the discrete wave number k=@pi@j/3 with an integer j. The magnetic field penetrating the torus surface change the dispersion relation E(k), while magnetic field through the hole shift the discrete wave number due to the AB effect. When the helical CNT is semi-metallic, it is possible that LUMO band bottom at k=0 is lower than the HOMO band over some k region.@footnote 2@ In that case, electron at the HOMO band makes a transition to the k=0 LUMO sate so that number of occupied levels with positive k is different from that with negative k. This causes the persistent current and large positive magnetic susceptibility, in spite of large negative magnetic susceptibility of graphite. @FootnoteText@@footnote 1@R. Tamura and M. Tsukada,Journal of Physical Society of Japan, Vol. 68, pp.910-922 (1999)@footnote 2@K. Akagi, R. Tamura, M. Tsukada, S. Itoh, and S. Ihara, Phys. Rev. B,Vol. 53, pp.2114-2120 (1996) .

NT-WeP19 Experimental and Theoretical Studies on the Ozone Reactivity with Carbon Nanotubes*, S. Picozzi, L. Lozzi, F. Di Gregorio, S. Santucci, C. Cantalini,* INFM and University of L'Aquila, Italy*; C. Baratto, G. Sberveglieri,* INFM and University of Brescia, Italy*; L. Valentini,* ***I. Armentano,*** University of Perugia, Italy*; B. Delley,* Paul Scherrer Institut, Switzerland

In a previous paper@footnote 1@ it has been reported how carbon nanotubes (CNTs) thin films deposited by plasma-enhanced chemical vapor deposition have a strong reactivity with NO2. In this work we investigate a CNT film as resistive gas sensors for O3. The sensor composed by the aligned CNT film with a thickness of 200 nm exhibits sensitivity to O3 gas at concentrations as low as 25 ppb, fast response time with a baseline drift that has been observed if the operating temperature of the sensor is increased over 70Â°C Upon the reaction with O3, the electrical resistance of the CNTs is found to decrease. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+O3 system within the density functional theory, using the all-electron Dmol3 (density functional theory for molecules and three-dimensional periodic solids) code.@footnote 2@ Our calculations show that the ozone molecule adsorbs on the tube with a binding energy of the order of 300 meV and gains about 0.1 electrons from the CNT. The calculated density of states shows that O3 adsorption gives rise to an acceptor peak at the Fermi level, which lies in correspondence to the tube valence band maximum, rendering the CNT+O3 system metallic. This is consistent with the experimentally observed increase in conductivity. The baseline shift of the sensor experimentally observed for the higher working temperatures may be ascribed to a consumption of the carbon nanotube under the ozone exposition at the defective sites.@footnote 3@ @FootnoteText@ @footnote 1@ L. Valentini, I. Armentano, J. M. Kenny, C. Cantalini, L. Lozzi, and S. Santucci, Applied Physics Letters Volume 82, Issue 6, pp. 961-963 (2003). @footnote 2@ B. Delley, J. Chem. Phys. 113, 7756 (2000); ibid. 92(1), 508 (1990) @footnote 3@ D.B. Mawhinney, V. Naumenko, A. Kuznetsova and J.T. Yates Jr., J. Am. Chem. Soc., 122, 2383 (2000).

NT-WeP20 Molecular Dynamics Study on the Non-equilibrium Flow of Small Molecules through Opened Carbon Nanotubes*, **K. Lee,** S.B. Sinnott,* University of Florida

Ultrafiltration membranes made of short, opened carbon nanotubes, which have relatively uniform nanometer-scale pore sizes and linear structures, may allow gases to selectively pass through the membrane. This potential selectivity can be predicted from atomistic simulations of the diffusion and adsorption of the gases into and within carbon nanotubes. The computational nanofluidics of hydrocarbons, oxygen, and carbon dioxide has been studied with molecular dynamics simulations in the work reported here. The microscopic behaviors of these gases can be simulated with multiple integrations of the interactions among the atoms in a system. The transport of gas molecules for long time periods is characterized by initial non-equilibrium states followed by equilibrium states. The non-equilibrium state is induced by the diffusive motion of the gas molecules from one end of the nanotubes into the vacuum or low-pressure region at the other end of the nanotubes, and lasts until the gases are evenly distributed in the nanotubes. During the non-equilibrium state, the gas molecules move back and forth through the nanotubes. It is found that this behavior, the time needed for the attainment of equilibrium, and the molecular motions at the openings of the nanotubes are affected by the density (or pressure) of gas molecules both inside and outside of the carbon nanotubes. When the gas molecules reach the end of the nanotubes, the attractive force between the tube end and the gas molecules prevent the molecules from leaving the nanotube. In order to leave the tube, the molecules must be acted on by a repulsive force, which is exerted by other gas molecules entering at the other end. The dynamics of these various nonequilibrium diffusion regions are characterized and will be discussed in detail. In addition, a discussion of how the results change with changes in nanotube chirality and diameter will be discussed. This work is supported by the NASA Ames Research Center.

Plasma Science and Technology
Room Hall A-C - Session PS-WeP
Poster Session

PS-WeP1 Experiemental Study of Real-Time Feedback Control of Ion Energy and Ion flux in Poly-Si Etch Process Using High Density Cl@sub 2@ Plasmas*, **K.C. Leou,*** National Tsing Hua University, ROC, R.O.C*; C.H. Chang, C. Lin,* National Tsing Hua University, ROC

In this study, we have demonstrated experimentally the real-time closed-loop control of both ion density and ion energy in a chlorine inductively coupled plasma etcher. To measure positive ion density, the trace rare gases-optical emission spectroscopy (TRG-OES) is used to measure the chlorine positive ion density. An rf voltage probe is adopted to measure the RMS rf voltage on the electrostatic chuck which is linearly dependent on sheath voltage. One actuator is a 13.56 MHz rf generator to drive the inductive coil seated on a ceramic window. The second actuator is also a 13.56 MHz rf generator to power the electrostatic chuck. The closed-loop controller is designed to compensates process drift, process disturbance, and pilot wafer effect and to minimize steady state error of plasma parameters. This controller has been used to control the etch process of unpatterned polysilicon. The experimental results showed that the closed-loop control had a better repeatability of plasma parameters compared with open-loop control. The closed-loop control can eliminate the process disturbance resulting from reflected power. In addition, experimental results also demonstrated that closed-loop control has a better reproducibility in etch rate as compared with open-loop control. Experiment results on SiO@sub 2@ etch show that real-time feedback control of both ion energy and flux also enhance the process stability of etch selectivity (Poly-Si to Oxide) in addition to the etch rate of poly-Si. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

PS-WeP3 Study of the Passivation Mechanisms Involved in the Silicon Deep Etching Cryogenic Process*, **X. Mellhaoui,** R. Dussart, A. Basillais, T. Tillocher, P. Lefaucheux, P. Ranson,* GREMI, France

Silicon etching is perfomed by cryogenic SF@sub6@/O@sub2@ plasma process. This process allows to obtain a high aspect ratio (depth/width > 10) and a high anisotropy. The plasma is created in an Inductively Coupled Plasma reactor. The silicon wafer is clamped on a chuck cooled with liquid nitrogen and controlled in temperature. A study of passivation mechanisms is necessary to perfectly control this process and to optimize the trench profiles. The passivating layer is a mixture of Si, F, O and S (SiO@sub x@F@suby@S@subz@). Previous XPS experiments have shown that the passivation layer is removed during the increase of temperature, which proves that the passivation layer is not mainly composed of SiO@sub2@. When destroyed, the passivation layer can be rebuilt with SiF@sub4@ and O@sub2@. This particular experiment was made and has revealed that the presence of sulphur is not necessary to build an efficient passivation layer.

Experiments to better understand the passivation layer reconstruction and composition will be presented at the conference. In overpassivating conditions (high O@sub2@ flow), black silicon phenomena appear in trench bottom. Roughness and black silicon pattern depend on several parameters (temperature, bias voltage, O@sub2@/SF@sub6@ ratio). A statistical study made on the black silicon pattern will be also presented.

PS-WeP4 Etching Characteristics in Novel Internal Linear Inductively Coupled Plasma Antenna for Flat Panel Display Applications*, G.Y. Yeom, **K.N. Kim**, Y.J. Lee,* Sung Kyun Kwan University, South Korea*; B.U. Cho, J.K. Lee,* Pohang University Science and Technology, Korea*; M.A. Lieberman,* University of California at Berkeley

The flat panel display (FPD) industry, especially for liquid crystal display (LCD) has been experiencing an impressive growth for the last 10 years, and moving to large generation sizes such a 1200mmX1500mm for reducing manufacturing costs, although third (550mmX650mm) and fourth generation (680mmX880mm) glass substrates are also available. Therefore, large-area plasma sources are needed to meet the plasma processing in display manufacturing plasma processing (PECVD, ETCH, and ASHING) and, to decrease the process time, high density plasma sources are required. In this study, large-area plasmas with inductive coupling of extended internal linear- antennas have been proposed promising candidate for the efficient high-density plasma source. The process chamber was designed as a rectangular mainly for FPD application and was made of stainless steel. The inner size of the chamber was 1020mmX830mm. To improve both the plasma density and the uniformity of internal ICP source, several internal-type linear antenna designs have been employed. In this presentation, the effects of various linear-antenna designs and process conditions on the plasma characteristics, such as plasma species and density, electron temperature, and plasma uniformity in this large area plasma source were investigated using a quadrupole masss spectrometer (QMS: Hidern Analytical Inc., PSM 500) and a Langmuir probe (Hiden Analytical Inc., ESP) located on the sidewall of the chamber. The results showed a strong relationship between the combination of the antenna configuration and plasma characteristics such as density and uniformity. The etch uniformities of SiO@sub2@ etched using C@sub4@F@sub8@(NF@sub3@)/He/O@sub2@ gas mixtures showed the similar trend as that of Ar@super+@ ion density.

PS-WeP6 Inductively Coupled Plasmas in Cl@sub 2@/O@sub 2@ Mixtures: Modeling and Experiment*, **A.M. Efremov**,* Ivanovo State University of Chemistry and Technology, Russia*; C.I. Kim, D.P. Kim,* Chung-Ang University, Korea

Microwave thin films resonators have been integrated with complex perovskite materials Ba(Mg@sub 1/3@Ta@sub 2/3@)O@sub 3@ (BMT) and Ba(Zn@sub 1/3@Ta@sub 2/3@)O@sub 3@ (BZT), which are very perspective materials due to excellent microwave properties. However, plasma etching in Cl-base gases is obstructed by two main problems. First problem is low etching rate due to low-volatility of metal-chlorides, which can be cleaned by strong ion bombardment. But, it is undesirable to avoid defects in structure. Second problem is the deviationsof stoichiometry on the surface after the etching due to various partial etching yields. The origins of these problems are also caused by low and different volatilities of reaction products. Therefore improvement of BMT and BZT etching technology should follow by the way of improvement of efficiency of chemical mechanism through the increasing of etching products volatility. In this way, Cl@sub 2@/O@sub 2@ mixture is very promising environment. The reason is that the formation of high-volatile metal-oxy-chlorides (M-ClO) is expected. We investigated plasma characteristics, plasma mass content and kinetic dependencies of both neutral and charged particle formation and decay in Cl@sub 2@/O@sub 2@ gas mixture. For these purposes we used a combination of experimental methods (OES, Langmuir probe, QMS) and a plasma modeling on the base of self-consistent solution of Boltzmann kinetic equation together with balance kinetic equations for neutral and charged particles in a quasi-stationary approximation. It was found that the change of O@sub 2@/(Cl@sub 2@+O@sub 2@) mixing ratio from 0 to 100% leads to an increase of electron average energy and electron energy distribution function deformation. The main mechanisms of Cl and O atom formation are the direct electron impact dissociation of corresponding molecules while the contribution of all possible secondary processes is not significant in the case of a relatively low O@sub 2@ addition.

PS-WeP8 Atomic Layer Etching of Silicon using a Low Angle Forward Reflected Ar Neutral Beam*, **S.D. Park**, D.H. Lee,* Sungkyunkwan University, Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea, South Korea

Atomic layer etching (ALE) is one of the important technologies for the fabrication of future nano-scale devices, because current dry etching techniques are not capable of etching with atomic layer resolution because of their high etch rates. In addition, relatively high energy of the ions can damage the crystal surface. Therefore, many studies on ALE of Si have been reported in recent years to develop a technique to etch materials layer-by-layer. But, these previous methods may show charging damage due to the charged particles such as positive ions and photons generated in the plasma. Therefore, in this study, ALE of Si was carried out using a sequential Cl@sub 2@ adsorption and an Ar neutral beam irradiation instead of ion beam. Low energy Ar neutral beam was generated by a low-angle forward reflected neutral beam technique. ALE of Si is a cyclic process consisting of 4 steps: (1) adsorption of Cl@sub 2@ on Si surface, (2) evacuation, (3) Ar neutral beam irradiation to the surface, (4) evacuation of etch products. The etch process parameters for optimizing the atomic layer etching of Si are Cl@sub 2@ gas exposure time, Ar neutral beam irradiation time, Ar neutral beam energy, etc. It is expected that the atomic layer etching of Si should be limited to 0.68 nm per cycle, which corresponds to the half mono-layer thickness of Si. The resulting step height and surface damage was estimated using transmission electron microscopy (TEM). The step height divided by the total number of ALE cycles yielded the etch rate per cycle. A scanning electron microscope (SEM) was used to observe as-etched Si profiles and an atomic force microscope (AFM) was used to analyze the surface topography.

PS-WeP9 Molecular Beam Mass Spectrometry of the Microwave Discharge in Methane/Argon Gas Mixture*, M. Misina, **P. Pokorny**,* Institute of Physics ASCR, Czech Republic

Mass spectrometry (MS) of the neutrals in a processing plasma requires extraction of a gas sample through an orifice, ionization, mass separation and detection. Radicals are detected by the appearance potential MS (APMS).@footnote 1@ APMS relies on the difference in the electron energy threshold for ionization of a radical by a simple electron impact ionization and for production of an fragment ion from a molecule by dissociative ionization. However, the absolute measurement of the radical density is complicated by the interaction of the radicals with the walls during the transport from the extraction orifice to the ionization source. This is especially true for species with a high sticking coefficient. Therefore, the molecular beam MS (MBMS) was developed.@footnote 2@ MBMS includes more stages of differential pumping with several orifices by which a beam of neutrals from the plasma is extracted into the ionization chamber of a MS. In this paper the concentration of radicals and the composition of the neutral gas in the microwave electron-cyclotron-resonance methane/argon plasma for DLC film deposition was measured by APMS and MBMS for a range of process parameters such as microwave power, working gas composition and total pressure. The total pressure in the experiment ranged from 0.1 to 1 Pa. The microwave power up to 800 W was used. The most abundant radical was methyl with a concentration of in the range of the order of 10@super 12@ cm@super -3@. A high degree of dissociation and consumption of the methane in the ECR discharge was observed. In fact, the hydrogen dissociated from the methane was the dominant component of the working gas at higher microwave powers. @FootnoteText@@footnote 1@ P. Kae-Nune, J. Perrin, J. Guillon, J. Jolly, Plasma Sources Sci. Technol. 4 (1995) 250-259.@footnote 2@ H. Singh, J. W. Coburn, D. B. Graves, J. Vac. Sci. Technol. A 17(5) (1999) 2447-2455.

PS-WeP10 Spatio-temporal Characterization of Pulsed, Electron Beam Produced Plasmas*, **S.G. Walton**, D. Leonhardt, C. Muratore, D.D. Blackwell, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

In plasma-based materials modification, regulating the flux of ion, neutral, and radical species at the substrate surface is a critical component of process control. The plasma density determines the flux and the electron temperature influences the energy of these species and so both can be used to regulate reactive species at the substrate. Modulated plasma production as well as remote plasma sources are often employed to control the relative ion flux and energy through temporal or spatial variations in the bulk plasma. In this paper, spatio-temporal characterizations of pulsed, electron beam-generated plasmas will be presented. Mass and time-resolved measurements of ion fluxes and energy distributions are presented and correlated to measurements of the plasma density and electron temperature. Previous work has shown that energetic electron beams are efficient at producing high-density plasmas (n@sube@

> 10@super11@ cm@super-3@) with low electron temperatures (T@sube@ < 1.0 eV) over the volume of the beam. Outside the beam, ion-neutral and electron-ion interactions alter the ion densities and flux. Temporal variations in the density, electron temperature, and flux have been observed during all phases of pulsed plasma production. Measurements are presented for a range of operating pressures, pulse widths, duty factors, and electron beam-to-electrode distances for plasmas produced in argon, nitrogen, and oxygen. The results are used to identify methods by which the ion fluxes and energies can be controlled. This work supported by the Office of Naval Research. @FootnoteText@ Muratore, C., ASEE/NRL Postdoctoral Research Associate; Blackwell, D.D., SFA Inc., Largo, MD.

PS-WeP11 Experimental Characterization of a Pulsed Inductively Coupled Plasma*, **C.H. Chang,*** National Tsing Hua University, ROC*; K.C. Leou,* National Tsing Hua University, ROC, R.O.C*; S.J. Wu, M.L. Gong, T.L. Lin,* National Tsing Hua University, ROC

The basic properties of a pulsed low pressure inductively-coupled plasma has been characterized by using various diagnostic tools, including a RF impedance meter, a Langmuir probe, a 36 GHz interferometer and optical emission spectroscopy. These tools have been modified from conventional ones to measure time resolved properties of the discharge. In addition to plasma density, plasma potential and electron temperature, the Langmuir probe has also been used to extract the electron energy probability function (EEPF) of the plasma. Measurement results show that high energy (roughly E > 10 eV) electrons are lost quickly after the driving RF power is turned off. The low energy part of the electrons remains nearly unchanged during the entire off period. The electron temperature thus drops quickly while plasma density changes little during RF off period as observed in other studies. Spatial-temporal behaviors of plasma density have also been measured. The radial distribution of plasma density only change slightly at different times of the RF on or off periods although the overall plasma density varies significantly. The electric properties of the discharge was measured by a home made impedance meter which detects the time varying amplitude and phase of the RF voltage and current, and thus net input RF power and complex impedance of the discharge. For different waveforms of modulation, such as square, triangular, sinusoidal and trapezoidal, impedance meter measurements show that, when the RF power is turned on, there is always a transient surge of RF voltage and current on the inductive coil, thus the net input power into the plasma. The temporal profiles of electric properties, however, do not vary significanly for different types of modulations. Comparison of probe and impedance meter measurements to interferometer and OES measurements will also be presented. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

PS-WeP12 Effect of Gas Heating in a High Density Pulsed Plasma Discharge*, D.J. Economou, **S.K. Nam,*** University of Houston

Owing to their importance, power-modulated plasmas have been studied both experimentally and computationally. However, the effect of gas heating in pulsed discharges has not been studied in detail. In contrast, there are numerous studies of gas heating in continuous wave discharges. A two-dimensional self-consistent model and simulation tool were developed to study the spatio-temporal dynamics of a pulsed power (square-wave modulated) inductively coupled argon discharge, with emphasis on gas heating effects. The coupled equations for plasma power deposition, electron temperature, charged and neutral species densities, and gas temperature were solved to obtain the space-time evolution of the discharge in a Gaseous Electronics Conference (GEC) ICP reference cell. The effect of control parameters such as power, duty ratio, pressure, and pulse frequency on the evolution of discharge properties (electron density, electron temperature, gas temperature) was investigated. Simulation results on discharge properties were in good agreement with available experimental data. @FootnoteText@ Work supported by the National Science Foundation.

PS-WeP13 A Model of Feature Profile Evolution for Nanometer-Scale Control of Etched Profiles and Critical Dimensions*, K. Ono, **Y. Osano**, A. Sano, K. Takahashi, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. The precise control of etched profiles and critical dimensions (CDs) is still one of the most important issues to be addressed, particularly in gate etch processes. In developing the technology to meet these demands, the modeling or simulation is an attractive approach, which significantly contributes to optimize complex processes in the fabrication of microelectronic devices. This paper presents a model of the feature profile evolution for nanometer-scale control of the profile and CD during etching of poly-Si gate electrodes in high-density chlorine- and bromine-containing plasmas. The model employs a full matrix approach with the volume density function in the entire computational domain for the materials being etched. This approach enables us to take into account surface reaction processes of enormous complexity that would occur during etching, particularly multilayer adsorption or reaction kinetics on feature surfaces, which the usual string algorithm with Langmuir adsorption scheme is hard to deal with. The model includes the transport and surface reaction kinetics of ions and neutrals in microstructures, based on our present understanding: neutral adsorption, geometrical shadowing, surface reemission or reflection of ions and neutrals, localized charging of feature surfaces, purely chemical etching, physical sputtering, ion-assisted reactions, and surface inhibitor deposition. The numerical results indicated that a thin passivation layer of surface inhibitors on feature sidewalls, surface temperature, and charging of mask layers play a key role in achieving the nanometer-scale control in gate etch processes.

PS-WeP14 Selected Modifications of PE and PTFE Surfaces by Means of a Modified RF N@sub 2@ Plasma*, **N. Vandencasteele**, F. Reniers,* Universite Libre de Bruxelles, Belgium

Plasma techniques are often used to modify polymer surfaces. However, due to the great variety of the species created in a plasma (neutrals, ions, electrons), the resulting surface modification is often poorly controlled, and the mechanisms of surface reaction poorly understood. In order to try to better control and undersand these processes, we have modified the geometry of a RF plasma chamber in order to be able to filter the species reaching the surface, allowing only the neutrals and the electrons to reach the surface, depending on the electrode bias. The selected effect of the nitrogen ions was the subject of another study.@footnote 1@ PE and PTFE surfaces have been exposed to this modified N@sub 2@ RF plasma. The plasma was characterized by optical emission spectrometry. A variation of the densities of the active species relative to the cathode position is evidenced. The samples were afterwards characterized by XPS, water contact angle measurements and AFM (for surface roughness). A strong correlation between the surface energy, the nitrogen concentration on the surface, the plasma characteristics (DC-bias and RF power) and the treatment time is shown. A deconvolution of the C1s and N1s peaks show a progressive functionalisation sequence of the surface. The effect of the polarity of the native bonds (C-H in PE and C-F in PTFE) on this sequence is studied. @FootnoteText@ @footnote 1@A. Wagner, D.H. Fairbrother, F. Reniers, Plasma and Polymers 8 (2003) 119-134.

PS-WeP15 Principle of a Beam Profile Controlled Linear Ion Beam Source and Application Examples*, **M. Nestler**, D. Roth,* Roth & Rau AG, Germany*; F Scholze, M. Tartz,* Institut f@um u@r Oberfl@um a@chenmodifizierung Leipzig e.V., Germany*; M. Zeuner,* Ion+Tech GmbH, Germany*; H. Neumann,* Institut f@um u@r Oberfl@um a@chenmodifizierung Leipzig e.V., Germany

We present a microwave excited ECR (electron cyclotron resonance) type low energy linear ion beam source with a special grid system for cleaning, surface treatment, etching, figuring, surface modification and thin film deposition. By means of a modular design with basic module length of 400 and 600 mm this source is easily scalable up to some meters for production environment. Fitting this source with a special designed, segmented multi-aperture three grid system and power supplies in combination with a variable electrical switcher, which allows a changing of the pulse length of the accelerator voltage applied on each segment, the profile of this low energy ion beam is adaptable on different process requirements. We discuss the measured beam profiles in correlation to the controlling principles by using inert and reactive gases and draw up the technological possibilities for this new broad beam ion source by means of selected examples. Its integration into an in-line production equipment is demonstrated.

PS-WeP16 Creation and Characteristics of Miniature Microwave Plasmas*, **J. Narendra**, T.A. Grotjohn, J. Asmussen,* Michigan State University

Small microwave generated plasma discharges are characterized to determine their properties for discharges with sizes ranging from 0.3 mm to 3 mm. The discharge characteristics investigated include microwave power density, plasma density, electron temperature and gas temperature. The outcome of this investigation is an understanding and quantification of the microwave power density needed to operate small discharges of specific sizes, shapes, pressures, and gas compositions. The microwave plasma source technology used in this investigation is a microstripline based plasma source with the discharge created in a quartz tube of 0.3 mm to a few mm in inside diameter. A microstripline is used to couple 2.45 GHz microwave energy into a discharge confined in a tube orientated perpendicular to the stripline conductor. The discharge formed often is a surface wave discharge. The plasma compositions investigated include argon, nitrogen, air, and hydrogen discharges. The pressure range investigated ranged from 100 mTorr to 1 atmosphere. The diagnostic measurements were performed using Langmuir probes and optical emission spectroscopy. The plasma characteristics measured and modeled indicate that as the characteristic dimension of the discharge decreases to less than 1 mm, the power densities approach and exceed 1000 W/cm@super 3@ and the plasma densities are above 10@super 13@ cm@super -3@. A specific application to be discussed is the plasma-assisted deposition of coatings on the inside of tubes.

PS-WeP17 Laboratory Exercises for a Technician-Level Course in Plasma-Aided Manufacturing, ***D.M. Hata***, Portland Community College

Portland Community College, through a grant from the National Science Foundation's Advanced Technological Education Program, has developed educational materials for a technician-level course in plasma-aided manufacturing and has prototyped a suite of supporting laboratory exercises. These educational materials were classroom tested during Winter Term of 2003 in PCC MT 240 RF Plasma Systems course. Thirty-three second-year students used the instructional materials and performed the laboratory exercises. Four faculty enhancement workshops are scheduled during the next year and a half to equip other community college faculty to teach a similar course at their institutions. This paper or poster session will provide an overview of the laboratory exercises developed to date.

Semiconductors

Room Hall A-C - Session SC+EM-WeP

Poster Session

SC+EM-WeP1 STM Observation of Dopant Atoms and Point Defects in the p-type GaAs (110) Surface at 5K, *B. Grandidier*, ***G. Mahieu***, *D. Deresmes, J.P. Nys, D. Stievenard,* IEMN-CNRS, France*; P. Ebert,* IFF-Julich, Germany

Cross-sectional scanning tunneling microscopy (STM) is used to study dopant atoms and point defects exposed on and in cleaved p-type doped GaAs (110) surfaces at 5K. While Zn dopant atoms have been already characterized in the past, spatial mapping of the conductance variation on individual dopants gives new insights in the origin of the triangular shaped features generally observed if the tip Fermi level is near the bottom of the conduction band. Combining empty and filled state images, we also identify As antisites and complex of vacancies. The stability of complex vacancies are discussed in the light of the available theoretical information.

SC+EM-WeP3 Metal-Oxide-Semiconductor Field Effect Transistors Investigated by Scanning Capacitance Force Microscopy, ***K. Kimura***, *K. Kobayashi, H. Yamada,* Kyoto University, Japan*; K. Usuda,* Toshiba Corporation, Japan*; K. Matsushige,* Kyoto University, Japan

We have recently developed a novel scanning probe technique, scanning capacitance force microscopy (SCFM) capable of measuring two-dimensional (2D) dopant profiling of semiconducting sample. SCFM, of which operating principle is based on the detection of an electric force between the conducting tip and sample, does@aa n@t utilize ultrahigh frequency capacitance sensor required for conventional scanning capacitance microscopy (SCM). In SCFM, an electric field alternating at an angular frequency @omega@ is applied between the tip and the semiconducting sample and then the induced electric force (ESF) oscillating at its third harmonic frequency (3@omega@) is detected using a lock-in amplifier as an SCFM signal. This is because the magnitude of the induced ESF is proportional to the square of the applied electric field and the capacitance of the semiconducting sample, which is also modulated at @omega@. Thus the amplitude-and-phase (Acos @phi@) signal of the induced ESF alternating at 3@omega@ contains information on the differential capacitance (dC/dV). We performed cross-sectional SCFM imaging of a n-channel metal-oxide-semiconductor field effect transistor (n-MOSFET). In source and drain regions, dopant density decreases from 10@super 21@ cm@super -3@ at the surface to 10@super 17@ cm@super -3@ at about 100 nm in the depth direction. Channel length is 500 nm and dopant density in channel region is 10@super 17@ cm@super -3@. We observed a drastic change in SCFM signal at about 100 nm in the depth direction of the source or drain regions. We also observed a characteristic contrast at the depleted area under the gate oxide corresponding to the channel region. In the presentation, we present SCFM images on MOSFETs obtained both in contact mode and dynamic mode. We discuss the interpretation of the obtained contrast and its dependence on the applied DC voltage. We also compare those SCFM images with SCM images and SIMS profiles.

SC+EM-WeP4 Effect of Mn Composition on Characterization of Zn@sub 1-x@Mn@sub x@Se Epilayers, ***Y.-D. Choi***, *Y.-M. Yu, D.-J. Kim, K.-J. Lee,* Mokwon University, South Korea*; Byungsung O, K.-S. Lee,* Chungnam National University, South Korea*; I.-H. Choi,* Chung-Ang University, South Korea*; M.-Y. Yoon,* Joongbu University, South Korea

ZnMnSe is one of II-VI diluted magnetic semiconductors, in which the cations of the host crystal are replaced with Mn@super 2+@ ions. Recently, ZnMnSe is used as a material to inject spin inside the quantum structures. The crystal structure of the bulk ZnMnSe is cubic in the range of the Mn composition for x0.05. The absorption and PL spectra at 10 K were compared. In the region of small range x, the band gap energy showed weak bowing effect. It was found that PL peak near the energy band gap was related to the free exciton from the absorption measurements. From Raman measurement at the room temperature, ZnSe-like LO phonon peak was observed, and with the increasing Mn composition x the blue shift of 3.5 cm@super -1@ was observed. The variation of the dielectric constants @epsilon@@sub 1@ and @epsilon@@sub 2@ as a function of Mn composition x by SE was measured. When x is small, it was found that the predominant transition took place in the critical point(CP) of each band structure, and with the increasing x, CP was shifted to low energy side.

SC+EM-WeP5 Linear Magnetoresistance in LaSb@sub 2@: The Role of Charge-Density Waves@footnote *@, *A. Acatrinei,* Louisiana State University*; J.W. Richardson,* Argonne National Laboratory*; D. Young, D. Browne, Y. Losovyj, P.T. Sprunger,* ***R.L. Kurtz***, Louisiana State University

LaSb@sub 2@ exhibits a giant linear magnetoresistance@footnote 1@ to very high fields (40T) yet it is composed of non-magnetic elements. This work reports on the role of charge-density waves (CDW) in providing a magnetic response within the two-dimensional constraints of this layered compound. Single-crystals of LaSb@sub 2@ were grown in an excess Sb flux using high-purity La and Sb and X-ray diffraction measurements confirm that it has an orthorhombic crystal-structure with a=6.38 b=6.23 and c=18.75Å. The layered structure of Sb planes separated by bi-layers of La-Sb chains gives the material a micacious appearance. X-ray measurements suggest a mosaic spread of ~0.5-1° and it is likely that the material is highly twinned. When the material is cleaved in uhv, STM studies give flat terraces mostly separated by the unit cell height and, occasionally, we observe half-unit cell steps. Neutron diffraction measurements show temperature-dependent peaks that are not from the orthorhombic structure but have been attributed to the CDWs. Further clues to the potential origin of charge-density waves come from a comparison of photoemission and density-functional studies. Photoemission studies show that the electronic structure is highly two-dimensional. Density functional theory predicts nearly square tube-like Fermi surfaces that extend along the c direction and provide the opportunity for a high degree of nesting within the basal plane. It is this nesting that provides an electronic mechanism to couple charge density oscillations to the electronic structure. A high-resolution study of the CDW gap opening at FS will be presented and discussed in terms of the role of CDWs in the magnetic response. @FootnoteText@@footnote *@We would like to acknowledge Argonne's IPNS, the LSU CAMD synchrotron light source, and the NSF for their support of this work. @footnote 1@ Bud'ko, Canfield, Mielke, et al., Phys. Rev. B 57, 13624 (1998).

SC+EM-WeP6 Ferromagnetic Co-Implanted Rutile TiO@sub 2@(110) for Spintronics Applications, ***V. Shutthanandan***, *S. Thevuthasan, T. Droubay, S.M. Heald, M.H. Englehard, L.V. Saraf, S.A. Chambers,* Pacific Northwest National Laboratory*; B.S. Mun,* Lawrence Berkeley National Laboratory*; R.P. Sears, B. Taylor, B.S. Sinkovic,* University of Connecticut

There is a growing interest in diluted magnetic semiconductor materials due to their potential applications in spintronics area. The ability to efficiently inject spins into multi-layer semiconductor device structures for room temperature operations creates new and exciting possibilities for utilizing DMS materials in semiconductor applications. Some of the dilute magnetic semiconductors with the potential for room temperature spintronics applications include Co-doped ZnO, Mn-doped GaN and Co-doped TiO@sub 2@. Although there are still some issues associated with the growth of single crystal Co-doped anatase TiO@sub 2@, recent experiments show that this material is the most promising candidate because of its room temperature ferromagnetism.@footnote 1,2@ Recently, we have investigated the Co doping in rutile TiO@sub 2@ using ion implantation as a function of implantation temperature and subsequent annealing. Co implantation at room temperature shows that the implanted Co stays as mostly Co metal in TiO@sub 2@(110). Subsequent annealing around 875 K in air promotes Co diffusion towards the surface. During this process Co gets oxidized in the near surface region. Although a portion of the implanted Co appears to be oxidized as a function of implantation temperature up to 875 K, the Co implantation at 1075 K indicates that the implanted Co is mostly oxidized. Some of the implanted Co at 1075 K appears to be substituting for Ti. These samples were characterized using several surface and bulk sensitive techniques including x-ray photoelectron spectroscopy (XPS), Co K and L edge x-ray absorption near edge structure (XANES), and Rutherford backscattering spectrometry (RBS)/channeling. These results with the room temperature vibrating sample magnetometer (VSM) and magneto-optical Kerr effect (MOKE) measurements from these samples will be discussed. @FootnoteText@@footnote 1@ M. Matsumoto et al., Science, 291, (2001) 854.@footnote 2@ S.A. Chambers et al., Appl. Phys. Lett. 79 (2001) 3467.

SC+EM-WeP7 The Crystallization Behavior and Interfacial Reaction between GeTe and Sb@sub 2@Te@sub 3@ Film for the Application to the Phase Change Memory

*, **E.J. Jung**, S.K. Kang, B.G. Min,* Yonsei University, South Korea*; H. Horii, Y.H. Ha, J.H. Park,* Samsung, South Korea*; D.H. Ko,* Yonsei University, South Korea

Flash memory has been widely used as a non-volatile memory, however, it has limitations, such as low speed and low write endurance. To supplement the limitation of flash memory, recently phase change memory(PCM) has been investigated using the class of elements known as chalcogenide. This technology is expected to allow chips that have SRAM speed, DRAM cost and FLASH power characteristic and non-volatility. Chalcogenide is a confirmed phase change material used in re-writeable CDs and DVDs. This material changes phases reversibly and quickly between an amorphous state with high resistivity and a crystalline state with low resistivity. Previously, GeSbTe system has been known as pseudobinary GeTe and Sb@sub 2@Te@sub 3@ alloys with different combinations, such as Ge@sub 2@Sb@sub 2@Te@sub 5@, Ge@sub 1@Sb@sub 2@Te@sub 4@, and Ge@sub 1@Sb@sub 4@Te@sub 7@. Recently GeTe-Sb@sub 2@Te@sub 3@ multi-layer structure is studied to improve crystallization time and rewrite cycle time in optical data storage. We investigated interface reaction and crystallization property between GeTe and Sb@sub 2@Te@sub 3@ thin film to observe a created composition at interface in variable annealing temperature and methods. The GeTe-Sb@sub 2@Te@sub 3@ film was deposited on SiO@sub 2@ by D.C. magnetron sputtering method with GeTe and Sb@sub 2@Te@sub 3@ alloy target. The thickness of each layer is 10nm. After the deposition of GeTe-Sb@sub 2@Te@sub 3@ film, TiN was deposited in a same chamber without breaking vacuum as a capping layer. Sample was annealed at temperature between 200°C and 700°C using furnace and RTP. To study crystallization behavior, XRD analysis were performed. In addition, the sheet resistance was measured by using 4-point probe. TEM analysis was performed to investigate interface reaction between GeTe and Sb@sub 2@Te@sub 3@ thin film. And to observe distribution of each element atom in interface reaction, AES depth profile and EDX were carried out.

SC+EM-WeP8 The Dependence of Charge Collection Efficiency on Metal Electrode in Polycrystalline CdZnTe(x=0.04) Material

*, **S.Y. Ahn**, K.H. Kim,* Korea University*; S.Y. An,* Korea Institute of Science and Technology*; J.K. Hong, K.N. Oh,* Korea University*; S.U. Kim,* Korea University, Korea

There is currently a growing interests on digital X-ray imagers. A direct methods that has several benefits over the indirect methods like convenient image acquistion, storage and transmission, digital image processing, computer-assisted diagosis, real time images, a better spatial resolution dose for equivalent images.@footnote 1@ To generate appropriate e-h pair in CdZnTe film on incident X-ray, thick CdZnTe film was required. Using thermal evaporation method that is generally adquate to deposit thick films, CdZnTe thick films was obtained having ~100 µm in thickness. We investigate the contact between CdZnTe thick film and a variety of metals with the aim of determining whether the choice of metal can improve the performance of X-ray imager detectors, in particular minimizing the dark current. The sample consist of 100 µm thick CdZnTe(x=0.04) with top electrodes formed from Au, In.@footnote 2@ The detection capability of the material has been demonstrated by time-of-flight(TOF) measurements performed on a device made by an n-CdZnTe epilayer. The analysis of the TOF collected charge as a function of the applied voltage give µ @tau@ ~ 10 @super -4@ cm@super 2@/V for this material.@footnote 3@ And we measured resistivity using four-point probe method. CdZnTe(x=0.04) thick film's resistivity is 3 x 10 @super 9@ @ohm@ cm. Au deposited sample is founded to have better properties than others in many respects such as low leakage current, chemicalstability. @FootnoteText@ @footnote 1@ Y. Eisen, A. Shor, J. Crystal Groeth 184/185 (1998) 1302.@footnote 2@ M. J. Mescher, J. F. Hoburg, T. E. Schlesinger, R. B. James IEEE Transactions on Nuclear Science, Vol. 46, NO. 6, December. (1999)@footnote 3@ X. J. Bao, T. E. Schlesinger, R. B. James, Semiconductors for room temperature nuclear detector applications, in: T.E. Schlesinger, R.B. James (Eds.), Semicounductors and Semimetals, Vol. 43, Academic Press, San Diego. (1995).

SC+EM-WeP9 Surface Passivation of HgCdTe by RF Sputtered Silicon Nitride

*, **S.Y An**,* Korea University*; Y.C. Joung,* Hanyang University, Korea*; S.H Lee,* Korea University*; S.H. Suh,* Korea Institute of Science and Technology*; J.S Kim,* Korea Institute of Science and Technology, Korea

There have been considerable advances in HgCdTe device technology. However, surface passivation and insulator/HgCdTe interface are still a subject of great interests.@footnote 1@ Up to now, there has been a lot of results reported on passivants for HgCdTe devices. Recently, silicon nitride (SiN@sub x@) deposited by ECR-PCVD has been reported as a passivant for HgCdTe.@footnote 1,2@ But, there was no research report on RF magnetron sputtered SiN@sub x@ for HgCdTe passivation. In this paper we briefly report some experimental results concerning about interface state and fixed charge density in metal-insulator-semiconductor (MIS) structures realized by RF magnetron sputtered SiN@sub x@ on HgCdTe surface. The electrical properties of MIS structure were studied as a function of sputtering power and working pressure of sputtering chamber. Capacitance-voltage (C-V) characteristics were measured at 1MHz and interface state densities were obtained by Terman's method. It was observed that conductivity type of HgCdTe is closely related with deposition rate of SiNx. The p-type conductivity of HgCdTe was converted to n-type conductivity at deposition rate of less than 25Å/min. To prevent p-type HgCdTe from type conversion, it is necessary to maintain high sputtering rate of SiNx at initial stage. The interface state density and fixed charge density of SiN@sub x@ film on HgCdTe were 1.9x10@super 10@cm@super -2@, and 1.5x10@super 11@cm@super -2@, respectively, at sputtering power of 175W. @FootnoteText@@footnote 1@O. P. Agnihotri, C. A. Musca and L. Faraone, Semicond. Sci. Technol. Vol. 13. 839 (1998). @footnote 2@Y. Nemirovsky and G. Bahir, J. Vac. Sci. Technol. A, Vol.7, No. 2, 450 (1989).@Footnote 3@G. Sudo, N. Kajihara, Y. Miyamoto and K. Tanikawa, Appl. Phys. Lett. Vol.51, No.19, 1521 (1987).

SC+EM-WeP10 Growth and Characterization of Thin Films of a New Semiconductor produced by Co-Sputtering of CdTe and Al@footnote 1@

*, **M. Melendez-Lira**,* Cinvestav-IPN, Mexico*; M. Zapata-Torres,* CICATA-IPN, Mexico*; S. Jimenez-Sandoval,* Cinvestav-IPN, Mexico*; M.A. Fuentes-Cabrera,* Carnegie Mellon University

The atomic elements Cd, Te and Al form the compunds CdTe, CdAl@sub 2@Te@sub 4@ and Al@sub 2@Te@sub 3@. CdTe and CdAl@sub 2@Te@sub 4@ are semiconductors and their room temperature band gap are 1.5 eV and 2.0 eV, respectively. The existence of these compounds prompted us to produce a new alloy based in CdTe and Al. We have produced thin films of Cd@sub x@TeAl@sub 1-x@ by rf co-sputtering employing targets of CdTe and Al under an argon atmosphere. Aluminum content in the films was controlled by the rf power applied to the aluminum target. The chemical, structural and optical properties of the thin films have been studied by EDS, X ray diffraction, AFM, optical transmission, photoreflectance, photoluminescence and Raman spectroscopies. EDS, X-ray diffraction and Raman results shown clearly that aluminum has been incorporated in the CdTe lattice, for low aluminum content an hexagonal structure is found. For low aluminum contents transmission spectroscopy results indicate a clear blue shift in the band gap of the alloy. Photoreflectance spectroscopy indicates the presence of a direct band gap of 1.6 eV; for an aluminum content of 6%. Band gap values are discussed taking in account theoretical results obtained by first principles employing the Local Density Approximation and Generalized-Density Functional Theory approaches. @FootnoteText@ @footnote 1@Work partially supported by CONACyT-Mexico.

SC+EM-WeP11 Current Mapping of GaN Films

, A.A. Pomarico, University of Lecce, Italy*; **J.C. Dickinson**,* Virginia Commonwealth University*; R. Cingolani,* University of Lecce, Italy*; H. Morkoc, A.A. Baski,* Virginia Commonwealth University

GaN-based devices have made remarkable advances recently, but still suffer from excessive current leakage, due in part to extended defects in the material and point defects which are not well understood. We have used the technique of conductive atomic force microscopy (C-AFM) to investigate how the local conductivity of GaN films is related to morphology.@footnote 1@ Our studies indicate enhanced conductivity for prismatic planes found around islands on as-grown samples, and on the edges of pits formed by post-growth chemical etching. In the case of etched HVPE samples, AFM images show hexagonal pits produced by the etching of defect sites on c-plane GaN. Simultaneous C-AFM images show detectable current only at the edges of such pits for forward-bias voltages below 4 V. This indicates that crystallographic planes tilted with respect to the c-plane have a significantly higher conductivity than surrounding areas. Although still under investigation, possible mechanisms for this enhanced electrical activity include extended defects, surface states, and modified Schottky barrier heights on prismatic planes. @FootnoteText@@footnote 1@ A.A. Pomarico et al., Appl. Phys. Lett. 82, 1890 (2003).

Surface Science
Room Hall A-C - Session SS-WeP
Poster Session

**SS-WeP1 High Temperature Catalytic Water Formation Studied with Laser-induced Fluorescence and Cavity Ringdown Spectroscopy*, S. Hemdal*, *A. Johansson, M. Forsth, M. Andersson, A. Rosen,* Goteborg University and Chalmers University of Technology, Sweden

Catalytic reactions are successfully studied with Laser-Induced Fluorescence (LIF) and valuable information about mechanisms and reaction paths can be obtained. However, due to the infamous quenching problem absolute concentrations are difficult to measure. Knowledge of exact concentrations of reactants and intermediates are valuable for successfully doing simulations. Cavity RingDown Spectroscopy (CRDS) is a laser absorption method suitable to measure exact concentration of reaction intermediates in trace amounts. In this study we have combined LIF and CRDS to study OH radicals in the water formation reaction desorbing from polycrystalline palladium and platinum catalysts. In CRDS a laser pulse is injected between two highly reflective mirrors that constitute the optical cavity. In each roundtrip some light will leak out and be detected as a function of time. Assuming single exponential decay, the ring down time @tau@ is defined as the time it takes for the intensity of the detected light to decrease to 1/e of its original intensity. By comparing the ring down times for on and off a resonant transition in the OH molecule, the number density can be obtained. The temperature of the catalyst was set to 1500 K, the pressure varied between 7 and 26 Pa and the flow was 100 SCCM. In this study we have successfully detected OH in the H@sub 2@/O@sub 2@ reaction with CRDS and calibrated the LIF profiles. From the CRDS data we have also calculated the rotational temperature of the OH molecule. The quenching rate for OH is also analysed.

SS-WeP2 Relevance of the Use of XPS and AES to Characterize the Electrochemical Interface*, F. Reniers,* Universite Libre de Bruxelles, Belgium

XPS and AES are often used in corrosion studies to identify the chemical composition of the interface. Moreover, the last developments of the technology makes available lateral resolutions of 10 nm in AES and 10 Âµm in XPS, which is interesting for grain boundary corrosion or pitting corrosion. These techniques are also used to characterize the surface of electrodes in fuel cell systems, or mixed (alloys) electrodes used for environmental purposes. AES and XPS are good complement to classical electrochemical techniques (cyclic voltammetry, coulommetry) which give access to the current flowing through the interface, as they can identify the nature and the number of surface atoms, as well as their chemical environment. However, as XPS and AES are UHV-based techniques, the physical nature of the interface probed is different from the original solid-liquid one, and transfer in air can modify the sample surface. This paper shows selected examples of coupled UHV-electrochemical studies (adsorption, corrosion, electrocatalysis), using transfer systems, and describes the information which can and which cannot be extracted from such studies. The persistence of the constituents of the electrical double layer and the nature of the electrode metal on the reliability of the results is discussed. A description of some transfer systems, designed to minimize the experimental artefacts, is proposed.@footnote 1@ @FootnoteText@ @footnote 1@F. Reniers, J. Physics D: Appl.Phys.35 (2002)R169-R188.

SS-WeP3 A Laser Plasma Vacuum Ultraviolet Light Source for Photo Desorption Studies*, I. Arakawa,* *J. Sato, T. Miura,* Gakushuin University, Japan*; T. Hirayama,* Rikkyo University, Japan

We have developed a laser-plasma vacuum ultraviolet light source (LPLS) as an excitation light source for the experimental studies of desorption induced by electronic transitions(DIET). Radiation from metal plasma, which is produced by laser beam focused on a metal surface, has a wide spectrum from infrared to X-ray and can provide a substitute for a conventional synchrotron radiation. In comparison with the synchrotron light source, LPLS has the advantage of being intense in short duration: the pulse width is the order of 10 ns, which is determined by a laser pulse. This distinctive feature makes it possible to obtain higher time resolution in a time-of-flight measurement of desorbed particles. The specifications of the Q-switched Nd-YAG laser we used in our LPLS are the followings; wave length: 532 nm with a second harmonic generator, maximum power: 210 mJ/pulse, pulse width: 10 ns, and repetition rate: 50 Hz. The radiation from the metal plasma is monochromatized by the three toroidal type gratings which cover the wavelength ranges of 4 - 12, 12 - 36, and 36 - 108 nm. We have choose Ta as the target metal for plasma source. This is because (1) a continuum like spectrum of primary radiation from plasma is expected in VUV range and (2) evaporated Ta will act as a getter pump in a vacuum chamber. The photon intensity of our LPLS apparatus is 10@super 7@ - 10@super 8@ photon/pulse in the pulse width less than 15 ns and with the resolution @lambda@/@DELTA@@lambda@ = 50 - 100 in the range of 12 - 108 nm. On application of our apparatus to the PSD experiment of a solid Ne, it was proved that the performance was satisfactory both in photon intensity and in time resolution for the DIET study.

SS-WeP4 Ellipsometric and XLEED Observation of Growth and Structure of Xenon and Krypton Films on the Surface of Silver Single Crystals*, A. Tosaka*, *T. Mitake, K. Ishii, M. Sato, T. Miura, I. Arakawa,* Gakushuin University, Japan

The layering growth and the structure of Xe and Kr films on Ag(111), Ag(100) and Ag(110) has been observed by means of ellipsometry and eXtremely-low-current Low Energy Electron Diffraction (XLEED) under the quasi-equilibrium condition from a submonolayer to a thick film. We chose the surfaces of Ag(111), Ag(100) and Ag(110) as the substrates in order to investigate the effect of the substrate geometry on the overlayer growth and structure. In the case of Xe/Ag(111) and Kr/Ag(111), it was confirmed that the overlayer is incommensurate with the substrate while the unit vectors of the Xe or Kr overlayer align with those of the substrate. This alignment is likely due to the pinning of overlayer at the steps of the substrate surface.@footnote 1@ We found that there were two types of alignment of a Xe or Kr overlayer on Ag(100): the unit vector of the overlayer was along of Ag in one alignment and along in the other. It was observed that Xe and Kr films on Ag(110) had centered-rectangular structure, which is uniaxially commensurate with [001] of Ag, just after the first layer condensation. In the case of Xe/Ag(110), lowering the sample temperature or raising the surrounding pressure brings out the uniaxial compression of Xe film along [110] of Ag. After this uniaxial compression along [110], the compression along [001] of Ag commenced. Finally, the Xe-Xe spacing reached to the bulk value before the second layer condensation. On the other hand, in the case of Kr/Ag(110), such compression did not observed in monolayer. @FootnoteText@ @footnote 1@G. S. Leatherman, R. D. Diehl, M. Karimi and G. Vidali: Phys. Rev. B 56 (1997) 6970.

SS-WeP6 Chemical Structure of the Pt/CdZnTe Interface, D.J. Gaspar,*** *M.H. Engelhard, D.E. McCready,* Pacific Northwest National Laboratory*; A.A. Rouse, Cs. Szeles,* eV PRODUCTS

We have determined the interfacial electronic and chemical structure for the Pt/CdZnTe system using scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD) and x-ray photolectron spectroscopy (XPS). XRD was performed on aggressively aged controls (such as Pt/Te, where PtTe@sub 2@ was formed) to elucidate the phases expected to form under normal annealing conditions. The presence of the phases was confirmed by looking at the specimens in cross-section with SEM/EDX. This was followed by XPS depth profiling experiments to determine binding energy shifts associated with the various phases, which were then used to determine the phases present in the more narrow interfacial regions of typical Pt/CZT structures for a variety of annealing conditions and for varying compositions.@FootnoteText@*This work supported by the DOE NNSA NA-22 program

SS-WeP7 Modeling Nano-Structure Evolution in the Continuum Step Model: Decay of Pb Crystallites@footnote1@*, **M. Degawa**, D.B. Dougherty, K. Th@um u@rmer, J.E. Reutt-Robey, E.D. Williams, T.J. Stasevich, T.L. Einstein,* University of Maryland

The evolution of crystalline nanostructures can be described accurately down to surprisingly small size scales using the continuum step model.@footnote 1@ Quantitative predictions for rates in general cases requires understanding the balance of competing kinetic mechanisms (step-edge attachment vs. terrace diffusion), competing driving forces (Gibbs-Thomson vs. step-step repulsions) and the influence of the initial shape and boundary conditions on the nanocrystal. Using numerical modeling, we demonstrate the evaluation of best fits in this multi-parameter space for the case of the relaxation of Pb crystallites after thermal quench@footnote 2@ and after triggered decay.@footnote 3@ The experimental system involves a volume-conserving change in the shape of the Pb crystal, which proceeds via cylindrically symmetrical layer-by-layer removal from the top facet of the crystal and transfer of mass to the sides of the crystal. The rate of peeling of all the layers yields non-unique combinations of the diffusion coefficient and attachment detachment rate, which can be limited by the range of physically reasonable the step-step repulsions. The time difference between sequential layer peelings, and the slow-down to the final state is governed by the choice of the boundary conditions and the step-step repulsions. The relationship of the best fit parameters to atomistic models for Pb, and the physical significance of the boundary conditions will be discussed. @FootnoteText@This work has been supported by the DOE-NNI and NSF-MRSEC.@footnote 1@A. Ichimiya, K. Hayashi, E.D. Williams, T.L. Einstein, M. Uwaha and K. Watanabe, Phys. Rev. Lett. 84, 3662 (2000). @footnote 2@K. Thurmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Emundts and H.P. Bonzel, Phys. Rev. Lett. 87, 186102-1 (2001). @footnote 3@D. B. Dougherty, K. Thurmer, M. Degawa, W.G. Cullen, J.E. Reutt-Robey and E.D. Williams, submitted for publication (2003).

SS-WeP8 Using Island Step-Edge Fluctuations to Determine Absolute Step Energies: Application to Pb(111)@footnote 1@*, **T.J. Stasevich**, F. Szalma, T.L. Einstein,* University of Maryland, College Park

It is well known that the equilibrium shape of an adatom or vacancy island can be used to extract the step free energy (or line tension) of the island step-edge up to a scale factor. Obtaining the absolute step energy, however, requires a deeper analysis. Recently it has been shown that by analyzing the island step-edge fluctuations about the equilibrium island shape, the desired absolute step energy can be obtained.@footnote 2,3@ We exploit this theoretical framework to analyze the temporal fluctuations of two-dimensional Pb(111) adatom and vacancy islands measured with scanning-tunneling microscopy.@footnote 4@ We report on our ongoing analysis and discuss the degree to which subtle transformations are needed to obtain eigenmodes from the conventinal multipole modes. With the aid of movies, we also discuss techniques used to find the equilibrium island shape, as well as tools used to analyze the fluctuations and, thus, determine the absolute step free energies. @FootnoteText@ @footnote 1@Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. @footnote 2@S. Kodambaka et al., Phys. Rev. B 67 (2003) 035409; S.V. Khare et al., Surf. Sci. 522 (2003) 75. @footnote 3@ F. Szalma and T.L. Einstein, submitted to SS1@footnote 4@ K Thürmer et al., Phys. Rev. Lett. 87 (2001) 186102.

SS-WeP9 Persistence Exponent for Terrace-Diffusion Limited Step Fluctuations: Numerical Simulation@footnote 1@*, **H. Gebremariam**, C. Dasgupta, T.L. Einstein,* University of Maryland, College Park

The strength of the step-step repulsion, one of the 3 key parameters of the step continuum model, is known to influence many properties of a vicinal surfaces. Motivated by experiments at Maryland on Ag(111) and Pb(111)@footnote 2@ and on Al/Si(111),@footnote 3@ we gauge the impact these interactions on the persistence exponent @theta@. (Here the steady-state persistence probability p(t) ~ t^(-@theta@) is the probability that a fluctuating step has not crossed a chosen rough initial position by time t.@footnote 4@) According to simple scaling based on Langevin arguments, @theta@ should be (1/2)[1+1/z] for evaporation-condensation (z=2) and (1/2)[1+3/(4z)] for periphery diffusion dynamics (z = 4).@footnote 4@ To investigate whether either of these relations also holds for terrace-diffusion-limited (TD) dynamics (for which z=3), we perform Monte Carlo simulations for an SOS model similar to that used for earlier investigations of step fluctuations.@footnote 5@ @FootnoteText@ @footnote 1@Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. @footnote 2@D.B. Dougherty et al., Surface Sci., in press [doi:10.1016/S0039-6028(03)00017-7]. @footnote 3@D.B. Dougherty et al., Phys. Rev. Lett. 89 (2002) 136102.@footnote 4@J. Krug et al., Phys. Rev. E 56 (1997 2702.@footnote 5@ N. C. Bartelt et al., Surface Sci. 312 (1994) 411.

SS-WeP10 Effects of Thickness Extension Resonance Oscillation of Acoustic Wave on Activity/Selectivity of Metal Catalysts with Two Layer Structures*, **Y. Oka**, Y. Nakajima, N. Saito, H. Nishiyama, Y. Inoue,* Nagaoka University of Technology, Japan

We have so far reported that the thickness-extension resonance oscillation (TERO) of acoustic wave generated on a ferroelectric crystal by a piezoelectric effect has the ability to markedly enhance the catalytic activity and to significantly change the reaction selectivity of metal-catalyzed reactions. The catalyst activation by TERO was associated with large and dynamic lattice displacement vertical to the catalyst surfaces. The TERO effects were different among the metal catalysts. In aiming at raising the efficiency of the TERO effects, it is of interest to examine the TERO effects on two-layer structure catalysts combining the different kinds of metal phases. In the present study, a metal catalyst combining Mo with Ag was employed. A ferroelectric z-cut LiNbO@sub 3@ single crystal was used as substrate, on which Ag film was deposited at a thickness of 100 nm, followed by the deposition of Mo with different thickness in the range 20-100 nm. Auger electron spectroscopic measurements showed that the two-layer structures were maintained during catalytic run. In ethanol decomposition on the Mo/Ag catalysts with different thickness of Mo layer, major gas phase products were ethylene and acetaldehyde. With turning TERO on, only the activity for ethylene production remarkably increased. The activation coefficient, defined as the ratio of the activity with TERO-on to that with TERO-off was 16 for 100nm, 17 for 75 nm, 24 for 50 nm, and 27 for 20 nm Mo layer, indicating that the TERO-inducing activation for ethylene production became larger as the thickness of Mo layer was smaller. Lattice displacement of Mo/Ag catalysts increased with decreasing thickness of the Mo layer. There was a correlation between the extent of lattice displacement and catalyst activation by the TERO in the two layer structures. These results have demonstrated that the combination of different metal phases is useful for extending TERO effects to catalyst activation.

SS-WeP11 Chemisorption of Sulfur on Au(111), Au(100) and Au(110) by Means of UHV and Electrochemical Adsorption*, **Y.W. Yang**, L.J. Fan,* National Synchrotron Radiation Research Center, Taiwan

Reaching a detailed understanding of the interaction between sulfur and gold surfaces has become more urgent due to their wide usage in constructing self-assembled monolayers in nanoengineering research. Here, we report on a detailed structural and energetic study of molecular S@sub 2@ adsorbed on Au(111), Au(100) and Au(110) surfaces by means of LEED, SR-XPS and TPD. A comparative study of sulfur adsorption from electrochemical (EC) deposition is also investigated with ECSTM. For all three surfaces, LEED study reveals the presence of a series of ordered adsorption structures. TDS data show the presence of strong repulsive interaction among sulfur adsorbates and, interestingly, the existence of several unusual binding states on all three surfaces. These binding states are characterized by sharp features of less than 30 K in desorption peak width. The overall change of S 2p core levels is found to be small in spite of a strong variation of adsorption structure and adsorption site among three gold surfaces. The observed S 2p@sub 3/2@ core levels fall between 161.0 and 161.3 eV. The rather constant S 2p@sub 3/2@binding energy suggests the importance of final-state metallic screening. ECSTM shows the presence of additional ordered structures not observable from UHV adsorption but stabilized by the coadsorbed ions from the solution. UHV and EC adsorption structure data will be discussed together.

SS-WeP12 Structure and Reactivity of Methyl Pyruvate and Butane-2,3-Dione on Pt(111) and Ni(111): Relevance to Enantiosective Hydrogenation at Surfaces*, **M.-A. Laliberte**, S. Lavoie, P.H. McBreen,* Universite Laval, Canada

Methyl and ethyl pyruvate are substrates in one of the rare examples of efficient enantioselective heterogeneous catalysis.@footnote 1,2@ The asymmetric hydrogenation of pryuvates to lactates occurs on chirally-modified supported platinum catalysts. Nickel catalysts are, in contrast, not active for the reaction. Data is now available in the literature for the chemisorption of pyruvates on both Ni(111)@footnote 3,4@ and Pt(111).@footnote 5-8@ An intriguing aspect of these results is that they show that the surface chemistry of pyruvates differs greatly between the two metals. We have previously reported a detailed RAIRS study of the coverage dependent orientation, conformation and surface chemistry of methyl pryuvate on Ni(111).@footnote 3,4@ The present study presents extensive new RAIRS data for methyl pyruvate on Pt(111), and butane-2,3-dione on Ni(111) and Pt(111), thereby enabling a detailed comparison to be made between the two surfaces. @FootnoteText@@footnote 1@Y. Orito, S. Imai, S. Niwa, N. G. Hung, J. Synth. Org. Chem. Jpn. 37, 173 (1979) @footnote 2@H. U. Blaser, H. P. Jalett, W. Lottenbach and M. Studer, J. Am. Chem. Soc. 122, 12675 (2000). @footnote 3@M. Castonguay, J.-R. Roy, S. Lavoie, A. Adnot, and P. H. McBreen, J. Am. Chem. Soc. 123,6429 (2001). @footnote 4@M. Castonguay, J. -R. Roy, A. Rochefort, and P. H. McBreen, J. Am. Chem. Soc. 122, 518 (2000). @footnote 5@T. Burgi, F. Atamny, R. Schlogl and A. Baiker, J. Phys. Chem. B, 104, 5953. (2000). @footnote 6@J. M. Bonello, R. M. Lambert, N. Kunzle and A. Baiker, J. Am. Chem. Soc. 122, 9864 (2000). @footnote 7@J.M.Bonello, E.C.H. Sykes, R. Lindsay, F.J. Williams, A. K. Santra and R.M. Lambert, Surf. Sci. 482 207 (2001) @footnote 8@J. M. Bonello, F. J. Williams, A. K. Santra, and Richard M. Lambert, J. Phys. Chem. B, 104, 9696 (2000).

SS-WeP14 QCM Studies of Phonon and Electron Scattering Effects for Monolayer Octane/Cu(111) and Octane/Pb(111) Interfaces*, **T. Coffey**, J. Krim,* North Carolina State University

The surface resistivity and sliding friction of thin films on metal surfaces has been linked to the scattering of conduction electrons from phonons and imperfections in the lattice. It is also believed that the damping of Frustrated Translational (FT) phonon modes are related to friction between adsorbates and substrates.@footnote 1@ The parallel FT modes are believed to be directly linked to sliding friction, but it is not clear how changes in the damping of perpendicular FT modes affects sliding friction. The perpendicular FT mode of octane adsorbed on Cu(111) has a damping constant that is twice as large as that of octane adsorbed on Pb(111).@footnote 2@ We are using QCM to study octane sliding on copper and lead surfaces to determine how the damping of perpendicular FT modes affect sliding friction. We have observed an increase in sliding friction as the damping of the perpendicular FT mode increased. @FootnoteText@ @footnote 1@ B.N.J. Persson, Sliding Friction, Physical Principles and Applications, Springer, Berlin (2000)@footnote 2@ D. Fuhrmann and Ch. Woll, Surface Science 368 (1996) 20-26. .

SS-WeP15 Photoemission Study of the Oxidation of Cu{111} with Hyperthermal O@sub 2@ Molecular Beam*, **K. Moritani**,* Japan Atomic Energy Research Institute, Japan*; M. Okada, S. Sato, S. Goto, T. Kasai,* Osaka University, Japan*; A. Yoshigoe, Y. Teraoka,* Japan Atomic Energy Research Institute

The oxidation of Cu has been of great interest because of the important role of Cu oxides in material science, for example, high T@sub c@ superconductors of cuprates and solar cells. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes have been little elucidated from the kinetics and dynamics points of view. In the present work, we studied the oxidation of Cu{111} with a hyperthermal O@sub 2@ molecular beam (HOMB) using X-ray photoemission spectroscopy (XPS) in conjunction with a synchrotron radiation (SR) source. All experiments were performed with the surface reaction analysis apparatus (SUREAC 2000) constructed in BL23SU at SPring-8. The kinetic energy of incident O@sub 2@ can be controlled by changing the O@sub 2@, He and/or Ar gas mixing ratios with the nozzle temperature kept at 1400 K. The incident direction of the HOMB is along the surface normal of the sample kept at 300 K. After the irradiation of a proper amount of HOMB, high-resolution XPS spectra were measured at 300 K using SR. We measured O-uptake curves, determined from the integration of O-1s XPS spectra, in the 2.3- and 0.6-eV HOMB irradiation on the Cu{111} surface. The efficiency of oxidation with HOMB is higher than that with ambient thermal O@sub 2@ gas. The kinetics of the dissociative adsorption in the HOMB incidence can be described well using a Langmuir-type adsorption model under @theta@ @<=@ 0.5 ML. On the other hand, further oxidation occurs rather inefficiently under @theta@ @>=@ 0.5 ML even for the 2.3-eV-HOMB irradiation. We found that such slow oxidation process of Cu can be interpreted in terms of a collision-induced-adsorption mechanism. We will discuss possible models of oxidation process of Cu based on the incident-energy dependence of the O-uptake curve.

SS-WeP16 Sulfur-oxygen Interactions on Cu(100) Revealed by Surface Resistivity Measurements*, **P.M. Baker**, R.G. Tobin,* Tufts University

Measurements of adsorption-induced changes in the electrical resistivity of thin Cu(100) films show that small amounts of preadsorbed sulfur dramatically reduce the resistivity caused by subsequently adsorbed oxygen. Previous measurements with sulfur and oxygen alone had shown that these two atoms, although chemically very similar, exhibited very different surface resistivity behavior.@footnote 1@ For oxygen the resistivity increases linearly with coverage, indicating minimal interactions between the oxygen atoms. Sulfur exhibits a strongly nonlinear coverage dependence, suggesting that at high coverages interactions between the adsorbed sulfur atoms reduce their cross section for scattering the metal's conduction electrons. In the present experiments the resistivity induced by oxygen was measured on 50 nm-thick Cu(100) films predosed with varying amounts of sulfur. For all sulfur coverages studied the oxygen-induced resistivity varies linearly with oxygen coverage, but the slope of the resistivity vs. oxygen coverage curve is strongly affected by the sulfur. This slope is a measure of the scattering cross section of each adsorbed oxygen atom. A sulfur coverage as low as 0.03 ML reduces the slope by a factor of two from its value on a sulfur-free surface. Evidently adsorbed sulfur atoms suppress the scattering cross section of coadsorbed oxygen even more strongly than they affect the cross section of other sulfur atoms. The saturation oxygen coverage is not significantly reduced at the sulfur coverages studied, indicating that site-blocking by sulfur is not involved. Rather the explanation must lie in changes in oxygen's electronic structure due to chemical interactions with the sulfur. @FootnoteText@@footnote 1@R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-WeP17 Adsorption and Reaction of NO and CO on CeO2(111) and Ce0.8Zr0.2O2(111) Surfaces*, **S. Azad**, M.H. Engelhard, J. Szanyi, C.H.F. Peden,* Pacific Northwest National Laboratory

The adsorption and reaction of NO and CO on oxidized and reduced CeO@sub 2@(111)/YSZ(111) surfaces have been studied using temperature-programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). NO desorbs molecularly from the fully oxidized and reduced surfaces, when adsorbed at 125 K, in three desorption states at 157, 196 and 300 K. NO reacts non-dissociatively on the fully oxidized surface. Reactivity of the high temperature annealed and sputtered surfaces, is significantly higher compared to the fully oxidized surface. Adsorption of NO on the reduced surfaces is followed by N-O bond dissociation producing adsorbed N and O atoms, which subsequently form a variety of products during TPD. A large fraction of CO molecules, adsorbed on the sputtered ceria surface, is oxidized to CO@sub 2@ whereas CO desorbs molecularly from the fully oxidized CeO@sub 2@(111)/YSZ(111) surface, when adsorbed at 125 K. These results will be compared with the ongoing studies on adsorption and reaction of NO and CO on Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111)/YSZ(111).

SS-WeP18 Electronic Properties of Au Nanoparticles Covalently Attached to Au{111} via 1,10-decanedithiol*, **D.J. Fuchs**, P.S. Weiss,* The Pennsylvania State University

1,10-decanedithiol molecules are inserted into a n-decanethiol [CH@sub 3@(CH@sub 2@)@sub 9@SH] self-assembled monolayer (SAM) on Au{111} and are characterized by scanning tunneling micrsocopy (STM). Bifunctional molecules are inserted into the SAM for the covalent attachment of monolayer protected gold nanoparticles. The gold nanoparticles are synthesized with short chain alkylthiol ligands to promote covalent attachment to the inserted 1,10-decanedithiol molecules and to reduce the probability of steric binding. Electronic properties of isolated gold nanoparticles are compared to proximate pairs and assemblies of gold nanoparticles.

SS-WeP19 The Decomposition of Ethylene on Rhodium(100): Theory and Experiments*, **A.P. Bavel**, D.L.S. Nieskens, D. Curulla Ferre, J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands

Hydrocarbon decomposition into C@sub x@H@sub y@ fragments is of great importance for understanding catalytic reactions of these species. We investigate the decomposition pathway of ethylene on the rhodium(100) surface, both on a clean surface and on a hydrogen presaturated surface. We use different experimental techniques: Temperature Programmed Desorption (TPD), Static Secondary Ion Mass Spectrometry (SSIMS), Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectroscopy (HREELS). It is known from literature that ethylene decomposition starts already at low temperatures (<200 K) and continues up to 700 K to give C on the surface. The nature of the intermediate species has been shown to depend on the amount of presaturated hydrogen. Several authors have shown, by using HREELS, the presence of CCH@sub 3@ species in an upright position and CCH species in a "bent" mode.@footnote 1,2,3@ Our LEED experiments indicate a p(2x2) structure for a saturation dosage of ethylene, implying a saturation coverage of 0.25 ML. The TPD spectra show a complicated pattern for the hydrogen desorption. We can distinguish several decomposition limited desorption processes for hydrogen. SIMS measurements show that CCH and CHCH species are present at relatively low temperatures. Some preliminary HREELS experiments in specular and off-specular mode have already been performed. In addition to the experiments we have used periodic DFT calculations to calculate the energy of all possible C@sub x@H@sub y@ species on the Rh(100) surface. We have used a p(2x2) unit cell in the calculations, thus mimicking a saturation coverage of ethylene. The calculations show that CCH@sub 3@ and CCH are the most stable species, in accordance with literature. We have also found, however, that the CHCH species is even more stable. At higher temperatures these species will decompose further into CH and finally carbon. @FootnoteText@@footnote 1@Slavin, A.J., Bent, B.E., Kao, C.T. and Somorjai, G.A., Surface Science 206 (1988) 124-144. @footnote 2@Kose, R., Brown, W.A. and King, D.A., Chemical Physics Letters 311 (1999) 109-116. @footnote 3@Egawa, C., Surface Science 454-456 (2000) 222-226.

SS-WeP20 The Adsorption of Benzene on Zr(0001)*, **N. Stojilovic**, R.D. Ramsier,* The University of Akron

The adsorption of benzene on Zr(0001) has been studied by temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) methods. Following adsorption at 150 K benzene desorbs at about 720 K. Low energy electron bombardment (500 eV) of adsorbed benzene neither affects the amount of desorbing species nor results in the production of new species. AES and secondary electron emission crystal current (SEECC) measurements indicate that carbon remains at the surface after thermal desorption. This work is part of an effort to investigate the possibility of forming zirconium carbide layers for selective surface passivation.

SS-WeP23 Step Edge Diffusion on Ag: Correlations and Persistence as a Function of Temperature**, **O. Bondarchuk**, M. Degawa, E.D. Williams, D.B. Dougherty, M. Constantin, S. Das Sarma, C. Dasgupta,* University of Maryland

The stochastic character of step-edge diffusion can be evaluated in terms of the persistence probability for step edge fluctuation, that is the probability that a fluctuating step does not return to a chosen initial position over a given time interval. Time dependent STM was used to observe temporal step fluctuations on Ag(111) thin film in temperature range from RT up to 450 K. The concept of persistence@footnote 1,2@ as well as the more usual time-correlation function have been used to analyze the step edge fluctuation on the surface in equilibrium and under electrical current stress. Experimentally measured persistence scales as a simple power law that is consistent with scaling predictions,@footnote 1@, and which also agrees with more rigorous tests of persistent behavior.@footnote 3@ The temperature dependence of the persistence prefactor is extremely weak, in contrast with the (diffusion constant dominated) Arrhenius behavior of the prefactor of the correlation function. Numerical calculations using the continuum Langevin equation confirm the weak temperature dependence. The physical significance of the persistence prefactor and the effects of discrete sampling and electrical current stress will be discussed. *This work has been supported by the NSF-NIRT and NSF-MRSEC. @FootnoteText@@footnote 1@J.Krug, H. Kallabis, S.N. Majumdar, S.J.Cornell, A.J. Bray, C.Sire, Phys.Rev. E56(1997)2702. @footnote 2@ D.B. Dougherty, O. Bondarchuk, M.Degawa, E.D. Williams, Surf.Sci. 527(2003)L213. @footnote 3@ M. Constantin, S.Das Sarma, C. Dasgupta, O.Bondarchuk, D.B. Dougherty, E.D. Williams, in press.

SS-WeP25 Growth and Characterization of Ultra-thin Lattice Matched Multilayers of Cr@sub x@Mo@sub 1-x@ and MgO*, I. Meyvantsson, S. Olafsson,* University of Iceland*; K. Johnsen,* Biopharmaceuticals, Iceland*; **J.T. Gudmundsson**,* University of Iceland, Iceland

We report on the preparation of a lattice matched hetheroepitaxial system in a magnetron sputtering discharge. Cr@sub x@Mo@sub 1-x@ thin films were grown on MgO(1 0 0) using DC power, and an MgO overlayer was grown on top by reactive sputtering using pulsed power. The composition of the binary metal alloy is chosen so that the interatomic distance along the direction approximates the lattice constant of MgO. Thus the film should exhibit negligible strain. The structure of the films was studied by ex situ X-ray diffraction (XRD) and the morphology by scanning electron microscopy (SEM). Low angle X-ray reflectivity measurements were performed to determine film thickness, and surface and interface roughness. The effect of substrate temperature during growth is discussed based on thermodynamics and kinetics of the growth process.The minimum thickness for continuity of the binary metal alloy film was determined using four point probe resistance measurements. The insulating properties of the MgO film as a function of thickness were assessed by measuring the tunnelling current I-V characteristics of a metal-insulator-metal structure.

SS-WeP26 Substrate Orientation Dependence for Ni Film Growth on Al Single Crystals: Comparisons of Atomistic Simulations with Experiment*, **R.J. Smith**, N. Winward, C.V. Ramana, V. Shutthanandan, N.R. Shivaparan, Y.W. Kim,* Montana State University*; G. Bozzolo,* NASA GRC and OAI*; J. Morse,* OAI

The structure and composition of metal-metal interfaces grown at room temperature is strongly dependent on a number of kinetically limited processes. Using ion scattering spectroscopy (LEIS and HEIS), we have studied the evolution of interface alloying for room temperature deposition of Ni on low-index surfaces of Al, and find that the thickness and composition of the Ni-Al interface varies remarkably for Al(100) as compared to Al(110) and Al(111) substrates. In the present work we have used Monte Carlo simulations with embedded-atom potentials to study the interface evolution of Ni on these three Al surfaces. The results are compared with measurements of interface formation obtained using MeV He ion backscattering and channeling (RBS/c), as well as low-energy He ion scattering (LEIS). Both simulation and experiment show a greater tendency for Ni to remain at the surface of Al(100) when compared to the more open Al(110) and more close-packed Al(111) surfaces. To further understand this unusual behavior the BFS method for alloys is used to calculate the strain and chemical energies associated with a series of Ni-Al surface configurations, and in this manner, to construct a likely scenario for the evolution of the Ni-Al alloy on the three surfaces. Work supported by NSF DMR 00-77534.

SS-WeP27 Theory of Uptakes in Thin-film Growth: Autocatalytic-reaction Model and Kinetic Monte-Carlo Simulation*, **M. Suemitsu**, H. Togashi,* Tohoku University, Japan*; T. Abe,* Tohoku Institute of Technology, Japan

In many thin film growth systems, the film grows via nucleation of 2D clusters, their growth, and coalescence. The process occurs with various time and space scales depending on the substrate temperature T and the impinging flux P of the precursors, which determines the uptake and morphology of the film. This T- and P-dependence arises from various T- and P-dependence of the surface processes behind the film growth: precursor adsorption and adatoms' migration and desorption. Migration and desorption are always thermally activated but with different activation energies. Adsorption may or may not be thermally activated but is consistently influenced by P. Reflecting this complication, thin film growth dynamics is a delicate function of both T and P. In high-P-low-T regime the growth proceeds with a random adsorption, which presents a Langmuir-type uptake of the film coverage. In low-P-high-T regime it proceeds with a 2D-island growth, which presents a sigmoid-function-type uptake. We have recently proposed autocatalytic-reaction (ACR) model as a rate equation for thin-film growth,@footnote 1@ which was successfully applied to various modes in dry oxidation at Si(001) up to one monolayer. With only two fitting parameters as it is, ACR bridges the gap between the two extremes of the behavior. To clarify the physics behind the model, we have conducted in this work a kinetic Monte Carlo (KMC) simulation assuming (1)adsorption of precursors only at the bare portion of the substrate, (2)finite residence time for the adatoms before desorption, (3)isotropic migration of adatoms, and (4)minimum stable clusters with two atoms. Quantitative agreement obtained between KMC and ACR allow us to discuss the development of the surface morphology using KMC. It was found that the success of the ACR model lies in its effective inclusion of nucleation, growth, and coalescence of adatoms. @FootnoteText@ @footnote 1@ M. Suemitsu, Y. Enta, Y. Miyanishi, N. Miyamoto, Phys. Rev. Lett. 82 (1999) 2334. .

SS-WeP29 Direct Observation of Key Interactions Between the Chiral Modifier, Substrate Molecule and Pt(111) Surface in the Enantioselective Hydrogenation of Methyl Pyruvate*, S. Lavoie, M.-A. Laliberte, **P.H. McBreen**,* Universite Laval, Canada

Methyl and ethyl pyruvate are substrates in one of the rare examples of efficient enantioselective heterogeneous catalysis. The asymmetric hydrogenation of these alpha-ketoesters to the corresponding lactates on chirally-modified supported platinum catalysts is known as the Orito reaction. The daunting complexity of this reaction may be appreciated by considering the fact that interactions between the chiral modifier and the metal surface, between the pro-chiral substrate and the metal surface, between the modifier and the pro-chiral substrate, and between the pro-chiral substrate and adsorbed hydrogen, must all be taken into account. A similar list can be made for interactions involving the half-hydrogenated ketoester-and all this ignores the role of the solvent. It then seems improbable that the uhv surface science approach can be used to profitably attack such a complex system. However, we will show that a uhv RAIRS study of methyl pyruvate on chirally modified Pt(111) reveals key information of relevance to any discussion of the reaction mechanism of the Orito reaction. In particular the RAIRS study permits the direct observation of hydrogen bonding between methyl pyruvate and the modifier. Furthermore, it shows how the interaction modifies the geometry and thermal stability of the adsorbed pyruvate. The results also reveal subtle effects due to spectator species, due to the modifier coverage and due to the adsorption conformation of methyl pyruvate. The combined new information on the 1:1 modifier-pyruvate interaction and on the pyruvate adsorption geometry suggests an important revision to the most widely accepted mechanism for the Orito reaction. In addition, data taken in a comparative study of methyl pyruvate on Ni(111) and Pt(111)-systems which display very different surface chemistries-will be used to comment on possible reasons why nickel is inactive for the Orito reaction.

Thin Films
Room Hall A-C - Session TF-WeP
Poster Session

TF-WeP1 A Plasma Enhanced Atomic Layer Deposition of Tungsten Nitride Diffusion Barrier for Copper Interconnect*, **H.S. Sim**, S.I. Kim,* Korea Institute of Science and Technology*; H. Jeon,* Hanyang University, Korea*; Y.T. Kim,* Korea Institute of Science and Technology, Korea

Tungsten nitride (W-N) was grown on tetraethylorthosilicate (TEOS) by pulse plasma enhanced atomic layer deposition (PPALD) from WF@sub 6@ and NH@sub 3@. It has been very difficult to deposit W-N film on the SiO@sub 2@ surface with ALD method by using WF@sub 6@ and NH@sub 3@ because WF@sub 6@ does not adsorb on the SiO@sub 2@ surface. In this work, however introducing NH@sub 3@ pulse plasma, which modify the SiO@sub 2@ surface to nitride surface, we can deposit the W-N film on the SiO@sub 2@ surface with the growth rate of ~1.3 monolayer/cycle at 350°C. N concentration is also uniformly distributed in the W-N film. This is due to the surface nitridation to enable the adsorption of WF@sub 6@ at the SiO@sub 2@ surface. As a diffusion barrier for the Cu interconnect, electrical measurement reveals that 22 nm thick W-N successfully prevents Cu diffusion after the annealing at 600°C for 30 min.

TF-WeP2 Atomic Layer Deposition of Iron Oxide Thin Films*, T.M. Klein,* ***L.A. Falco**,* University of Alabama

Atomic layer deposition (ALD) has been successfully used in various thin film applications such as electroluminescent (TFEL) flat panel displays, electrochemical solar cells, gas sensors, optical coatings, and microelectronics materials. Thin epitaxial films for super lattices and quantum wells have also been demonstrated by ALD. A wide variety of metal oxide materials have been investigated, however, Fe@sub 2@O@sub 3@ has not been studied extensively. In this poster, we will present the properties of atomic layer deposited hematite (Fe@sub 2@O@sub 3@) thin films on MgO and Al@sub 2@O@sub 3@ substrates using iron (III) acetylacetonate, a solid which sublimes at 110 °C and 2 torr. Iron oxide films may be useful on solid oxide membranes to modify surface selectivity in fuel cell applications.

TF-WeP3 Spatially Regulated Growth of SnO@sub 2@ Thin Films on Si-C Linked Monolayer Template Based on Self-Assembly Technique: Fabrication of Micro Sensor Arrays*, **N. Shirahata**, A. Hozumi, Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology, Japan*; W.S. Seo,* Advanced Materials Analysis & Evaluation Center, Korea*; K. Koumoto,* Nagoya University, Japan

Increasing attention has recently been paid to the low temperature deposition of SnO@sub 2@ thin films due to its excellent gas sensitivity. The micropatterning of such a conductive material is crucial in order to apply it to microelectronics devices, for example, gas sensor. Unfortunately, due to high chemical reactivity, SnO@sub 2@ is difficult to micropattern with conventional processes using chemical etching. Therefore, the development of an alternative method to fabricate SnO@sub 2@ microstructures having a high resolution is strongly desired. In this study, we report a novel approach to fabricate SnO@sub 2@ micro-array based on the molecular recognition between the precursor molecules and the Si-C linked monolayer. The hydrophobic Si-C linked monolayer substrate was micropatterned by the use of 172 nm vacuum ultraviolet (VUV) light lithography. The VUV irradiated regions became hydrophilic due to the formation of silicon oxide (SiO@sub x@) layer. This micropatterned substrate was immersed into solution containing one of two types of precursors, i.e., SnF@sub 2@ and SnCl@sub 2@Â·2H@sub 2@O (0.03-0.1 M and pH=1.7-5) and kept at less than 80 °C for several hours. After immersion, each sample was sonicated in ethanol in order to remove the physisorbed precursors onto the OD-monolayer (ODM) surface. As confirmed by SEM, AFM and XRD, SnO@sub 2@ thin films with cassiterite structures grew preferentially on the SiO@sub x@ surface while rarely depositing on the ODM surface. As-deposited films consisted of small grains having several tens nm in diameter. Although the crystallinity of the films increased with a decrease of pH values, gas sensitivity of as-formed films to hydrogen molecules was insufficient without annealing. In our case, at least annealing temperature of 300 °C was required in order to attain sufficient gas sensitivity.

TF-WeP4 The Effect of Temperature on the Materials Properties of Low k Films Deposited from Organosilicon Precursors*, **M.L. O'Neill**, A.S. Lukas, R.N. Vrtis, J.L. Vincent, E.J. Karwacki, B.K. Peterson, M.D. Bitner,* Air Products and Chemicals, Inc.

Organosilicate glass (OSG) materials are the leading interlayer dielectric (ILD) candidates for current and future technology nodes for integrated circuit manufacture. Current leading edge ILD films are deposited by plasma enhanced chemical vapor deposition (PECVD) with dielectric constants (k) in the range of 2.7-3.2. Future generation ILDs with k < 2.6 require the introduction of porosity. However integration issues caused by the reduced mechanical strength of these materials have delayed their introduction into manufacturing. Although there are numerous ways in which to introduce porosity to a material, the common goal for the processing of these materials is the means to optimize the networking forming process. Herein we examine the effect of temperature on material properties for films produced by PECVD from various OSG precursors. Recently developed codeposition methods use plasma polymerizable organic materials to template porosity in an OSG network during the deposition process. The process requires lower temperature depositions (150-300 °C) to deposit a discrete porogen phase along with the OSG network. Reduced deposition temperatures further compromise material mechanical strength by increasing the number of non-network forming groups in the film. A detailed comparison of film structure and properties with deposition temperature is used to identify the critical components of the precursor in providing the optimal OSG network. Balance between electrical and mechanical properties will provide the maximum opportunity for extension to future generation porous OSG dielectric materials.

TF-WeP5 Photocatalytic Activity and Surface Wettability of TiO@sub 2@/SnO@sub 2@ Heterojunction System*, **N. Kanai**, C. Saiki,* The University of Tokyo, Japan*; Y. Fukunaga, M. Abe,* Tokyo University of Science, Japan*; K. Hashimoto, T. Watanabe, H. Ohsaki,* The University of Tokyo, Japan

Photocatalytic efficiency of TiO@sub 2@/SnO@sub 2@ (TiO@sub 2@ overcoated with SnO@sub 2@) heterojunction system was investigated. TiO@sub 2@ and SnO@sub 2@ thin film stacks were deposited on sodalime glass by reactive DC magnetron sputtering using Ti and Sn metal targets. Photocatalytic efficiency of TiO@sub 2@/SnO@sub 2@ thin film stacks was evaluated by gas-phase isopropanol (IPA) photodegradation with UV light irradiation. Photocatalytic efficiency of TiO@sub 2@/SnO@sub 2@ thin film stacks depends on electric conductivity and packing density of overcoating SnO@sub 2@. This result suggests that photogenerated holes might work as a main photocatalysis actor; oxygen defects in SnO@sub 2@ trap photogenerated holes. The results also indicate that the interface between TiO@sub 2@ and SnO@sub 2@ has a great influence on photocatalytic efficiency. Surface wettability of TiO@sub 2@/SnO@sub 2@ thin film stacks was dramatically improved.

TF-WeP6 Characterization of PECVD Low-k Films by Positronium-Annihilation Lifetime Spectroscopy*, **T. Ohdaira**, R. Suzuki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Y. Shioya, K. Maeda,* Semiconductor Process Laboratory (SPL), Japan

Positronium-annihilation lifetime spectroscopy (PALS) was used to measure pore size distributions in porous SiOCH films for low-k interlayer dielectrics and Cu-diffusion barriers, which were grown by plasma-enhanced chemical vapor deposition (PECVD) with source gases of HMDSO (hexamethyldisiloxane). In the PECVD, the dielectric constants (k) of the films change with the deposition conditions (pressure, flow rate, RF power, temperature, etc). The PALS analysis showed that the PECVD-grown SiOCH films with k in the range from 2.6 to 4 contain pores with average sizes from 0.4 to 1.2 nm, and that the k values of the films correlate strongly with the pore sizes. The PALS depth profiling was also carried out for the

SiOCH low-k films with post plasma treatments and UV irradiations. For the plasma treated films, it is found that the size of the pores in a few 10 nm beneath the surface decreases significantly, indicating that a thin dense layer is formed on the surface.

TF-WeP7 Structural and Electronic Properties of (CdTe)@sub x@(In@sub 2@Te@sub 3@)@sub 1-x@ Thin Films Grown by RF Co-Sputtering@footnote 1@, ***S. Jimenez-Sandoval****, M. Melendez-Lira,* Cinvestav-IPN, Mexico*; M. Zapata-Torres,* CICATA-IPN, Mexico

The semiconductor CdTe and In@sub 2@Te@sub 3@ can be employed to form the ternary compound (CdTe)@sub x@(In@sub 2@Te@sub 3@)@sub 1-x@. The compounds CdIn@sub 2@Te@sub 4@ and In@sub 2@Te@sub 3@ have a band gap of 1.12 eV and 1.0 eV respectively. A band gap modulation toward low energies could be achieved by the incorporation of In in the CdTe lattice. Potential applications for this ternary semiconductor can be thought of in near-IR optoelectronics and photovoltaic heteroestructures. Trying to obtain a gradual incorporation of In in CdTe we produce (CdTe)@sub x@(In@sub 2@Te@sub 3@)@sub 1-x@ thin films by co-sputtering of CdTe and In@sub 2@Te@sub 3@ targets. A previous evaluation of the sputtering yield allow us to control the x parameter through the rf power deliver at each target. We present the results of the chemical, structural and electronic characterization, of a set of eleven thin films, obtained by EDS, X ray diffraction, optical transmission, photoreflectance, photoluminescence, IR and Raman spectroscopies. EDS results indicates that the In content changes between 0 and 38 at%; Cd between 50 and 0 at % and Te between 50 and 62 at %. X ray diffraction showed a gradual change in the CdTe peak positions as In contents increases but for the higher In contents samples were amorphous. Transmission spectroscopy indicates a gradual change of the absorption band edge making difficult to assign the band gap value. Band gap values were obtained by photoreflectance spectroscopy for samples with indium contents up to 17%, indicating a direct band gap. For some samples two transitions were detected. It is possible that for the substrate temperature employed in our system CdTe-rich and In@sub 2@Te@sub 3@-rich compounds were produced with band gap values around 1.43 eV and 1.19 eV, respectively. The results are discussed taking in account the results of the vibrational properties of the thin films. @FootnoteText@@footnote 1@Work partially supported by CONACyT-Mexico.

TF-WeP9 P-Type Semiconducting Cu@sub 2@O-NiO Thin Films Prepared by Magnetron Sputtering*, T. Minami, H. Tanaka,* ***T. Shimakawa,*** Kanazawa Institute of Technology, Japan

This report describes the preparation of p-type semiconducting thin films consisting of a new multicomponent oxide, Cu@sub 2@O-NiO. The Cu@sub 2@O-NiO films were deposited on glass substrates at a temperature of 200-500@super o@C by r.f. magnetron sputtering carried out at a pressure of 0.2-2.0 Pa in an Ar or O@sub 2@ gas atmosphere with an r.f. power of 80 W using a powder target. A mixture of Cu@sub 2@O and NiO powders calcined at 1000@super o@C in an Ar or air atmosphere for 1 h was used as the target: Ni contents (Ni/(Cu+Ni) atomic ratio) in the range from 0 to 100 at.%. The obtained electrical and optical properties of Cu@sub 2@O-NiO thin films were strongly dependent on the deposition conditions as well as the Ni content of the target. P-type semiconducting Cu@sub 2@O-NiO thin films could be prepared at 500@super o@C in a pure Ar gas atmosphere at a pressure of 0.4 Pa using targets calcined in Ar: All the prepared Cu@sub 2@O-NiO thin films were found to exhibit positive hole conduction, as evidenced from Hall measurements and the Seebeck effect. The resistivity of the Cu@sub 2@O-NiO thin films prepared under the above conditions increased markedly as the Ni content was increased up to about 30 at.%, remained relatively constant in the range of about 30 to 60 at.%, and then increased markedly with further increases of Ni content. In the Cu@sub 2@O-NiO thin films prepared with an increasing Ni content in the range from 0 to 30 at.%, the obtained resistivity increased from 70 to 4×10@super 4@@ohm@cm, resulting from decreases in both Hall mobility and hole concentration, and band-gap energy increased from 2.6 to 2.9 eV. In contrast, the Cu@sub 2@O-NiO thin films prepared with a Ni content in the range from 30 to 50 at.% exhibited a relatively constant resistivity on the order of 3×10@super 4@@ohm@cm; these films were identified as the ternary compounds NiCuO@sub 2@ or Ni@sub 2@CuO@sub 3@, by x-ray diffraction analyses. The multicomponent oxide Cu@sub 2@O-NiO thin films prepared by r.f. magnetron sputtering with a Ni content in the range from 0 to 100 at.% were found to be p-type semiconductors with a resistivity that was increased by increasing Ni content. From spectroscopic ellipsometric measurements, it was found that the band-gap energy of Cu@sub 2@O-NiO films can be controlled in the range from 2.6 to 4 eV.

TF-WeP10 Photocatalytic Related Properties and Structure of Titanium Oxide Films, ***C.B. Shiu,*** *M.C. Yang, T.S. Yang,* National Dong Hwa University, Taiwan, ROC*; M.S. Wong,* National Dong Hwa University, Taiwan, ROC, Taiwan, R.O.C

Titanium dioxide (TiO2) films were prepared with ion-assisted electron-beam evaporation technique using rutile TiO2 powder as a source material. Various oxygen flows and ion bombardments were applied to adjust and to modify the composition and the structure of the growing films. Various characterization methods such as ellipsometry, Raman spectroscopy, UV-Visible spectroscopy, XRD, SEM, and TEM were used to measure the crystallinity, morphology, optical and mechanical properties of the films. The photocatalytic related properties under UV and visible lights were characterized by water-contact angle measurement, oxidation of methylene-blue solution, and reduction of Ag from AgCl solution. In general anatase TiO2 films exhibited overall the best photocatalytic performance. However, variations in thickness, composition, phase and crystallinity in the films made a difference in their catalytic behaviors. The effects of film processing parameters on the structure and properties of the oxides will be discussed.

TF-WeP11 Influence of the Microstructure on the Sputter-etching Characteristics of Pulsed-laser Deposited Strontium-titanate-oxide Thin Films*, L. Stafford,* Universite de Montreal, Canada*; M. Gaidi,* INRS-Energie, Canada*; O. Langlois,* Universite de Montreal, Canada*; M. Chaker,* INRS-Energie, Canada*;* ***J. Margot****,* Universite de Montreal, Canada*; M. Kulishov,* Adtek Photomask Inc., Canada

Strontium-titanate-oxide (STO) thin films are of great interest for several photonic applications such as high-speed electro-optic elements for next-generation all-optical networks. Obviously, the integration of STO layers into such devices requires a simultaneous optimization of the deposition method and of the patterning process. In this context, we have investigated the influence of the deposition parameters on the etching characteristics. For this purpose, in a first step, stoichiometric SrTiO3 thin films with the crystallographic perovskite structure were grown on a silicon substrate using a Pulsed-Laser Deposition (PLD) technique. The microstructural properties of the films were studied as a function of the buffer gas pressure (O2). In a second step, we have examined the sputter-etching characteristics of the as-deposited films using a high-density argon plasma operated at very low pressure (1 mTorr) and a substrate bias of 100 V. The etch rate of the STO thin films is found to increase with the O2 deposition pressure, a feature that can be related to the microstructural properties of the film (grain size, lattice parameter, etc.) induced by changes in growth conditions. We will show that the etch rate is actually related to the macroscopic film density (film porosity) rather than to its microscopic density (unit cell volume of the film).

TF-WeP12 Ferroelectric Properties of Highly Oriented BLT Films for Ferroelectric-gate Field-effect Transistors*,* ***J.M. Lee****, C.I. Kim, K.T. Kim,* Chungang University, Korea

Ferroelectric thin films such as Bi-based layered perovskite (SrBi@sub 2@ Ta@sub 2@ O@sub 9@, Bi@sub 4@ Ti@sub 3@ O@sub 12@, Bi@sub 3.25@ La@sub 0.75@ Ti@sub 3@ O@sub 12@, etc.) and Pb(Zr,Ti)O@sub 3@ thin films have been extensively investigated for non-volatile ferroelectric random access memory (FeRAM) devices. Metal-ferroelectric-semiconductor field-effect-transistors (MFSFETs) have advantages of high switching speed, nonvolatility, and high density. However, the MFSFETs have been problem such as interdiffusion between the film and Si. To suppress them, a metal-ferroelectric-insulator-semiconductor (MFIS) structure has been demonstrated. The most important thing in developing a MFIS structure is to find a good insulator that acts as a buffer between the Si substrate and the ferroelectric material, and have relative high dielectric constants, low leakage current, good interface characteristics, and compatibility. The MFIS capacitors were fabricated using a metalorganic decomposition method. Thin layers of Al@sub 2@ O@sub 3@ were deposited as a buffer layer on SiO@sub 2@ /Si and BLT thin films were used as a ferroelectric layer. The electrical and structural properties of the MFIS structure were investigated by varying the Al@sub 2@ O@sub 3@ layer thickness. X-ray diffraction was used to determine the phase of the BLT thin films and the quality of the Al@sub 2@ O@sub 3@ layer. AES and TEM show no interdiffusion that suppressed by using the Al@sub 2@ O@sub 3@ film as buffer layer. The width of the memory window in the C-V curves for the MFIS structure increased with increasing thickness of the Al@sub 2@ O@sub 3@ layer. The experimental results show that the BLT-based MFIS structure is suitable for non-volatile memory FETs with large memory window.

TF-WeP13 The Ferroelectric Properties of Lanthanide-doped Pb(Zr, Ti)O@sub 3@ Thin Films Prepared by using a Sol-gel Method*, C.I. Kim,* ***Y.H. Son****, K.T. Kim,* Chung-Ang University, Korea

The PZT film has a large polarization and a low crystallization temperature. However, there are some problems in the PZT film, such as fatigue with Pt electrodes and poor retention. In this study, lanthanide (Eu, Dy, Tb, Er)-doped lead zirconium titanate(PZT) thin films on the Pt/Ti/SiO@sub 2@/Si substrates prepared by a sol-gel method. According to the ionic radius, lanthanide (Ln) tends to occupy the A-site of PZT perovskite structure and acts as a donor that generates Pb vacancies. Ln doping was found to alter significantly the dielectric and ferroelectric properties. We investigated the effect on the structural and electrical properties of PZT films as a function of Ln concentrations. The structure and the morphology of PZT films were analyzed by x-ray diffraction (XRD), atomic force microscope (AFM), and scanning electron micrograph (SEM). The depth profile of the interfaces between PZT films and electrode materials were examined using Auger electron spectroscope (AES). SEM and AFM showed uniform surface of PZT films. The dielectric constant and the dielectric loss of Ln-doped PZT thin films decreased with the increasing Ln content. Ln-doped PZT thin films showed improved fatigue characteristic comparing to the undoped PZT thin film.

TF-WeP14 Amorphous Transparent Conductive Oxide Films of In@sub 2@O@sub 3@-ZnO with Additional Al@sub 2@O@sub 3@ Impurities*,* ***K. Tominaga****, H. Fukumoto, Y. Hayashi, K. Murai, T. Moriga, I. Nakabayashi,* Tokushima University, Japan

In@sub 2@O@sub 3@-ZnO films were deposited by facing target sputtering system of ZnO:Al and In@sub2@O@sub3@ targets. Two targets were sputtered simultaneously in Ar gas at 1 mTorr, and electric current ratio @ganma@=I@sub Zn@/(I@sub Zn@+I@sub In@) was adopted as a deposition parameter to change film composition. Discharge current of each target was changed from 0 to 80 mA in order to change the contents of Zn and In in the film. Compositional ratios of Zn/(Zn+In) in films were nearly equal to @ganna@ value according to the data estimated by X-ray fluorescence analysis. Five ZnO:Al targets containing 0,1,2,3 and 4 wt% Al@sub 2@O@sub 3@ were used for Al adding in the films. In@sub 2@O@sub 3@-ZnO films in amorphous phase were deposited between Zn/Zn+In=0.2-0.6. The lowest resistivity of 1.5x10@super -4@ @ohm@cm was attained in amorphous phase films deposited from In@sub 2@O@sub3@ and ZnO:Al (Al@sub 2@O@sub 3@=2 wt %). Carrier mobility did not depend on Al@sub 2@O@sub 3@ content in ZnO:Al target. Carrier concentrations at the lowest resistivity in amorphous In@sub 2@O@sub 3@-ZnO had the highest value for 2 wt% Al@sub 2@O@sub 3@ content, but decreased at above 3 and 4 wt%. Optical bandgap energy shifted to higher energy side for the film of 4 wt% Al@sub 2@O@sub 3@ content. These results indicate that the energy shift of optical bandgap for amorphous phase film is not ascribed to Burstein-Moss shift. The role of Al in amorphous films is different with that of donors in crystalline In@sub 2@O@sub 3@:Sb and ZnO:Al. On the other hand, Al@sub2@O@sub3@ doping in homologous phase of In@sub 2@O@sub 3@ film decreased carrier concentration, independent on the levels of Al@sub 2@O@sub 3@ doping. This indicates that Al did not act as donor impurities in homologous Zn@sub k@In@sub 2@O@sub k+3@ crystalline films.

TF-WeP15 Luminescence Behavior of Li-doped Gd@sub 2@O@sub 3@ : Eu@super 3+@ Thin Film Phosphors Grown by Pulsed Laser Ablation*,* ***S.S. Yi****,* Silla University, Korea, South Korea*; J.S. Bae, H.J. Seo, B.K. Moon,* Pukyong National University, Korea*; J.H. Jeong,* Pukyong National University, Korea, South Korea*; P.H. Holloway,* University of Florida

Gd@sub 2@O@sub 3@ : Eu@super 3+@ and Li-doped Gd@sub 2@O@sub 3@ : Eu@super 3+@ luminescent thin films have been grown on Al@sub 2@O@sub 3@ (0001) substrates at substrate temperatures in the range of 500 ~ 700 °C and oxygen pressure in the range of 100 ~ 300 mTorr using a pulsed laser deposition technique. The films grown under different deposition conditions have been characterized using microstructural and luminescent measurements. The photoluminescence brightness data obtained from Li-doped Gd@sub 2@O@sub 3@ : Eu@super 3+@ films grown under optimized conditions have indicated that sapphire is a good substrate for the growth of high quality Li-doped Gd@sub 2@O@sub 3@ : Eu@super 3+@ thin film red phosphor. The luminescence of the Gd@sub 2@O@sub 3@ : Eu@super 3+@ films is highly dependent on the crystallinity and surface roughness of the films. In particular, incorporation of Li@super +@ ions into the Gd@sub 2@O@sub 3@ lattice induces a remarkablely enhanced crystallinity and photoluminescence. The diffraction data suggest that the (222) surface is preferentially oriented parallel to the substrate for films grown on Al@sub 2@O@sub 3@ (0001). In addition, the full width at half maximum (FWHM) of the diffraction peaks is narrower (~20 %) for films grown with versus films grown without Li-doping. The root mean square roughness of these films was found to vary from 7.5 to 16.1 nm depending upon the Li-doping. The highest emission intensity was observed with LiF-doped Gd@sub 1.84@Li@sub 0.08@Eu@sub 0.08@O@sub 3@, whose brightness was increased by a factor of 2.3 in comparison with that of Gd@sub 2@O@sub 3@ : Eu@super 3+@ films. This phosphor is promising for the flat panel displays.

TF-WeP16 Luminescent Characteristics of Se-doped ZnGa@sub 2@O@sub 4@:Mn Thin Film Phosphors Grown by Pulsed Laser Ablation*,* ***J.H. Jeong****,* Pukyong National University, Korea, South Korea*; J.S. Bae,* Pukyong National University, Korea*; I.W. Kim,* University of Ulsan, Korea*; J.S. Lee,* KyungSung University, Korea*; S.S. Yi,* Silla University, Korea*; P.H. Holloway,* University of Florida

Mn-doped ZnGa@sub 2@O@sub 4-x@Se@sub x@ thin film phosphors have been grown using pulsed laser ablation(PLA) under various growth conditions. The structural characterization was carried out on a series of ZnGa@sub 2@O@sub 4-x@Se@sub x@ : Mn@super 2+@ films grown on MgO(100) substrates using Zn-rich ceramic targets. Zn-rich ceramic targets have been prepared to compensate for the vaporization loss of Zn during PLA. The oxygen pressure was fixed at 100 mTorr and substrate temperatures were varied from 500 to 700 °C. The luminescence results indicated that MgO (100) is a promising substrate for the growth of high-quality of ZnGa@sub 2@O@sub 4-x@Se@sub x@ : Mn@super 2+@ films. The crystallinity and surface roughness of the ZnGa@sub 2@O@sub 4-x@Se@sub x@ : Mn films are highly dependent on the growth conditions, in particular the substrate temperature and the composition ratio of targets. Epitaxial films were obtained on MgO (100) substrates due to the low lattice mismatch between ZnGa@sub 2@O@sub 4@ and MgO. The crystallinity of the films is improved with Se doping. The root mean square surface roughness of these ZnGa@sub 2@O@sub 4-x@Se@sub x@ : Mn@super 2+@ films were found to initially increase from 3.25 nm (x=0.00) to 10.92 nm (x=0.075) then decrease to 8.43 nm (x=0.10) as the amount of Se increases. Incorporation of Se into the ZnGa2O4 lattice led to a remarkable increase of photoluminescence. The highest green emission intensity was observed with ZnGa@sub 2@O@sub 3.925@Se@sub 0.075@ : Mn@super 2+@ films whose brightness was increased by a factor of 3.1 in comparison with that of ZnGa@sub 2@O@sub 4@ : Mn@super 2+@ films. This phosphor is promising for application in flat panel displays.

TF-WeP17 Low-Resistivity Polycrystalline ZnO:Al Thin Films Prepared by Pulsed Laser Deposition*, T. Minami,* ***H. Tanaka****, K. Ihara, T. Miyata,* Kanazawa Institute of Technology, Japan

Recently, a very low-resistivity Al-doped ZnO (ZnO:Al, AZO) films comparable to ITO films were attained on glass substrates by pulsed laser deposition (PLD) method. In this report, we describe the preparation of low resistivity AZO thin films, including a description of conditions necessary to obtain the low resistivity on the order of 1×10@super -4@@ohm@cm. The AZO films were deposited on glass substrates by PLD using an ArF excimer laser. The deposition was carried out under the following conditions: pressure, 10@super -4@ Pa; substrate temperature, 180-350@super o@C; target-substrate distance, 50 mm; substrate, OA-2 glass; and target, sintered ZnO+Al@sub 2@O@sub 3@(1-3 wt.%). All AZO thin films prepared with a thickness of 200 to 700 nm exhibited an average transmittance above 85% in the visible range. In order to obtain low-resistivity AZO films, it was necessary to optimize the relationship between the target sintering conditions and the deposition conditions. The obtained resistivity decreased as the substrate temperature was increased, reached a minimum at a temperature of about 240@super o@C, and then increased with further increases of the temperature. The decrease of resistivity associated with the increase of temperature to about 240@super o@C resulted from an increase of Hall mobility, whereas the increase of resistivity with higher temperatures resulted from a decrease of carrier concentration. The Hall mobility increase was found to be correlated to an increase of crystallite size, as evaluated from the (0002) x-ray diffraction peak. On the other hand, the Al content in the films increased gradually as the substrate temperature was increased. The decrease of carrier concentration was ascribed to an increase of oxygen content in the films. As another example, the resistivity decreased as the film thickness was increased. As above, the resistivity decrease was also correlated to a Hall mobility increase resulting from an increase of crystallite size. It is concluded that differences in obtainable Hall mobility can be attributed to differences in the crystallinity such as crystallite size.

TF-WeP18 Deposition of ITO Film using the DLC Buffer Layer between Plastic Substrate and ITO Layer*, **M.G. Kim**, H.S. Jeong, Y.W. Seo,* ITM Inc., Korea

Recently organic electro luminescence displays(OELD) using a plastic substrate such as PET and PES are emerging as a strong new candidate for flat panel displays. In this study we make diamond like carbon(DLC) films as a buffer layer between plastic substrate and transparent conducting oxide(TCO). The DLC is characterized by high hardness, flatness, and low gas permeability to moisture and oxygen. The unipolar pulse mode of the power supply(IBP1030, ITM, Inc.) was used on a graphite target, and the argon-methane mixed gas was used. Indium tin oxide films were deposited on the DLC buffer layer of the plastic substrate in a horizontal single ended in-line sputter system equipped with a pulsed dual magnetron sputter. Two ITO targets of In@sub2@O@sub3@(90 wt%):SnO@sub2@(10 wt%) were used. To understand the properties of the ITO films deposited by pulsed dual magnetron sputtering processes, we investigated the electrical resistivity, film structure, optical transmission, surface roughness, and gas permeability. @FootnoteText@ This work was supported by the Ministry of Science and Technology of the Republic of Korea through the National Research Laboratory program.

TF-WeP19 Deposition of ZnO:Al Gradient Composite Films Using Dual Magnetron Sputtering*, **H.S. Jeong**, H.J. Lee, M.S. Hwang, Y.W. Seo,* ITM Inc., Korea*; S.J. Kwon,* Kyungwon University, Korea

ZnO:Al films with compositional gradient were prepared by dual magnetron sputter deposition technique of in-line sputter system. The films of compositional gradients are achieved by the angle of dual magnetron sources and the moving direction of carrier substrate. The symmetric pulse mode of the power supply(IAP1010, ITM, Inc.) was used to simultaneously sputter a ZnO target and an Al target. We varied the duty of the pulses to control the ratio of ZnO:Al in the thin films. The electrical and optical properties of the films were measured with a surface profiler, an UV/Visible spectrophotometer, a 4-point probe, X-ray diffraction spectroscopy, and atomic force microscopy. Also to observe the depth profile of the compositional gradient film, the film was analyzed by Auger Electron Spectroscopy. The special attention is paid to the surface roughness, electrical resistance, and optical transmittance.

TF-WeP20 ZnO Layers Grown by ns and subps Lasers in Nitrogen Atmosphere*, **M. Jelinek**, L. Soukup,* Institute of Physics AS CR, Czech Republic*; A. Klini,* Foundation for Research and Technology - Hellas (FORTH), Greece*; M. Cernanský, J. Oswald,* Institute of Physics AS CR, Czech Republic*; C. Fotakis, D. Anglos,* Foundation for Research and Technology - Hellas (FORTH), Greece*; R. Zeipl,* Institute of Radio Engineering and Electronics AS CR, Czech Republic*; A. Santoni,* ENEA, Centro Ricerche Frascati, Italy

Thin ZnO films and nitrogen doped ZnO films were grown by subpicosecond (450 fs) and nanosecond (20 ns) KrF pulsed laser deposition (PLD) and by PLD combined with radiofrequency (RF) discharge. Discharge (13.56 MHz) was situated between two RF electrodes placed parallel to plazma plume. Doped ZnO layers were fabricated in mixture of nitrogen and oxygen, for various T@sub s@ and RF power. As substrate fused silica was used. Films were transparent from ~ 350 nm. Highly oriented peaks with FMWH (2? 0.15o was detected by XRD. Films grown in RF discharges were nanocrystalline with crystallites size of 10nm. Hall constant, Hall mobility and resistivity were measured by Van der Pauv method. In dependence on deposition conditions the Hall constant in the range of 1 x 10@super -7@ 2 x 10@super -3@ m@super 3@/As, mobility from 6 x 10@super -2@ to 18.2 cm@super 2@/Vs and resistivity 5.9 x 10@super -5@ to 20 @OMEGA@m were obtained. XPS and WDX results and experimental details will be also presented. @FootnoteText@ The authors thank to the Czech Grant Agency for financial support under contract S1010203.

TF-WeP21 Orientation Selective Epitaxy of CeO@sub 2@(100) or CeO@sub 2@(110) Thin Films on Si(100) Substrates by Magnetron Sputtering with Substrate Bias*, **T. Inoue**, N. Sakamoto, M. Ohashi, A. Horikawa, S. Shida,* Iwaki Meisei University, Japan*; Y. Sampei,* Fukushima Technology Centre, Japan

From studies on the epitaxial growth of CeO@sub 2@ layers on Si(100) substrates using reactive dc magnetron sputtering enhanced with an inductively coupled rf plasma, it is found that the epitaxial CeO@sub 2@ layer with (100) or (110) orientation is selectively grown by controlling substrate bias and plasma power. Although many reports have been made on the growth of CeO@sub 2@(110)/Si(100), recently CeO@sub 2@(100) layers have been reported to grow on atomically cleaned Si(100) surfaces with a 2x1 reconstructed structure in an ultra-high vacuum. Our method has superiority in the requirement of only practical H-terminated surfaces obtained by the usual wet cleaning process. Adopting two step growth method; ultrathin metallic Ce layer deposition at room temperature followed by silicidation process at several hundreds degree C, and subsequent reactive sputtering in an Ar/O@sub 2@ mixture environment using Ce metal target at elevated temperature, the CeO@sub 2@(100) layer epitaxy is attained applying either positive or negative substrate bias of 15 - 20 V, whereas CeO@sub 2@(110) layers are grown without substrate bias. The orientation selection is found to be also dependent on plasma power, in other words the growth rate: the low growth rate leads to (100) orientation and vice versa. This orientation selective epitaxial growth technique will be useful for device applications. Details on the growth parameters of both substrate bias and plasma power and the characterization including RHEED, XRD, XTEM and AFM will be presented.

TF-WeP23 Analysis and Modeling of Low Pressure CVD of Phosphorus-doped Poly-silicon in Commercial Scale Reactor*, **R. Shimizu**, M. Ogino,* Fuji Electric Corporate Research and Development, Ltd., Japan*; M. Sugiyama, Y. Shimogaki,* University of Tokyo, Japan

Poly-silicon is a key material for all kinds of semiconductor devices. The main issue for its deposition technology is how to get the uniform deposition rate and dopant concentration on silicon wafers. In this work, to investigate the poly-silicon CVD mechanisms that control the uniformity in a commercial scale LPCVD reactor, we analyzed the elementary reaction of silane based CVD with the doping gas of phosphine. We used longitudinal type CVD reactor of 6inch manufacturing scale. Under the standard condition, sample wafers were fully charged with a spacing of 4.1mm and the 100% silane and 0.8% phosphine gases with nitrogen carrier gas were introduced to the reactor. The growth temperature was kept 550°C along 700mm length hot-zone and the total pressure was 100Pa in the reactor. On the basis of the diffusion model of chemical species into the wafer-gaps, two precursors were found to contribute the profile of deposition rate, and their sticking probabilities were deduced together with the one of silane. The activation energy of direct surface reaction and gas phase reaction rate constant of silane were experimentally derived from the dependencies of the deposition rate on the growth temperature and wafer spacing, respectively. The diffusion model also gave the relative concentration distributions of the two precursors, which were examined with the elementary reaction analysis based on the Ho's model.@footnote 1@ The effect of phosphine gas on the silane reaction was found to be rather large notwithstanding the small concentration of phosphine gas, as in the studies by others.@footnote 2@ The analysis of this phenomenon will show the detail of the chemical reaction system composed of silane and phosphine gases, and give us a useful predictive model of poly-silicon CVD process. @FootnoteText@ @footnote 1@P. Ho, M. E. Coltrin, and W. G. Breiland, J. Phys. Chem., 98, 10138 (1994)@footnote 2@B. S. Meyerson and W. Olbricht, J. Electrochem. Soc., 131, 2361 (1984).

TF-WeP24 A Study of the Growth Front of Au Policristalline Films and its Relation with the Bulk Structure of the Films*, C. Munuera, J.A. Aznarez, E. Rodriguez,* CSIC, Spain*; A.I. Oliva,* Centro de Investigaciones y Estudios Avanzados del IPN Unidad de Merida, Mexico, Mejico*; M.A. Aguilar, **J.L. Sacedon**,* CSIC, Spain

The surface roughness of Au polycrystalline films with a high (111) texture has been studied using STM images. The growth front has been characterized in samples with thickness from 30 to 1800 nm by measuring the interface width and the coarsening of apparent rounded mounds. In this analysis any isotropic or self-affine hypothesis has been avoided. In addition, the fracture of the thickest films have been analysed by SEM. The films have been obtained by thermal evaporation on native SiO@sub 2@ terminated Si(100) substrates maintained at room temperature. The rate of growth was 1.0 nm/s. The SEM images show a competitive columnar growth for thicknesses from <90nm to 1800 nm. They also show that the mound round shaped structures correspond to the top of the columns. The interface width scaling behaviour obtained from STM images shows two growth regimes, the more advanced starts at 60 nm and corresponds to a constant morphological slope regime.In this advanced stage, the value of the interface width and coarsening scaling exponents are close to 1/3. The exponent values and fracture structures agree with the parametric model of E.V. Albano et al.(PRB 59,7354 (1999)). This model is based on the concept that surface diffusion phenomena controls the bulk structure of the film. Local slopes along the surface profiles are compatible with a significant step down atomic current component, which is necessary to allow the burial of the less competitive columns. The linear boundaries of the surface structure suggest a relaxation of the columnar boundaries to crystalline planes causing the weak hexagonal symmetry observed in the height to height correlation functions.

TF-WeP26 Structure and Properties of Nanolaminate Chromium/ Titanium Oxide Films by Pulsed-DC Reactive Sputtering*, M.S. Wong,* National Dong Hwa University, Taiwan, ROC, Taiwan, R.O.C*; M.C. Yang, H.B. Chou,* National Dong Hwa University, Taiwan, ROC*; M.E. Graham,* Northwestern University

The outstanding optical, semiconducting and mechanical properties of titanium and chromium oxides have made them useful for many applications. Ion-assisted, high-rate, reactive, pulsed-dc magnetron sputtering is used to deposit the nanometer-scale multilayered oxide films. RF substrate bias was applied to induce ion bombardment to modify the structure of the growing films. Various characterization methods such as ellipsometry, Raman spectroscopy, UV-Visible spectroscopy, XRD, SEM, TEM, hardness and stress measurement techniques were used to measure the crystallinity, morphology, optical and mechanical properties of the films. Under suitable conditions, the sputtered metal atoms will react with the partial pressure of supplied oxygen to form stoichiometric and transparent oxide films. Crystalline Cr2O3 and anatase TiO2 were deposited as single-layer films, and as Cr/Ti-oxide multilayers. When the period of the multilayer was below ~7 nm, the multilayer structure was not observed, and Cr-Ti-O alloy films appeared to be formed instead. The energy gaps for Cr2O3, Cr-Ti-O and TiO2 films are ~2.1, ~2.5 and ~3.2 eV, respectively. The Cr2O3 and Cr-Ti-O films possess high hardness, over 20 GPa. The effects of substrate bias and multilayer period on the structure and properties of the oxides will be discussed.

TF-WeP27 Absorption Properties of Thin Film Getter for Impurity Gas in High Vacuum Environment*, K.C. Kim,* *Y.J. Yoon,* Yonsei University, Korea*; S.M. Lee,* Kangwon National University, Korea*; H.K. Baik,* Yonsei University, korea, South Korea

Recently, getters have been widely used in vacuum microelectronics requiring high vacuum. The conventional bulk getters required high temperature activation processes for proper action as a getter, where the device was contaminated by outgassing of different gases, e.g., H@sub 2@O, O@sub 2@, H@sub 2@O, CO, CO@sub 2@. The conventional bulk getter itself was not suitable for the microelectronic devices due to size limitations. As a resolution to such problems, thin film getters, small enough for microelectronic applications, with excellent resonant gas absorption characteristic and requiring no activation, have been fabricated and analyzed. In this research, Zr was used as a getter material, and Ni and Pt were used for catalysis and protection of the getter against oxidation. Thin film getters were fabricated by the introduction of Pt and Ni layers, which exhibited excellent absorption characteristic of impurity gases in high vacuum, without high temperature activation. Realization of thin film getters, by solution of the size limitations of the bulk getters, enabled getter to apply to the microelectronic devices.

TF-WeP28 Control of Crystalline Evolution in Aluminum Nitride Thin Films Deposited by Magnetron Sputtering*, V.M. Pantojas,* *E. García, N.R. Ramos, W. Otaño,* University of Puerto Rico at Cayey

There is considerable interest in the growth of Aluminum Nitride (AlN) thin films for the fabrication of mechanical, optical and surface acoustic wave devices. The properties of polycrystalline AlN thin films depend strongly on the crystallographic orientation and texture of the grains and it is important to have an adequate control of the crystalline characteristics in order to achieve good performance for specific properties. Thin AlN films were prepared using magnetron sputtering. The relationship between the sputtering deposition process parameters and the coating characteristics, and properties, were investigated using Response Surface Design methodology. The deposition pressure, gas composition and substrate temperature were used as factor levels to characterize the response of the most important characteristics, crystallinity and stoichiometry. The evolution of crystal orientation in AlN thin films was analyzed using an x-ray diffraction system with a general area detector. The two dimensional, position sensitive area detector allows for fast collection of the x-ray scattering data and provides the unique capability of directly imaging the orientation of the diffraction pattern. The degree of crystal orientation of the AlN samples varied from completely polycrystalline to highly oriented depending on the deposition conditions. In order to quantify the degree of crystallinity, an integration method was used. The three main peaks of hexagonal AlN were integrated along a rectangular slit at the center of the detector to quantify the degree of in-plane orientation and a texture coefficient was calculated for each crystal orientation.

TF-WeP29 Synthesis and Electrochemical Characteristics of Boron Carbon Nitride Films Deposited by Magnetron Sputtering*, E. Byon,* Korea Institute of Machinery and Materials, Korea*; M. Son,* Samgsung Techwin Co. Ltd, Korea*; N. Hara, K. Sugomoto,* Tohoku University, Japan*; S.-K. Kwon,* Korea Institute of Machinery and Materials

Boron-Carbon-Nitrogen (BCN) system is an attractive ternary material since it has not only an extremely high hardness but also a number of other prominent characteristics such as chemical inertness, and low thermal expansion. In this paper, we prepared ternary BC@sub x@N@sub y@ films on Si by r.f. magnetron sputtering of boron and graphite targets. With increasing of the graphite target power, FTIR and XPS showed that the structure of the BC@sub x@N@sub y@ films was changed from the cubic BCN to the hexagonal BCN. The corrosion resistance of BCN thin films in aqueous solution was investigated. BCN films with different composition were deposited on a platinum plate in the thickness range of 150-280 nm. In order to understand effect of pH of solutions on the corrosion resistance of the film, BC@sub 2.4@N samples were immersed in 1 M HCl, NaCl and NaOH at 298 K respectively. BCN films with different carbon content were also immersed at 1 M NaOH solutions to investigate effect of chemical composition on the corrosion resistance. The thinning rate of the film thickness was measured at various potentials in 1 M NaCl by using in-situ ellipsometry. From the results, the corrosion resistance of B@sub 1.0@C@sub 2.4@N@sub1.0@ films were NaOH>NaCl>HCl in that order. With increasing carbon content in BCN films, the corrosion resistance of BCN films is enhanced. The lowest corrosion rate was obtained for B@sub 1.0@C@sub(3.2-4.4)@N@sub 1.2@ films. The anodic polarization in 1 M H@sub 2@SO@sub 4@, 1 M HCl and 1 M NaCl showed similar behavior with Pt substrate. Hydrogen overvoltage in the cathodic region was higher than Pt substrate. No active dissolution of the films was occurred in the range of â€“0.2 V to 0.1 V of potential in 1 M NaOH, but the film thickness reduced with increasing potential. The current density of the films is directly proportional to the dissolution rate of B1.0C2.4N1.0 film over 0.2 V of potential.

TF-WeP30 Mechanical Properties of Ultranano-, Nano- and Poly-crystalline Diamond Films and Membranes*, A. Moon,* *T.A. Grotjohn,* Michigan State University and Fraunhofer Center for Coatings and Laser Applications*; M.K. Yaran, T. Schuelke,* Fraunhofer Center for Coatings and Laser Applications*; D.K. Reinhard, J. Asmussen,* Michigan State University and Fraunhofer Center for Coatings and Laser Applications

The mechanical properties of polycrystalline materials can vary substantially depending on the material's grain size, surface morphology and grain boundary properties. In the case of diamond films the crystal grain size and surface morphology can range from ultrananocrystalline (grain sizes of less than 10nm) to nanocrystalline (grain sizes of 10's nm) to polycrystalline (grain sizes of 100's nm to microns). The Young's modulus of films and the deflection characteristics and fracture strength of membranes are characterized in this study for a range of diamond films/membranes deposited with grain sizes ranging from ultrananocrystalline to polycrystalline. The Young's modulus of diamond films with thickness from 0.1 µmm to 2 µmm is measured on the substrate by using a pulsed laser to generate surface acoustic wave which are evaluated by Fourier analysis. The Young's modulus and membrane deflection characteristics are characterized as function of the thickness of the film, film nucleation/seeding technique, grain size, surface morphology, and synthesis chemistry. Measured Young's modulus values were as high as 900-1000 GPa.

TF-WeP31 Improvement of Corrosion Resistance of Transparent Conductive Multi-layer Coatings Consisting of Silver Layers and Transparent Metal Oxide Layers*, K. Koike,* *F. Yamazaki, T. Okamura, S. Fukuda,* Mitsui Chemicals, Inc., Japan

We have investigated transparent conductive multi-layer sputter coatings consisting of silver (Ag) layers and transparent metal oxide layers. We could expect versatile applications for the multi-layer sputter coatings, such as a transparent electrode and a transparent electromagnetic waves shield. The multi-layer sputter coatings including the silver layer is very sensitive to surrounding atmosphere. For example we would find discolored points on the multi-layer sputter coatings, possibly caused by a silver atom migration in silver layers, after an exposure test. In our investigation, we modified a top surface of the multi-layer sputter coatings with transition metals to improve a corrosion resistance of the multi-layer coatings. Specifically we deposited the transition metals with 0.5 to 2nm thickness on the top surface of the multi-layer coatings by sputtering. We chose indium tin oxide (ITO) as the transparent metal oxide. We applied the multi-layer sputter coatings of 7 layers formed on a polyethylene terephthalate (PET) film substrate. A cross-sectional structure of the film with the multi-layer coatings is PET film / ITO / Ag /ITO / Ag / ITO / Ag / ITO. We evaluated the corrosion resistance by a salt water immerse test. In the test we immerse the film with multi-layer coatings into salt water, and then evaluate an appearance, a transmittance and an electrical resistance of the multi-layer coatings. We investigated several transition metals as the modifying material, and we found that titanium and tantalum drastically improved a resistance of the multi-layer coatings against the salt water without a significant decline of a transmittance. We also investigated a relation between an elapsed time after the depositing the modifying materials and the resistance against the salt water. Further we investigated effects of a heat treatment and an oxide plasma treatment on the resistance against the salt water.

TF-WeP32 Anisotropic Film Growth during PVD on Substrates in Planetary Motion*, G.C.A.M. Janssen,* Delft University, The Netherlands*; **J.-D. Kamminga***, NIMR, The Netherlands*; P.F.A Alkemade,* Delft University, The Netherlands*; S.Yu. Grachev,* NIMR, The Netherlands

Chromium films were deposited in an industrial PVD machine, designed to coat 3-D objects. The machine is equipped with a substrate table that allows a planetary motion of the substrates in front of the target. Films with thickness ranging from 30 nm to 10 Âµm were deposited on Si wafers. All films are under tensile stress. The thinner films exhibit a 110 fiber texture. The curvature of the substrates with the thinner films is radially symmetric. Therefore the stress is radially symmetric. The thicker films exhibit an in plane "single crystal" type texture. For these films the stress is no longer radially symmetric. The curvature of the wafers with the thicker films is distinctly different in the plane of planetary motion and perpendicular to that plane. A SEM top view of the thicker films shows an anisotropy in grain shape. We discuss the coinciding occurrence of anisotropy in stress and microstructure.

TF-WeP33 Combined RF Magnetron Sputtering and Ion Implantation for the Synthesis of Silicon Carbonitride Thin Films*, **M. Bruns**, H. Lutz,* Forschungszentrum Karlsruhe GmbH, Germany*; M. Rudolphi, H. Baumann,* Universitaet Frankfurt, Germany

Silicon Carbonitride thin films have been the subject of great interest in recent years due to the expected improvement of surface properties for a lot of applications. Various precursor based techniques have been employed to synthezise the pure materials. However, most of these efforts result in amorphous films or tiny crystals embedded in amorphous matrices of deficient nitrogen content and considerable hydrogen and oxygen impurities, respectively. In contrast, RF magnetron sputtering as well as ion implantation have been proven suitable means to achieve high-purity ternary systems of up to 57 at.% nitrogen content, e.g. Si@sub 2@CN@sub 4@. However, carbon rich compounds (i.e. SiC@sub 2@N@sub 4@) are not attainable on this way. For that the combination of both means seams to be a promising approach. Defined and reproducible Si/C ratios within the films can be obtained using co-sputter targets of different Si/C areas. In a second step surface modification by high fluence implantation of @super 15@N ions into these Si-C films result in suitable nitrogen content up to the theoretical amount. Severalfold implantation at different energies calculated from Monte-Carlo-simulations enable us to synthesize layers with homogeneous element depth-distribution up to the surface. @paragraph@The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy (XPS). In addition, Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry (n-RBS). Resonant nuclear reaction analysis (NRRA) provides non-destructive depth profiles of @super 15@N. The morphology after subsequent annealing was studied by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Vacuum Technology
Room Hall A-C - Session VT-WeP

Poster Session

VT-WeP1 Temperature Characteristics of a New Static Expansion Vacuum Standard*, J.C. Greenwood, **P. Carroll**,* National Physical Laboratory, UK

The uncertainty in the pressure generated in vacuum standards is often dominated by temperature contributions. In equilibrium, gradients across the system vessels make it difficult to assign a temperature to the gas contained inside. Gradients between vessels can also contribute to errors in the calculation of the generated pressure. To investigate the temperature characteristics of a new Static Expansion vacuum standard at NPL a series of measurements were made using an array of thermister thermometers located at over 100 distinct locations. This level of monitoring is not practical for normal operation, however, the temperature distribution for the system has been mapped so that probe locations for representative temperature measurements have been identified for normal operation. An indication of the worst case error is given together with the improvement in uncertainty for optimally located temperature probes.

VT-WeP2 Thermodynamic Effects on the Pumping Performance of a Dry Scroll Vacuum Pump*, **T. Sawada**, S. Kamada, W. Sugiyama, M. Yabuki,* Akita University, Japan*; M. Fujioka, M. Tsuchiya,* ANEST IWATA Corporation, Japan

The theory we proposed before gives the ultimate pressures closely consistent with the values from the actual machine at the rated speed, but gives smaller values than the actual machine does, for lower orbiting speed. This discrepancy increases as the orbiting speed decreases. The theory also seems to be incomplete for other gases than nitrogen, especially for a light gas like helium. It has been confirmed experimentally that this is caused by the difference in clearance between the theoretical analysis and the actual machine. The clearance is constant in the theoretical analysis regardless of the orbiting speed and the type of gases; however, the clearance in the actual machine changes with the temperature changes accompanying variations in orbiting speed and the differences in the thermophysical properties of gases. We propose a thermodynamic model expressing the temperature distributions on the orbiting and fixed scrolls. Since the heat generated in a suction side pockets is very small, it is considered that the heat generated by gas compression is carried adiabatically to around the shaft and then conducted to the orbiting scroll and the fixed scrolls. The temperature of the orbiting scroll rises higher than that of the fixed scrolls because the fixed scrolls are cooled more easily than the orbiting scroll. Then, we obtain the clearance change under the obtained temperature distribution and predict the ultimate pressure of the pump having the changed clearance. The predicted ultimate pressure agrees pretty well with the measured one throughout the experimented range of orbiting speed for all tested gases (nitrogen, argon and helium).

VT-WeP3 Novel Calibration Apparatus for Precise Barometer and Vacuum Gauge*, **S.Y. Woo**,* Korea Research Institute of Standards and Science, Korea*; S.H. Kang, I.M. Choi, Y.J. Lee,* Korea Research Institute of Standards and Science

In order to calibrate accurate absolute pressure gauges such as barometer and vacuum gauge, laser or ultrasonic mercury manometers have been used. However, complexity, harmfulness of mercury vapor, and cost of mercury manometers made it difficult to use in most calibration laboratories. As a substitute, a gas-operated pressure balance is used for calibration of such gauges. However, commercially available pressure balances cannot be suitable because consequent exposure of the piston and masses to the atmosphere raises the problem of contamination and the ingress of dust particles to the gap between the piston and cylinder. Moreover a lot of time is being spent in changing the mass combinations on the piston and breaking the vacuum each time when a different pressure point is required. To overcome these difficulties, we manufactured a novel weight-loading device for changing the masses in situ without breaking the vacuum. This device made it possible to add or remove weights easily in vacuum, thereby greatly reducing the time between measurements. Using this device, we could easily calibrate precise quartz resonance barometers from 940 hPa to 1050 hPa. Moreover we also found that with new calibration technique this device could be used very efficiently for the calibration of vacuum gauge in the range of 100 hPa full scale. In this paper, practical calibration results are presented for a precise barometer (Paroscientific, Model 760-16B) and a vacuum gauge (MKS, CDG 100 Torr).

VT-WeP4 Photon Stimulated Desorption Study for a NEG-Coated Insertion Device Vacuum Chamber for TLS*, **G.-Y. Hsiung**, J.-C. Lee,* National Synchrotron Radiation Research Center, Taiwan*; J.-R. Chen,* National Synchrotron Radiation Research Center and NTHU, Taiwan

An aluminum alloy vacuum chamber, 4.6 m in length, for a narrow gap insertion device at Taiwan Light Source (TLS) is coated with the Zr-Ti-V Non-Evaporable Getter (NEG) film on the inner surface. The chamber, after NEG-coating, was installed in the 19B(PSD) beam line at TLS for synchrotron radiation exposure measurement. The yield of photon stimulated desorption (PSD), measured by the throughput method, illustrates a lower value but slowly decayed curve at the earlier exposure beam dose. The desorbed gas species, measured by a quadrupole mass spectrometer, contain the CH@sub 4@, H@sub 2@, CO, CO@sub 2@, as well as Ar. The behavior of pumping and desorption from the NEG coated surface will be discussed.

VT-WeP5 The Effect of Environmental Humidity on Thermal Outgassing Rate*, **C.-K. Chan**, Y.-C. Ou, G.-Y. Hsiung, J.-R. Chen,* National Synchrotron Radiation Research Center, Taiwan

This work investigates how humidity of environment affects thermal outgassing rate of an A6063 aluminum alloy chamber. The throughput method was used to measure the thermal outgassing rate of a test chamber exposed to the air with different moistures. The aluminum chamber was then exposed to dehumidified-air under an airshower located at downstream of an oilless compressor. Experimental results indicate that by controlling the humidity around the chamber adequately, the thermal outgassing rate achieved without baking is comparable to that after in-situ bakeout.

VT-WeP6 Vacuum Pump Oil Tests at the National Synchrotron Light Source to Minimize Oil Waste@footnote 1@*, **C.L. Foerster**, J.-P. Hu, E. Haas,* Brookhaven National Laboratory

In order to reduce the large amount of oil waste produced during normal operation of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), an oil-testing project was established to determine if synthetic vacuum pump oil could be used effectively with longer oil change intervals. Due to the large number of oil-sealed rotary vane pumps that are used at the NSLS, a longer oil change interval would reduce maintenance costs as well as oil waste. Initially, two basic types of vacuum pump oils, mineral and synthetic, were selected for direct comparison. Three of the same size two-stage mechanical pumps were set up to run simultaneously with the same gas load. ConvectronR gauges, cold cathode gauges, and isolation valves were connected to a central vacuum chamber having a common inlet pressure control and a sampling valve for residual gas analysis. To simulate oil degradation produced by long-term mechanical pump operation, the system air load was manually controlled with an air bleed valve on the common vacuum chamber and was periodically adjusted to run at 500 mTorr. This easily tolerated pressure range for mechanical pumps was suggested by oil suppliers to expedite the oil viscosity change, acid buildup, and pump-wear debris production. Major advantages are that the testing time will be much quicker and that any back streaming of oil is minimized at this operating pressure. The detailed test data for the resulting oil properties, oil degradation, visual comparison, vacuum conditions, and pump characteristics will be presented for comparison of the pump oils used at NSLS and for estimation of the resulting oil waste reduction.@footnote 1@ Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VT-WeP7 Plasma Sensors for Control of PVD Processes for Nanostructured Me-C:H Coatings@footnote 1@*, **C.C. Klepper**, E.P. Carlson, R.C. Hazelton, E.J. Yadlowsky,* HY-Tech Research Corporation*; M.A. Taher, B. Feng,* Caterpillar, Inc.*; B. Shi, W.J. Meng,* Louisiana State University

To improve the reproducibility of metal-containing amorphous hydrogenated carbon (Me-C:H) coatings deposited by physical vapor deposition (PVD) techniques such as reactive sputtering, various plasma probes are of interest as in-situ sensors integrated with a closed-loop deposition control system.@footnote 2,3@ In a series of Design-of-Experiment (DoE) test runs on an unbalanced magnetron sputtering setup, various plasma probes were tested for their sensitivity to process input factors and as candidates for a feed-back control system. These include optical emission and absorption spectroscopy of metal atoms, conventional and electron emissive Langmuir probes (LP), and hydrogen atomic line emission (H@alpha@). Of particular interest are combinations of the outputs of these probes. For example, the H@alpha@, divided by the product of the electron density from the LP and the hydrogen partial pressure from a residual gas analyzer (RGA), can be used as a measure of the excitation temperature of the plasma. This factor scales differently from the electron temperature from the LP, which is representative of the cold component that dominates the electron energy distribution function in low-T plasmas. The plasma potential measured from the LP is also of interest, since it, together with the applied substrate bias, determines the energy of ionic species bombarding the substrate. This measurement is primarily sensitive to plasma composition, especially in the reactive phase. Details and interpretation of these dependences, as well as their importance in the design of the closed-loop control system, will be presented. @FootnoteText@@footnote 1@ Partial support for this project came from NIST ATP 70NANBH0H3048 through a subcontract with Caterpillar Inc.@footnote 2@ M. A. Taher, et al., contributed talk in this conference. @footnote 3@ B. Shi, W. J. Meng, Journal of Applied Physics, in press (2003).

VT-WeP10 Adsorption Force Control with Surface Roughness Modification for Smooth Sliding in a Vacuum*, **A. Kasahara**, M. Goto, T. Oishi, M. Tosa,* National Institute for Materials Science, Japan

Vacuum friction measurement system based on Bowden-Leben type system has been successfully developed that can evaluate sliding friction force under changing load from 1.96N to 0.98mN and under changing atmospheric pressure from 1E+5 Pa to 1E-8 Pa. Friction measurement was carried out on typical vacuum materials as type 304 austenitic stainless steel sheets after such surface treatments as chemical polishing or electrochemical buffing. We have shown that the materials with surface roughness around 100nm can offer as smooth sliding in a vacuum as at an atmospheric pressure. This smooth sliding may arise from absorption gas as lubricant kept in hollows of surface nanoscopic asperities. We accordingly tried to estimate absorption force by decrease in sliding load with the friction measurement system to study the effect of surface roughness on adsorption force and the contribution to smooth sliding in a vacuum. We found existence of absorption force about 20mN on a sample with surface roughness about less than 600nm, at an atmospheric pressure. The sample with the surface roughness under 40nm also showed adsorption force below 0.98mN in a vacuum, while sample with the surface roughness around 100nm showed higher adsorption force over 0.98mN even in a vacuum. The surface roughness can also slow desorption rate of absorption gas layer and keep friction small in a vacuum. It is therefore concluded that the surface with 100nm roughness exhibiting similarly low friction in a vacuum as at an atmospheric pressure is ideal modified surface for trapping adsorbed gases strongly to act as vacuum lubricant. The surface roughness about 100nm will be a good candidate surface for smooth movement in a vacuum.

Applied Surface Science
Room 324/325 - Session AS-WeA
Fuel Cell & Battery Materials/Corrosion

Moderator: B. Beard, Akzo Nobel Chemicals Inc

2:00pm **AS-WeA1 Development of Multi Layered Oxide Nanofilms for Fast Oxygen Ionic Conduction***, **S. Thevuthasan**, S. Azad, O.A. Marina, C.M. Wang, V. Shutthanandan, L.V. Saraf, D.E. McCready, I. Lyubinetsky, A. El-Azab, C.H.F. Peden,* Pacific Northwest National Laboratory

There has been considerable interest in solid oxide fuel cell (SOFC) devices since they provide relatively clean alternative energy to the conventional fossil fuels. Several research groups are working on developing electrolyte materials with higher oxygen ionic conductivity at low temperatures to improve the efficiency of SOFC device at low temperatures. It is well known that nanoscale materials often display properties very different from the base coarse-grained bulk materials. In particular, it has been recently demonstrated that a nanoscale lamellar structure of two different fluorides (calcium fluoride and barium fluoride) can exhibit significantly higher ionic conductivity along the interfacial directions at moderate temperatures.@footnote 1@ If such a remarkable finding could be transferred into practice, it would provide the ability to design similar structures from oxygen ion conductors to enhance the performance of SOFC devices at temperatures substantially lower than the current operating temperatures. In this study, we investigated the effect of multiple interfaces on oxygen ionic conductivity in Gd-doped single crystal ceria/zirconia multi layers as a function of Gd concentration. Pure and Gd-doped ceria and zirconia films were grown by oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and characterized by reflection high-energy electron diffraction (RHEED), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and high-resolution transmission electron microscopy (HRTEM). The preliminary results are encouraging and four layered Gd-doped ceria/zirconia multi layered structure shows higher oxygen ionic conductivity compared to two layered structures. @FootnoteText@ @footnote 1@N. Sata, K. Eberman, K. Eberl and J. Maier, Nature 408 (2000) 946.

2:20pm **AS-WeA2 Surface Science Studies of Model Fuel Cell Electrocatalysts***, **P.N. Ross**,* Lawrence Berkeley National Laboratory**INVITED**

Progress in the understanding of the electrocatalytic reactions in fuel cells will be reviewed. The emphasis is on the study of model electrocatalysts with in-situ surface spectroscopies. It is shown that Pt single crystals and well-characterized Pt bimetallic bulk alloys have been used with some success as models for real(commercial) catalysts. The electrode reactions discussed include hydrogen oxidation evolution, oxygen reduction, and the electrooxidation of C1 compounds (carbon monoxide, formic acid, and methanol). Surface spectroscopies discussed are infrared reflection absorption spectroscopy (IRRAS), scanning tunneling/atomic force microscopy (STM/AFM), and surface x-ray scattering (SXS). The discussion will focus on the relation between the energetics of adsorption of intermediates and the reaction pathway and kinetics, and how the energetics and kinetics are effected by extrinsic properties of the model system, e.g. surface structure and composition. Finally, we conclude by discussing some limitations of these model systems and suggest some directions for studying more realistic systems with the same rigor.

3:00pm **AS-WeA4 Identifying Factors Responsible for Capacity and Power Loss in Lithium-ion Cells***, **D. Abraham**,* Argonne National Laboratory **INVITED**

High-power battery technology is crucial to the commercial success of hybrid electric vehicles. In the United States, high-power lithium-ion batteries are being studied as part of the Advanced Technology Development (ATD) program. Lithium ion-cells, ranging in capacity from 1 mAh to 1Ah, are built and tested to determine suitable electrode-electrolyte combinations that will meet the calendar life, safety and cost goals of the ATD program. The cells are aged, cycled, and/or abused according to established test procedures. After test completion, the cell components are examined by various diagnostic tools to determine the nature and extent of physical, chemical, and structural changes that resulted from the testing conditions. These diagnostic results are used to improve cell chemistries and cell designs of the next generation of lithium-ion batteries. The capacity and power loss of lithium-ion cells are governed by the chemical and electrochemical side reactions that occur at the electrode-electrolyte interface. The formation of a Solid Electrolyte Interface (SEI) layer on negative electrodes that are polarized below electrolyte reduction potential (~0.8 V vs. Li/Li+) is a well-known phenomenon. The SEI layer, which contains various organic and inorganic electrolyte decomposition products, protects the negative electrode from further reduction and allows stable lithium-intercalation processes at low potential. Capacity loss appears to result from changes and growth of the SEI layer during cell aging. The cell power loss results from impedance increases at the positive electrode, which may be the consequence of changes in the electrode surface films. Data from X-ray photoelectron spectroscopy, secondary ion mass spectroscopy, transmission electron microscopy, electron energy loss spectroscopy, and nuclear magnetic resonance analysis will be presented to support the conclusions of our study.

3:40pm **AS-WeA6 The Chemical Nature of LiCoO@sub 2@, LiNiO@sub 2@ and LiCo@sub 0.5@Ni@sub 0.5@O@sub 2@ Surfaces by X-ray Photoelectron Spectroscopy***, **M.A. Langell**,* University of Nebraska*; A.W. Moses,* University of California*; J.G. Kim,* University of Nebraska

Many lithium metal oxides find use in lithium batteries as a result of their Li@super +@/Li redox properties coupled to their high lithium conductivity and their ability to be multiply cycled between the near-stoichiometric and severely de-lithiated electrode material. In its stoichiometric form, LiCoO@sub 2@ presents a straightforward picture in charge balance. Lithium is formally Li@super +@, cobalt is Co@super 3+@ and, with the exception of the occasional defect, the lattice oxygen is comparable to that found in 3d transition metal monoxides, O@super 2-@. By simple analogy, LiNiO@sub 2@ should contain nickel formally in its 3@super +@ oxidation state. Ni@super 3+@ is not as thermodynamically favored as the low-spin, octahedrally-coordinated Co@super 3+@, however, and this tends to destabilize the LiNiO@sub 2@ surface composition. We present results from XPS and Auger electron spectroscopy that show LiCoO@sub 2@ forms stable, stoichiometric surface compositions once surface hydroxylation and carboxylation are properly taken into account. These latter surface adsorbates are variable, depending upon the history of the material and the surface pretreatment prior to UHV analysis. LiNiO@sub 2@, however, is not as well behaved, even when XRD indicates that the bulk is well-ordered. The surface is severely depleted in lithium and phase separation to NiO and cubic LiNiO@sub 2@ is common. Adding cobalt to the lattice does not completely stabilize the structure and LiCo@sub 0.5@Ni@sub 0.5@O@sub 2@ substrates behave much like LiNiO@sub 2@ from the viewpoint of the nickel with nickel found predominantly in the Ni@super 2+@ state. In contrast to literature reports that nickel is 2@super +@ in LiNiO@sub 2@, with charge compensation resulting from a localized Ni@super 2+@ - O@super -@ adjacent lattice ion pairs, we see no evidence that the oxygen is significantly different in the three materials, at least within the near-surface area.

4:00pm **AS-WeA7 Formation of Protective Coatings on Depleted Uranium - 0.75 wt% Titanium Alloy***, **D.F. Roeper**, C.R. Clayton, D. Chidambaram, G.P. Halada,* SUNY at Stonybrook

The process of enriching uranium for nuclear power plants results in the formation of a toxic and mildly radioactive waste. Exposure to this byproduct called depleted uranium (DU) may have deleterious health effects.@footnote 1@ The leaching of uranium into the environment and its prevention have become issues of concern. Protective coatings could prevent leaching of DU as well as prevent localized corrosion. In this study, we explore the formation of silicate-based coatings on DU-0.75 wt% Ti alloy (0.75 wt% Ti, less than 0.2 wt% @super 235@U and ~0.0008 wt% @super 234@U, rest being @super 238@U with some trace impurities); a common DU alloy. These coatings are compared with a molybdate-based coating that has been demonstrated earlier.@footnote 2@ The optimal concentrations of the inhibitors and activators have been used, as determined from the earlier study. The morphological information has been obtained using optical microscopy and scanning electron microscopy. While open circuit potential measurements and potentiodynamic polarization have been utilized for characterization of the electrochemical behavior, the use of X-ray photoelectron spectroscopy has provided the chemical information regarding the coatings. Our results indicate the primary constituent of the coating to be an oxide complex. We discuss the approach currently undertaken to develop protective complex coatings on the alloy surface. The characteristics of these coatings have been compared with other coatings similarly formed using different inhibitors and accelerators. @FootnoteText@ Acknowledgement: The U.S. Army Research Laboratory under contract DAAD190110799 supported this work. Dr. Derek J. Demaree, PhD., has served as contract officer.@footnote 1@ S. Jones, I. lowles and A. Smith, Lancet, 357 1532 (2001).@footnote 2@ C.R. Clayton, D.F. Roeper, D. Chidambaram and G.P. Halada, 203@super rd@ Meeting of the Electro Chemical Society, Abstract No. 318, April 30, 2003 Paris, France.

4:20pm **AS-WeA8 The Mechanism of Protection of Mechanical Damages to Chromate Conversion Coatings Formed on Aluminum Alloys***, **D. Chidambaram**, C.R. Clayton, G.P. Halada,* State University of New York at Stony Brook

Inhibitive action of dichromate based solutions have been known for nearly a century. Hexavalent chromium present in these coatings is toxic and a well-known mutagenic agent. Aluminum alloys used widely in the aerospace industry are given a treatment to form chromate conversion coatings (CCCs). The development of alternative coatings requires the precise knowledge of the underlying mechanisms of protection offered by hexavalent chromium, which are unclear. Defects or mechanical damages in CCCs are protected without further treatment by "self-healing" properties. "Self-healing" has been associated with migration of chromates to actively corroding sites. The formation of a protective Al(III)-Cr(VI) complex at damaged sites was first suggested by Abd Rabbo et al. Electrochemical techniques have been used in this study to provide a direct observation of the repassivation of a scratch. XPS analysis of pure aluminum exposed to chromate solution indicates the presence of high amount of hexavalent chromium at higher depth of analysis. This result is in agreement with theories proposing the formation of stable Al(III)-Cr(VI) compounds. Atomic force microscopy (AFM) confirmed the physical presence of these compounds. Synchrotron infrared micro spectroscopy (SIRMS) clearly showed the formation of Al(III)-Cr(VI) complex in these regions. Al(III)-Cr(VI) complex was found to form at active regions and protect the surface irrespective of the nature of the chromate source (adsorbed chromate film or CCCs). A novel study involving scratching of AA2024-T3 prior to the formation of CCC was performed. The surface morphology studied using scanning laser confocal microscopy showed the physical presence of some compounds in the scratches. The increase in the hexavalent chromium content with the number of scratches as observed using XANES explained the mechanism of protection of mechanical damages to the CCCs formed on aluminum alloys.

4:40pm **AS-WeA9 The Role of Hexafluorozirconate in the Formation of Chromate Conversion Coatings on Aluminum Alloys***, D. Chidambaram, **C.R. Clayton**, G.P. Halada,* State University of New York at Stony Brook

Alodine 1200SÂ® process is widely used to form chromate conversion coatings (CCCs) on aluminum alloys. Potassium hexafluorozirconate (K2ZrF6) forms a major component of Alodine. Although the roles played by most of the other components of the treatment bath are known, there is no knowledge about the interaction of hexafluorozirconate with aluminum alloys. Electrochemical and surface analytical techniques have been employed to study the nature of interactions between hexafluorozirconate and constituents of aluminum alloy AA2024-T3. AA2024-T3 is widely used in the aerospace industry. Studies on the interactions between major components found in AlodineÂ® with aluminum alloys showed maximum activation to occur in the case of hexafluorozirconate pretreatment. This is contrary to the belief that sodium fluoride, another major component of AlodineÂ®, acted as an activator. Contact angle measurements have also been performed. Hexafluorozirconate was found to decrease the interfacial tension besides leading to increased surface wetting. The results obtained from electrochemical techniques have also been compared with similar studies conducted using other fluoride components found in Alodine such as sodium fluoride and potassium fluoborate. X-ray photoelectron spectroscopy (XPS) has been used to study the surface chemistry of the alloys after exposure to hexafluorozirconate, thereby giving an insight into the mechanism of activation and surface wetting. The results indicate hexafluorozirconate to play an important role in the formation of chromate conversion coatings on aluminum alloys. This will be useful to the development of coatings based on benign components. Acknowledgements The U. S. Air Force Office of Scientific Research under contract F49620-96-1-0479 supported this work. Lt. Col. Paul Trulove, Ph.D. served as the contract officer.

Biomaterial Interfaces
Room 307 - Session BI+SS-WeA

Biomolecular Surface Science and Microfluidics

Moderator: M. Grunze, Universität Heidelberg, Germany

2:00pm **BI+SS-WeA1 Soft X-ray SpectroMicroscopy of Bio-interfaces***, **A.P. Hitchcock**, C. Morin, T. Araki, J.L. Brash, R. Cornelius,* McMaster University, Canada*; S.G. Urquhart, U.D. Lanke,* University of Saskatchewan, Canada*; N. Samuel, D.G. Castner,* University of Washington **INVITED**

We are using scanning transmission x-ray microscopy (STXM) and X-ray photoemission electron microscopy (X-PEEM) to study the adsorption of biological and bio-active species on naturally and artificially patterned polymer and molecular substrates. In one area, the thrust is to investigate fundamental issues of protein - polymer interactions relevant to blood compatibility. In a second area, we are providing feedback for the development of patterned bio-active surfaces. Both synchrotron-based microscopies provide chemical speciation by near edge X-ray absorption spectroscopy (NEXAFS). STXM provides quantitative chemical mapping at a spatial resolution of 50 nm, with the possibility of detecting proteins on polymer thin films with monolayer sensitivity in the presence of an aqueous overlayer of the protein solution.@footnote 1@ X-PEEM has greater surface sensitivity than STXM but requires placing the sample in vacuum. Our X-PEEM studies of fibrinogen adsorption on a model polymer substrate, phase segregated polystyrene-poly(methylmethacrlyate) (PS/PMMA),@footnote 2@ indicate clear preference for adsorption on the PS domains when adsorption is performed from a phosphate buffer solution, but preference for adsorption at the PS-PMMA interface when using non-buffered solutions. The strengths, limitations, and future potential of soft X-ray microscopy for studies of bio-interfaces will be discussed.@footnote 3@ @FootnoteText@ @footnote 1@ A.P. Hitchcock et al., J. Biomaterials Science, Polymer Ed. 13 (2002) 919.@footnote 2@ C. Morin et al, J. Electron Spectroscopy 121 (2001) 203.@footnote 3@ X-ray microscopy carried out at the Advanced Light Source (supported by DoE under contract DE-AC03-76SF00098) and the Synchrotron Radiation Centre (supported by NSF under award DMR-0084402). Research supported financially by NSERC (Canada) and the Canada Research Chair Program. We thank the PEEM-2 staff (A. Scholl, A. Doran) for assistance in these studies.

2:40pm **BI+SS-WeA3 Interaction of Protein Solutions with Biocompatible Organic Monolayers: An In Situ Neutron Reflectometry Study***, **R. Dahint**, D. Schwendel,* University of Heidelberg, Germany*; F. Schreiber,* University of Oxford, UK*; M. Grunze,* University of Heidelberg, Germany

Oligo(ethylene glycol) (OEG) terminated self-assembled monolayers (SAMs) effectively prevent the adsorption of proteins from biological solutions. Yet, efforts are still being made to elucidate the mechanisms of protein resistance on a molecular level. For proteins deposited on the tip of an atomic force microscope (AFM), long range repulsive forces have been observed upon approaching protein resistant methoxy-terminated tri(ethylene glycol) undecanethiolate SAMs (EG3-OMe) on gold.@footnote 1@ However, as proteins adsorbed on the tip may undergo significant structural changes, it is not obvious that the same strength and type of interaction is experienced by freely moving, dissolved molecules. We, therefore, used neutron reflectometry to investigate protein/surface interactions employing biomolecules in their native state and natural environment. Room temperature measurements on protein resistant films of EG3-OMe in contact with bovine serum albumin (BSA) solutions reveal the presence of an extended protein depletion layer with a thickness of about 50 nm between the SAM and the bulk protein solution. The results are compared to the strength and range of repulsive forces measured by AFM. Temperature dependent studies on the EG3-OMe/water interface reveal, that a previously observed, density reduced water phase in the vicinity of the SAM cannot account for the protein resistant properties of the films. @FootnoteText@@footnote 1@ K. Feldman, G. Hähner, N. D. Spencer, P. Harder, M. Grunze, J. Am. Chem. Soc. 1999, 121, 10134.

3:00pm **BI+SS-WeA4 Characterization of Lipid Bilayers on Functionalized Surfaces***, **T.W. McBee**, S. Saavedra,* University of Arizona

The utilization of planar supported lipid bilayers (PSLBs) for technological applications is limited by their fragility. They can be destroyed by a variety of conditions, including exposure to air, surfactants, and mechanical stress such as elevated temperatures. One way to overcome this limitation is to introduce polymerizable groups into the tail region of the lipid molecules and stabilize the bilayer structure through polymerization, which results in a very stable film when formed on silica. We have been investigating the characteristics of lipid bilayers, both polymerized and unpolymerized, on a variety of functionalized surfaces, including self-assembled monolayers (SAMs) as well as self-assembled polymer multilayers compared to bilayers formed on silica. This talk will focus on our investigations of PSLBs on Î³-aminopropyl silane (GAPS) monolayers as well as on mixtures of polyaniline/poly(acrylic acid). These types of surfaces are of interest due to their potential for energy transduction and sensing applications.

3:20pm **BI+SS-WeA5 Intact Vesicle Adsorption and Supported Biomembrane Formation from Vesicles in Solution Studied by a Combined SPR and QCM-D Instrument, and AFM***, E. Reimhult*[1]*, F. Höök,* ***B. Kasemo,*** Chalmers University of Technology, Sweden

Two biomembrane model systems receiving high interest are unilamellar phospholipid vesicles and supported planar phospholipid bilayers. We have investigated the adsorption kinetics of small unilamellar POPC vesicles with a setup, combining the Quartz Crystal Microbalance with Dissipation technique and Surface Plasmon Resonance techniques in parallel. Using this instrument we have for the first time simultaneously and in real time measured the acoustic (hydrated) and optical (dry) mass for vesicle adsorption on SiO@sub 2@ and oxidized Au. These measurements have significantly extended our understanding of intact vesicle adsorption on surfaces, as a function of surface chemistry,@footnote 1@ temperature,@footnote 1,2@ vesicle size,@footnote 3@ and osmotic stress.@footnote 1@ We have been able to distinguish between the mass response due to adsorbing intact vesicles and that of planar bilayers formed on the surface via vesicle rupture. Furthermore, we have; determined the critical coverage required for vesicle rupture on SiO@sub 2@, obtained a measure of the amount of trapped water and deformation of intact vesicles on the surface, studied the kinetics of the final part of the supported planar bilayer formation process on SiO@sub 2@ and detected loss of lipids on its completion. The latter two are critical for the quality of the formed bilayer, i.e. limiting the number of defects. We also intend to present results from atomic force microscopy studies of vesicle adsorption on heterogenous (patterned) surfaces, with focus on the behavior at phase boundaries, separating planar bilayer forming and intact vesicle adsorbing areas. @FootnoteText@ @footnote 1@ E. Reimhult, F. Höök, and B. Kasemo, Langmuir 19, 1681 (2003)@footnote 2@ E. Reimhult, F. Höök, and B. Kasemo, PRE 66, 051905 (2002).@footnote 3@ E. Reimhult, F. Höök, and B. Kasemo, JCP 117, 7401 (2002).

3:40pm **BI+SS-WeA6 Microfluidic Systems for Applications in Chemistry and Biochemistry*, A. Manz,*** Imperial College, UK **INVITED**

Fluid handling integrated into microsystems has been in use now for a number of years. Mostly, research has focused on micro pumps, valves, sensor flow cells and electrophoresis.@footnote 1,2,3@ However, the underlying idea of shrinking the whole analytical chemistry or biochemistry lab down to chip size will make it necessary to talk about interfacing these modules properly and efficiently. Recently, we have proposed a concept for a chemical microprocessor.@footnote 4,5@ This concept is related to an earlier attempt to define an analytical chemistry microsystem, micro-TAS (miniaturised total analysis system).@footnote 6@ Scaling laws predict 100x faster mass and heat transport, if a known system is miniaturized by a factor 10 (linear). This is particularly useful in capillary electrophoresis, chromatography and continuous-flow reactors. We have presented several examples in the past few years. I plan to show a few examples of recent chip developments taken from my lab: A horseradish peroxidase assay (400ms incubation), isoelectric focusing of a peptide in continuous flow (100x higher concentration in 300ms focusing time) and an air monitor based on a plasma emission chip. @FootnoteText@ references @footnote 1@Micro Total Analysis Systems 2000, A.van den Berg, W.Olthuis, P.Bergveld, eds., Kluwer Academic Press, ISBN 0-7923-6387-6 (2000). @footnote 2@D.R.Reyes, D.Iossifidis, P.A.Auroux, A.Manz, Anal Chem 74, 2623-2636 (2002) @footnote 3@P.A.Auroux, D.Iossifidis, D.Reyes, A.Manz, Anal Chem 74, 2637-2652 (2002) @footnote 4@A.Manz, H.Becker, Transducers 97, Chicago, June 16-19, 1997, Digest of technical papers (1997) 915-918. @footnote 5@M.C.Mitchell, V.Spikmans, A.Manz, A.J.de Mello, J.Chem.Soc., Perkin Trans.1 2001 (2001) 514-518. @footnote 6@A.Manz, N.Graber, H.M.Widmer, Sens. Actuators B1 (1990) 244-248.

4:20pm **BI+SS-WeA8 Interfacial Engineering for Protein Biochips in Proteomics Applications*, H. Lu,*** *P. Kernen, P. Wagner,* Zyomyx, Inc.

Proteomics is increasingly dependent on analytical tools that focus on quantification of protein expression, biomolecular-protein interactions, and functional activity. The large numbers of proteins and complexity involved in proteomics applications present tremendous challenges for the development of analytical platforms and specifically interfacial engineering schemes. Zyomyx has developed a novel protein biochip platform that facilitates rapid, precise, highly multiplexed analysis with minimal sample requirements and has integrated several sophisticated interfacial engineering strategies. The biochip architecture consists of a three-dimensional array structure designed to provide consistent feature size and defined placement, while eliminating spot-to-spot cross contamination. We will focus on details of biochip development with an emphasis on organic layer compositions for optimal packing density, molecular orientation, selective immobilization of capture reagents, and low non-specific protein adsorption. Examples on high-level quantitative protein analysis will focus on Zyomyx human Cytokine Biochip capable of fully multiplexed and quantitative protein analysis based on sandwich-immunoassay configurations.

4:40pm **BI+SS-WeA9 Arrays of DNA-tagged Vesicles Based on Spontaneous Sorting to a DNA-array Template*, I. Pfeiffer,*** *S. Svedhem, F. Höök,* Chalmers University of Technology, Sweden

We have developed a surface-modification protocol that allows sorting of DNA-tagged vesicles (where DNA is anchored via a cholesterol moiety) to arrays of cDNA-modified Au-spots on a SiO@sub 2@ surface. Biotinylated albumin (biotin-BSA) was chosen to functionalize Au spots surrounded by SiO@sub 2@, while supported phospholipids bilayers was formed on the surrounding SiO@sub 2@, thus representing an inert background. This allowed subsequent coupling of biotinylated DNA strands via neutravidin bound to biotin-BSA only on Au spots. Eventually, a cDNA array created in this way was proven compatible with specific immobilization of differently DNA-tagged vesicles utilizing complementary DNA hybridization. The surface functionalization protocol was established using the quartz crystal microbalance technique with dissipation monitoring (QCM-D), allowing quantification of the different immobilization steps, while fluorescence microscopy was used to analyze the vesicle sorting. The compatibility of the vesicles to act as carriers for proteins was proven using scFv-antibodies, anchored to the DNA-tagged vesicles via nitrilotriacetic acid (NTA)-functionalized lipids. These results thus open up the prospect to use surface directed sorting of functionalized vesicles for construction of protein arrays, avoiding complicating and/or destructive microfluidics or microdispensing protocols. The work also includes a number of alternative approaches towards the creation of DNA arrays being compatible with the above described principle for spontaneous vesicle sorting, including improvements in the strength of the cholesterol-DNA based coupling and the dimension of the arrays, which has the potential to be down-scaled to the length of the DNA probes and the size of the vesicles, typically being less than 100 nm.

5:00pm **BI+SS-WeA10 Immobilization of Oriented Protein Molecules on High-density Poly(ethylene glycol) Coated Si(111)*, T. Cha,*** University of Minnesota*; A. Guo,* MicroSurfaces, Inc.*; X.-Y. Zhu,* University of Minnesota

The success of DNA microarray technology has motivated the development of similar tools for proteins. One of the key challenges in this chip-based assay is how the liquid-solid interface is engineered to minimize nonspecific adsorption, to control protein conformation and orientation, and to present high specificity for protein attachment. We demonstrate the synthesis of high density poly(ethylene glycol)-coated Si(111) and its application as an excellent substrate for protein microarray technology. The surface is obtained from the reaction of a multi(8)-armed PEG (mPEG) molecule with a chlorine terminated Si(111) surface to give a PEG film with thickness of 5.2 nm. Four out of the eight arms on each immobilized PEG molecule are accessible for linking to the chelating iminodiacetic acid (IDA) group which binds Cu2+ ions (2.7x10^13/cm2). The resulting Cu2+-IDA-mPEG-Si(111) surface is shown to specifically bind 6x-histidine-tagged protein molecules, including green fluorescent protein and sulfotransferase, without the need of pre-purification. In the case of 6xHis-GFP, this immobilization strategy can lead to a closely packed monolayer of protein molecules. Background tests show that the surface retains its inertness towards non-specific protein adsorption in the absence of either a poly-His tag on the protein molecule or metal ions on the surface. Both the inertness of the chemical surrounding and the controlled orientation contribute to an ideal environment for the immobilized protein molecule to retain its native conformation and reactivity. Enzyme activity for surface immobilized sulfotransferase are measured and compared to solution phase values. Such a kinetic experiment essentially extends a 2-dimensional array to the third dimension-time.

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

Electronic Materials and Devices
Room 310 - Session EM+SC+OF-WeA

Future Issues in Electronics and Optoelectronics
Moderator: C.R. Eddy, Jr., Naval Research Laboratory

2:00pm **EM+SC+OF-WeA1 Materials Issues in Solid-State Lighting**, ***J.Y. Tsao,*** Sandia National Laboratories **INVITED**

A quiet revolution is underway. Over the next 10-15 years inorganic-semiconductor-based solid-state lighting (SSL) technology is expected to outperform first incandescent, and then fluorescent and high-intensity-discharge, lighting.@footnote 1@ Nevertheless, SSL is in its infancy, and significant challenges must be met for SSL to achieve its potential for general white lighting. In this talk, we give an overview of these challenges, and of the prospects for overcoming them. We will focus especially on challenges related to the wide-bandgap AlGaInN family of materials: increasing their electrical-to-optical power conversion efficiency, and increasing their range of emitted colors. And, where possible, we will try to connect these challenges to fundamental physical properties, including: high piezoelectric coefficients, high dopant and exciton ionization energies, high microscopic internal strain and chemical immiscibility, and large differences between the bond strengths of the product materials and the chemical precursors used to grow them. @FootnoteText@@footnote 1@J.Y. Tsao, Ed., "Light Emitting Diodes (LEDs) for General Illumination Update 2002" (Optoelectronics Industry Development Association, Washington D.C., 2002); A. Zukauskas, M.S. Shur, and R. Caska, "Introduction to Solid-State Lighting" (Wiley and Sons, New York, 2002); and M.R. Krames, H. Amano, J.J. Brown, and P.L. Heremans, Eds., Special Issue on High-Efficiency Light-Emitting Diodes, IEEE Journal of Selected Topics in Quantum Electronics, Vol. 8, Issue 2 (Mar-Apr 2002).

2:40pm **EM+SC+OF-WeA3 Organic Light Emitting Diodes as a Source of Light for General Illumination**, ***M. Stolka,*** Consultant **INVITED**

Organic Light Emitting Diodes (OLEDs) have a potential to become a technology of choice for general illumination of commercial and residential buildings. There exist no fundamental obstacles to achieve the required power efficiency (>>100 lm/W), lifetime (>50,000 hrs), and the quality of emitted white light with high rendition index. OLEDs will be ten times more energy efficient as incandescent, and twice as efficient as fluorescent lamps. Recent discovery that triplet excitons can be harvested to produce photons with nearly 100% internal quantum efficiency represents a major breakthrough towards achieving the goal. Based on a spin statistics, only 25% of excitons are singlets, which were thought to be the only excitons capable of relaxing the energy as photons, by fluorescence. The remaining 75% of the excitons in triplet states were considered ineffective since the energy, gained by recombination of charges, is typically dissipated as heat. This was thought to impose a 25% fundamental limit on the internal quantum efficiency of photon generation. It was found that phosphorescent emitters, such as complexes of Pt or Ir, enable the utilization of triplet excitons as sources of photons as well. High energy efficiency, flexibility, conformability to any shape and form, light weight, distributed nature of the light sources, and the ability to emit any color including white are the main attractive features of OLEDs. However, significant challenges still remain. The outcoupling efficiency has to be increased beyond the current ~20%. The stability, especially of blue emitters, has to be improved. Better protection against the access of moisture has to be found, etc., etc. Strategies for increasing the power efficiency, increasing the lifetime of OLEDs, and methods of obtaining white light will be discussed.

3:20pm **EM+SC+OF-WeA5 Future Issues in Spintronics**, ***M.E. Flatté,*** University of Iowa **INVITED**

Metallic spintronics, the control of electrical signals through the flow of spin-polarized current, has progressed from a research discovery in 1988 to a key information technology and commercial success. Almost every computer now contains at least one spintronic device - such as the read head for a hard disk drive. Encouraged by this success researchers have explored other material systems, especially those of semiconductors. New possibilities available from semiconductor spintronics include high-speed coupling of spin dynamics to light (optospintronics), nonlinear transport and gain (spin transistors), exceptionally long spin coherence times, and electrical control of ferromagnetism. Progress in these areas has been rapid, and has led to new perspectives on the optical and electrical manipulation or detection of information stored in magnetic systems. Quick summary examples of such new physical and material functionality within semiconductors will be shown. Semiconductor spintronics, however, cannot do without metallic magnetism, for metals provide an exceptional combination of high conductivity and high Curie temperatures. New spintronic devices probably will depend on hybrid structures, where each component is chosen for optimal properties from metallic, inorganic semiconducting, and organic semiconducting materials.

4:00pm **EM+SC+OF-WeA7 Growth and Applications of Epitaxial Metal-semiconductor Nanocomposite Structures**, ***A.C. Gossard,*** *M. Hanson, D. Driscoll,* University of California, Santa Barbara **INVITED**

We explore the growth and ovegrowth of nanoscale semi-metallic islands in GaAs-based semiconductors. MBE-grown ErAs and ErSb islands grow epitaxially and coherently on the semiconductor surfaces with particle dimensions that are controlled by the deposition growth parameters. The islands can be overgrown with epitaxial semiconductors, and further layers of islands and semiconductor films can be grown to form superlattices of layers of metallic islands. The distribution of islands governs the electrical and optical properties of the nanocomposites, including Fermi level position, carrier mobility, photocarrier lifetimes, plasma properties, barrier formation and carrier tunneling.

4:40pm **EM+SC+OF-WeA9 Electronic Devices from Single Crystal CVD Diamond**, ***J. Isberg,*** Uppsala University, Sweden; *D.J. Twitchen, G.A. Scarsbrook, A.J. Whitehead, S.E. Coe,* Element Six Ltd., UK **INVITED**

Diamond is well known as being the hardest of all materials making it useful in various mechanical applications. Perhaps less well known are the extreme electronic and thermal properties of diamond, which have raised considerable speculation over its usefulness as a semiconductor material in a number of applications. The high charge-carrier mobilities, dielectric breakdown field strength and thermal conductivity of high purity diamond makes it especially well suited in devices where high frequencies are required in combination with high power, high temperatures, or high voltages. Nevertheless, despite more than two decades of research, the breakthrough of diamond-based electronics has not yet happened, largely due to the difficulty of synthesising free-standing, high-quality, single crystal diamond. We will describe recent advances in growing single crystal intrinsic and boron doped diamond intended for electronic applications. The material was grown under conditions of extreme purity, resulting in films of exceptionally low defect densities. In the intrinsic material we have measured room temperature drift mobilities of 4500 cm@super 2@/Vs for electrons and 3800 cm@super 2@/Vs for holes. These mobility values were determined by using the time-of-flight technique on thick intrinsic diamond plates. The high values for the electron and hole mobility, as well as a measured carrier lifetime in excess of 2 @mu@s, indicates a huge improvement in the electronic quality of free-standing, single crystal chemical vapor deposited (CVD) diamond. At present commercially available electronic applications of diamond include UV and radiation detectors, X-ray dosimeters, photoconductive switches and surface acoustic wave (SAW) filters. These applications are mainly based on undoped diamond. We argue that even the lack of a shallow n-type dopant does not stop diamond from having an impact in high power and high frequency electronics because effective unipolar devices such as schottky diodes and MESFETs can be made. Many difficulties concerning the fabrication of diamond devices remain to be solved and a number of process technologies need to be developed such as reliable ion-implantation, etching, annealing, surface termination and contact fabrication technologies. However, the improvement in the electronic quality of diamond indicate that the potential of single crystal CVD diamond as a wide bandgap semiconductor is substantial and will eventually allow the expansion of the boundaries of device technology. @FootnoteText@ J. Isberg et al., Science, 6 Sept, 297 (2002) p1670.

Electronic Materials and Devices
Room 321/322 - Session EM-WeA

Diamond/Contacts to SiC
Moderator: J.P. Pelz, The Ohio State University

2:00pm **EM-WeA1 Electron Transport Mechanisms in Thin B-doped CVD Diamond Films**, ***J.E. Yater,*** *A. Shih, J.E. Butler, P.E. Pehrsson,* Naval Research Laboratory

Diamond possesses unique bulk and surface properties that can be exploited for electronic device applications. Of particular interest, diamond is a promising cold emitter material for vacuum electron devices because of the negative electron affinity (NEA) observed at specific surfaces. In this study, we use electron transmission measurements to examine the electron transport characteristics of NEA diamond. Specifically, we inject conduction electrons into thin CVD diamond films using a 0-20 keV electron gun, and we measure the intensity and energy distribution of low-energy electrons transmitted through the films. In measurements from films of varying thickness (0.15-5.0 microns) and B concentration, we observe two distinct transmission distributions. One distribution is consistent with emission from the diamond conduction band, with an energy spread of about 0.7 eV (although in some cases the distribution is affected by the doping properties). Transmission yields (i.e. number of transmitted electrons produced by each incident electron) are measured as high as 2-5 in this regime. The other distribution has an energy spread of about 3 eV with associated yields that are very low (~0.05). This distribution exhibits characteristics that are consistent with emission from graphitic material, and the energy distribution is relatively insensitive to the doping properties. An analysis of the data suggests that electron transport along graphite-containing grain boundaries is the primary transport mechanism when the electron escape distance is greater than 1 micron, while conduction band transport becomes increasingly dominant for transport distances less than 1 micron.

2:20pm **EM-WeA2 On the Peculiarity of Depletion Layer in Diamond pn-junction***, **Y. Koide,*** National Institute for Materials Science (NIMS), Japan

The p-type Diamond has been easily obtained by doping with boron, and high-quality p-type diamond film was often grown on (100) diamond substrates by a microwave plasma-assisted chemical vapor deposition (MPCVD) technique. Recently, a growth method fabricating undeniable n-type diamond films was established by the MPCVD technique. The fabrication of the pn-junction structure widened a possibility of application of diamond to electronic and photonic devices. Therefore, understanding of characteristics of diamond pn-junction is our mandatory. Dependence of temperatures on carrier densities measured by Hall effect provided the ionization energies of P donor and B acceptor to be as large as 600 meV and 370 meV, respectively. Since both the dopants have deep nature, characteristics of the pn-junction are predicted to be very different from that of pn-junction which involves shallow dopants The purpose of the present paper is, as a first step to understand the pn-junction physics of diamond, to analyze the deep dopant effect of the pn-junction involving deep P donor and B acceptor. The theoretical analysis will predict a limit of performance of diamond bipolar transistor, in which the deep nature of donor and acceptor will play an important role. The analysis of space charge and carrier profiles in the pn-junction was simply carried out by solving one-dimensional Poisson equation including compensation and carrier distribution. Profiles of ionized dopants and carriers in pn-junction of diamond with deep phosphorus donor and boron acceptor were calculated. Widths of depletion layer were around two times longer than those of space charge layer since there existed a transition region at the depletion layer edge. The difference between both the widths was reduced with increasing temperatures. It was predict that a static saturation property of bipolar pnp-junction transistor was affected by the deep nature of dopants.

2:40pm **EM-WeA3 Highly Conductive N-type Ultrananocrystalline Diamond: Materials Properties and Devices***, **J.E. Gerbi,** O. Auciello, J. Birrell,* Argonne National Laboratory*; S. Curat,* University College London, UK*; D.M. Gruen,* Argonne National Laboratory*; R.B. Jackman, O.A. Williams,* University College London, UK*; J.A. Carlisle,* Argonne National Laboratory

Ultrananocrystalline diamond (UNCD) is a fine-grained (3-5 nm) diamond material. Synthesized by MPECVD using Ar-rich Ar/CH@sub 4@ plasmas, the electronic, structural, and tribological film properties of UNCD can be tailored by doping with a controlled amount of N@sub 2@. These changes correspond with clear transformations in the film structure, as both the grain size and grain boundary width of the UNCD films increase with nitrogen doping. In addition, we hypothesize that modifications in the bonding of the grain boundaries themselves occur. Together, these changes result in an n-type, highly conductive film that can retain the excellent tribological and structural properties of undoped UNCD. The conduction mechanism of nitrogen-doped UNCD is different than that of single-crystal diamond, with specific nitrogen-carbon and dangling bond complexes in the grain boundaries playing a crucial role. In this work, we discuss this unique conduction mechanism in the context of the UNCD film structure and growth process. We present recent device fabrication results and new Hall measurement results, performed with a field switching setup at variable temperatures, which provide incontrovertible evidence of the n-type conduction and significant mobilities of this material. For example, a film grown with the relatively low nitrogen doping level of ~ 0.2 at.% displays an electron carrier concentration of ~ 5 x10@super 17@ cm@super -3@ and a mobility of greater than 6 cm@super 2@/Vs , while retaining the excellent tribological, chemical, and structural characteristics necessary for conductive MEMS/NEMS and bioelectronics applications. Films with much higher conductivities and doping concentrations can also be produced; doping levels as high as 1.1 at. % N will also be discussed in the context of thin-film diamond electronics. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

3:00pm **EM-WeA4 Raman Spectroscopy of Ultrananocrystalline Diamond Thin Films***, **J. Birrell,** J.E. Gerbi, O. Auciello,* Argonne National Laboratory*; J. Johnson, X. Xiao,* Argonne National Laboratory, U.S.*; J.A. Carlisle,* Argonne National Laboratory

Raman spectroscopy is often used as an efficient and non-destructive way of determining the bonding structure of diamond thin films. However, interpretation of the Raman spectrum of carbon materials with small grain sizes and a large number of grain boundaries, such as in nanocrystalline, ultrananocrystalline (UNCD), and amorphous diamond, is not straightforward. In order to correctly interpret the Raman spectral features of UNCD thin films, a series of films spanning the range of structures from microcrystalline to UNCD was studied using visible and UV Raman spectroscopy, as well as scanning and transmission electron microscopy. For UNCD, we find that although the sample has been found to be composed of ~95% @super" sp@super 3@-bonded carbon by other techniques including near-edge adsorption fine structure (NEXAFS) and TEM, none of the spectral features observed using visible Raman spectroscopy can be attributed to @super" sp@super 3@-bonded carbon. As the UNCD grains appear purely crystalline in TEM, we identify the disordered carbon at the grain boundaries of UNCD as responsible for all spectral features observed. This enables us to probe the grain boundary structure of UNCD specifically, which is of great utility for understanding the electronic and structural properties of the material. Finally, we interpret the changes in the Raman spectra of UNCD grown under various growth conditions, including low temperature growth; as well as with nitrogen doped UNCD, which results in a large increase in the conductivity of UNCD films. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

3:20pm **EM-WeA5 Silicon on Diamond Technology***, **A. Aleksov**, N. Govindaraju, F. Okuzumi, G.N. Yushin,* North Carolina State University*; S.D. Wolter, J.T. Prater,* Army Research Office / AMSRL- RO-PM*; Z. Sitar,* North Carolina State University

The roadmap for the development of Si-based high-speed low-power electronics for digital applications shows that Moore's law predicting an exponential increase in the speed operation of digital ICs will remain valid in the near future, yielding ever shrinking devices and larger integration scales, necessitates a decrease of the supply voltage to limit the loss power and an increase in the complexity of heat management. Silicon on Diamond (SOD) is proposed as an alternative to SOI to overcome the severe thermal limitations imposed by SOI, but at the same time retain the advantages of SOI in respect to increased device speed and carrier confinement. SOD technology is beneficial for both digital Si-applications as well as for high-power high-frequency Si-devices. This technology utilizes the unique physical properties of diamond i.e. the highest thermal conductivity (up to 22 W/cmK) and a high specific resistance (10@super 12@ Î©cm range). In our SOD approach, the insulating layer is a highly-oriented diamond (HOD) film with bulk-like properties, which can be grown on large area Si substrates. Following the diamond growth, another Si wafer is bonded to the diamond in UHV at a pressure of around 32 MPa and a temperature of 950°C. The bonded Si wafer is then thinned to the desired thickness. The bonded interface has been studied by TEM and EELS to assess structural and chemical character of the interface, respectively. Metal strip heater devices fabricated on SOD samples confirm the heat spreading efficiency of the diamond layer and benefits of SOD. For comparison, the same device structures have been fabricated on a SOI wafer. The experimental results are accompanied by finite element thermal simulations of the experimental set ups enabling the direct comparison of theoretical and experimental data.

3:40pm **EM-WeA6 Metallizing a Semiconductor Surface with Hydrogen***, **P.G. Soukiassian**, V. Derycke,* Commissariat à l'Energie Atomique, France*; F. Amy, Y.J. Chabal,* Agere Systems*; M. D'angelo, H. Enriquez, V.Yu. Aristov, M. Silly,* Commissariat à l'Energie Atomique, France*; M. Pedio, P. Perfetti,* Insituto di Struttura della Materia, Italy

Passivation of semiconductor surfaces against chemical attacks can be achieved by terminating the surface-dangling bonds with a monovalent atom such as hydrogen. Such passivation has invariably leads to the removal of all surface states in the band gap, and thus to the termination of non-metallic surfaces. Here, the first observation of semiconductor surface metallization induced by atomic hydrogen is reported.@footnote 1@ This surprising result, established using atom resolved scanning tunneling microscopy (STM) and spectroscopy (STS), core level and valence band photoelectron spectroscopy (XPS,UPS) and multiple reflection infrared absorption spectroscopy (MR-IRAS) is achieved on the Si-terminated 3C-SiC(100) 3x2 cubic silicon carbide surface,. The metallization is evidenced through band gap closing in STS, Fermi level built-up in UPS and specific related spectral features in MR-IRAS. In addition, core level photoemission spectroscopy using synchrotron radiation gives fine details about interatomic charge transfers within the surface and sub-surface regions. The metallization process results from competition between hydrogen termination of surface dangling bonds and hydrogen-generated steric hindrance below the surface. Understanding the ingredient for hydrogen-stabilized metallisation directly impacts the ability to eliminate electronic defects at semiconductor interfaces critical for microelectronics, provides means to develop electrical contacts on high band-gap chemically passive materials, particularly exciting for interfacing with biological systems, and gives control of surfaces for lubrication, e.g. of nanomechanical devices. @FootnoteText@ @footnote 1@ V. Derycke, P. Soukiassian, F. Amy, Y.J. Chabal, M. D'angelo, H. Enriquez and M. Silly, Nature Materials 2, 253 (2003).

4:00pm **EM-WeA7 Macroscopic and Microscopic Electronic Behavior of Cubic Inclusions in 4H-SiC***, **K.-B. Park**, Y. Ding, J.P. Pelz,* The Ohio State University*; K.C. Palle, M.K. Mikhov, B.J. Skromme,* Arizona State University*; A. Los, M.S. Mazzola,* Mississippi State University

Double-stacking-fault cubic inclusions in n-type 4H-SiC@footnote 1@ were studied with ballistic electron emission microscopy (BEEM) in ultra high vacuum where the inclusions intersect a Pt/SiC Schottky barrier (SB) interface. We confirmed prior proposals@footnote 2@ that the inclusions behave as quantum wells, and found a propagating two-dimensional quantum well conduction band minimum (CBM) at ~0.53 eV below the CBM of the bulk 4H-SiC host. This agrees well with calculations of the quantum well state@footnote 3@ and is close to the SB height lowering found with macroscopic I-V and C-V measurements.@footnote 4@ The macroscopic C-V SB heights were found to be quite similar to macroscopic I-V measurements, which is interesting because less than 5% of the Pt/SiC interface is on the low-barrier-height inclusions. We believe this similarity between C-V, I-V, and BEEM measurements can be explained by the actual SBH of the inclusions at the Pt/SiC interface, along with changing occupation of the quantum well states away from the interface during C-V measurements. We are currently developing electrostatic modeling to quantify this hypothesis. We will also discuss the first "hole BEEM" measurements of SiC on a Pt/p-type 4H-SiC (presently without inclusions) SB interface. We found a 1.40 eV p-type SB height, compared with 1.54 eV of Pt on n-type 4H-SiC, as well as a double threshold, suggesting a possible second valance band maximum. @FootnoteText@@footnote 1@R. S. Okojie, M. Zhang, P. Pirouz, S. Tumakha, G. Jessen, and L. J. Brillson, Appl. Phys. Lett. 79, 3056 (2001).@footnote 2@T. A. Kuhr, J. Q. Liu, H. J. Chung, M. Skowronski, and F. Szmulowicz, J. Appl. Phys. 92, 5863 (2002).@footnote 3@H. Iwata, U. Lindefelt, S. Oberg, and P. Briddon, J. Phys. C 14, 12733 (2002).@footnote 4@B. J. Skromme, K. Palle, C. D. Poweleit, L. R. Bryant, W. M. Vetter, M. Dudley, K. Moore, and T. Gehoski, Mater. Sci. Forum 389-393, 455 (2002).

4:20pm **EM-WeA8 Improved Titanium / Nickel Ohmic Contacts on N-Type 4H Silicon Carbide***, **J.H. Park**, P.H. Holloway,* University of Florida

Nickel (Ni) contacts are the most commonly used ohmic contacts to n-type silicon carbide (SiC). Unfortunately, the Ni contacts exhibit rough interface morphology after high temperature annealing. In addition, the reaction to form the silicide liberates carbon, which can segregate to the metal-semiconductor interface. These two factors limit the reliability of the Ni contacts to n-SiC for high temperature and power applications. The electrical and structural properties of electron-beam evaporated nickel/titanium metal contacts to n-type 4H SiC were studied by current-voltage (I-V), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and X-ray diffraction (XRD) techniques. Nickel/titanium metal contacts on the 4H SiC were rectifying as deposited but turned to ohmic after rapid thermal annealing (RTA) at 1000°C for 2 minutes in nitrogen. The nickel/titanium contacts were converted to the layer sequence of titanium carbide/nickel silicide/SiC by annealing. This structure had a low specific contact resistance of 10@super -5@ @ohm@-cm@super 2@. A shallower and smoother nickel silicide/SiC interface was obtained as compared to the conventional only-nickel contacts. The nickel silicide layer was formed on SiC by a nickel-SiC reaction during high temperature annealing which left excess carbon at the interface between the silicide and SiC. Titanium reacted with the carbon to form a titanium carbide layer on the nickel silicide, which led to reduced carbon excesses at the interface and lower resistance of the ohmic contacts. The phase inverting mechanisms and the effects of nickel/titanium thickness on this process have been studied. Phase analysis of the nickel silicides and titanium carbides using XRD and TEM will be reported.

4:40pm **EM-WeA9 Correlation Between Electrical and Microstructural Properties of Low Resistance TiAl-based Ohmic Contacts to p-type 4H-SiC***, **S. Tsukimoto**, K. Nitta, M. Moriyama, M. Murakami,* Kyoto University, Japan

In order to understand a contact formation mechanism for TiAl-based contacts, the electrical properties and microstructure of conventional Ti/Al and recently developed Ni/Ti/Al ohmic contacts to p-type 4H-SiC were correlated. The Ti/Al and Ni/Ti/Al ohmic contacts were prepared by depositing sequentially Ni, Ti, and Al on the SiC substrates doped with Al at 4.5x10@super 18@cm@super -3@, and subsequently annealing in an ultra high vacuum at 1000°C for 2min and 800°C for 10min, respectively. These contacts provided the lowest contact resistances of 1x10@super -5@ and 7x10@super -5@ @ohm@-cm@super 2@, respectively. X-ray diffraction and cross-sectional transmission electron microscopy were used to identify reacted layers formed at the ohmic contacts/SiC interfaces. For the Ti/Al contacts, ternary Ti@sub 3@SiC@sub 2@ compound layers with a hexagonal structure were formed to grow epitaxially on the substrates. For the Ni/Ti/Al contacts, hexagonal Al@sub 4@C@sub 3@ compound layers were also formed to grow epitaxially on the SiC in addition to other binary compounds. The formation of these epitaxial carbide layers was found to have a strong influence on the contact resistances to the SiC, and was essential to prepare low resistance TiAl-based contacts. The present experiment indicated that both the Ti@sub 3@SiC@sub 2@ and the Al@sub 4@C@sub 3@ layers played a role of intermediate semiconductor layers (ISL) between p-type SiC and the contact metals, which reduced the barrier height and/or depletion region.

Homeland Security Topical Conference

Room 309 - Session HS+MM-WeA

Detection of Explosives and Other Chemicals for Homeland Security

Moderators: R. Cavanagh, National Institute of Standards and Technology, R.T. Lareau, Transportation Security Administration

2:00pm **HS+MM-WeA1 MEMS Chemical Sensors for Homeland Security***, **D.C. Meier**,* National Institute of Standards and Technology*; C.J. Taylor,* Pomona College*; R.E. Cavicchi, Z. Boger, S. Semancik,* National Institute of Standards and Technology

Chemical sensors capable of accurate detection of trace quantities of chemical warfare (CW) agents would provide a potent tool for perimeter security, treaty verification, and battlefield threat detection. Ideally, such sensors would be highly sensitive, selective, compact, and require low power. Since many CW agents are lethal at µmol/mol (ppm) concentrations, reliable trace detection is the critical prerequisite to the employment of life-saving countermeasures. In order to meet these goals, microsensors consisting of CVD TiO@sub 2@ and SnO@sub 2@ sensing films on MEMS array platforms have been fabricated. Their response measurements to the CW agents GA (tabun), GB (sarin), and HD (sulfur mustard) in dry air at concentrations between 5 and 200 nmol/mol (ppb), as well as to CW agent simulants CES (chloroethyl ethyl sulfide) and DFP (diisopropyl fluorophosphate) between 250 and 3000 ppb are reported. The devices yield both excellent signal-to-noise and good reproducibility for similar devices. Detection in backgrounds of common battlefield interferants is also discussed. The temperature of each sensor element is independently controlled by embedded microhotplate structures that drive both the CVD process (375 °C) and sensor operation at elevated temperatures (325 to 475 °C). The concentration-dependent analyte response magnitude is sensitive to sensing film growth conditions. Long-term stability studies verify stable sensor responses to GB and HD for 14 hours of agent exposure. Use of fast (200 ms) temperature programmed sensing (TPS) over a broad range (20 to 480 °C) enhances analyte selectivity, since the resulting signal trace patterns include only kinetic data that are unique for each agent tested. Recursive training of an artificial neural network (ANN) assembles the set of most relevant inputs from the TPS data; subsequent validation of the trained ANN verifies positive agent and simulant identification and quantification.

2:20pm **HS+MM-WeA2 Development of a Piezoelectric Microphone for Trace Gas Detection***, **R.G. Polcawich**, P. Pellegrino,* U.S. Army Research Laboratory

Escalating environmental awareness has led to more restrictive regulations on air quality in both the workplace and the environment in general. As a result, there is an increasing desire to have portable trace gas analyzers especially for chemical and biological agent detection. To meet these goals, a gas detection system must be miniaturized allowing large scale production of affordable small sensing systems. Initial examination of the scaling principles associated with photoacoustic spectroscopy (PAS) in respect to microelectromechanical system (MEMS) dimensions indicate the photoacoustic signals would remain at similar or greater sensitivities commonly found in macro-scale devices.@footnote 1@ Several other issues including: increased stability, noise avoidance, small source-to-detector distances and monolithic sensor construction support the idea that a MEMS photoacoustic chemical sensor can be realized.@footnote 2@ Our current research efforts have focused on fabrication of a piezoelectric microphone for trace gas sensing using a MEMS PAS. Using lead zirconate titanate (PZT) thin films as the piezoelectric sensor, 500 to 2000 micrometer diameter acoustic sensors have been fabricated and have an unamplified sensitivity of 0.1 to 1.0 µmV/Pa, depending on geometry. Using a limit of detection determined from the noise floor of the PZT microphone, it is anticipated that a PZT based acoustic sensor should detect SF@sub 6@ at slightly less than 1 ppb. Our presentation will cover the fabrication, packaging, and testing of a piezoelectric microphone for use in a MEMS based PAS detector. @FootnoteText@ @footnote 1@ S.L. Firebaugh, K.F. Jensen, and M.A. Schmidt, Miniaturization and integration of photoacoustic detection, J. Appl. Phys., vol 92, pp.1555-1563 (2002).@footnote 2@ P. Pellegrino and R. Polcawich, Evaluation of a MEMS Photoacoustic Sensor, submitted to 2002 Joint Service Scientific Conference Chemical Biological Defense Research, Hunt Valley.

2:40pm **HS+MM-WeA3 Fabrication, Packaging and Testing of Micronozzles for Gas Sensing Applications***, **S. Li**,* University of Maryland, College Park*; C.B. Freidhoff, R.M. Young,* Northrop Grumman Electronic Systems Inc.*; R. Ghodssi,* University of Maryland, College Park

There has been recent, rapid development of MEMS-based gaseous microfluidic devices (GMDs) working under standard atmospheric conditions. One of the applications considered for the GMD is for a frontend of a miniature chemical sensor to improve its sensitivity. We report a fabrication technology for developing linear converging-diverging micronozzles using low temperature wafer-level adhesive bonding with SU-8. The process is quick, repeatable and relatively insensitive to presence of particles on the wafers to be bonded. A selection of wafer bonding tests with SU-8 as the intermediate bonding material has been performed to investigate the influence of different parameters on the bonding of structured wafers. A crack-opening method is used to evaluate the surface energy of bonded wafers to be in the range of 0.42-0.56 J/m@super 2@. Based on the results of wafer bonding test with SU-8, sealed micronozzles with throat widths as small as 3.6 µm are fabricated successfully. For the purpose of comparison, micronozzles of same geometries and dimensions are also fabricated using deep reactive ion etching (DRIE) and silicon-glass anodic bonding techniques. The micronozzles are packaged to interface with a gas flow test setup using capillary needles, O-rings and flexible tubing. Gas flow rates and pressure distributions in the micronozzles are measured and compared with those predicted from the one-dimensional isentropic flow model, which demonstrate that these developed techniques may extend the flexibility of fabricating and packaging microfluidic devices for gas sensing applications. The detailed fabrication process and testing results will be presented.

3:00pm **HS+MM-WeA4 Characterization of Portal-Based Trace Explosive Detection Systems***, **G. Gillen**, R.A. Fletcher, S.V. Roberson, C. Zeissler, E.S. Etz, J. Verkouteren, M. Verkouteren, E.S. Windsor, G.A. Klouda,* National Institute of Standards and Technology*; R.T. Lareau,* Transportation Security Administration

In collaboration with the Transportation Security Agency's (TSA) Trace Explosive Detection Group, the NIST Chemical Science and Technology Laboratory (CSTL) has been working to build a chemical metrology program to help support the widespread operational deployment and effective utilization of trace explosives detection devices throughout the United States. A second objective is to develop at NIST the specialized measurement expertise that will be needed to support the next generation of explosive detection equipment. Of particular interest for this work is the characterization of walk-through trace explosive detection portal (TEDPâ€™s) systems currently under evaluation by the TSA. The low volatility of most high explosives makes direct analysis of vapors impractical. Therefore, many detection systems are based on either airborne or surface swipe collection of micrometer-sized explosive particles with subsequent thermal vaporization of the particles into an ion mobility spectrometer for identification. The effective collection and thermal desorption of the explosive particles is the critical front-end process for the successful and reproducible detection of explosives. In order to understand this process in detail we are employing a number of microanalytical techniques including: SIMS and TOF-SIMS, SEM, Raman, Optical and Fluorescence Microscopy, Infrared Thermometry and Optical Particle Counting. These techniques are being used to study, at the single particle level, the collection and removal of individual explosive particles from surfaces and the chemical and morphological changes that occur during sampling. This presentation will review the NIST-TSA project and will present our recent findings with an emphasis on chemical characterization of individual explosive particles.

3:20pm **HS+MM-WeA5 Polymer Electronics for Ultra-Sensitive Chemical and Biological Sensors***, **T.M. Swager**,* Massachusetts Institute of Technology **INVITED**

This presentation will describe the design of electronic polymers that have the ability to undergo self-amplified responses.@footnote 1@ Optimal energy and charge transport properties are key to the amplifying ability of these materials. Design principles have been developed that can be used to improve the mobility and lifetime of excitons will be presented. To elicit a selective sensor response different molecular recognition principles have been integrated into the polymers. Effective implementation of recognition elements requires effective transduction events that are compatible with the amplifying ability of the polymers. Designs based upon energy transfer, quenching, and excimer formation will be presented for the detection of DNA, Proteins, Chemical Warfare Agents, Explosives, and Ions. I will also discuss our continuing efforts in the design of sensory materials that utilize molecular recognition events to product changes in conductivity. In many cases we use transition metal ions are redox active elements in these materials and I will outline the design principles for producing conducting polymers that utilize the metal ions as part of the conducting pathway. These materials have allowed us to produce new sensors for nitric oxide, a signaling agent in biological systems. @FootnoteText@ @footnote 1@ (a) Swager, T. M. "The Molecular Wire Approach to Sensory Signal Amplification" Accts. Chem. Res. 1998, 31, 201-7. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. "Conjugated Polymer Sensory Materials" Chem. Rev. 2000, 100, 2537-2574. (c) Self-Amplifying SemiconductingPolymers for Chemical Sensors Swager, T. M.; Wosnick, J. H. MRS Bulletin, 2002, June, 446. (d) J.H. Wosnick and T.M. Swager, "Molecular Photonic and Electronic Circuitry for Ultra-Sensitive Chemical Sensors" Curr. Opin. Chem. Biol. 4 (2000) p. 711.

4:00pm **HS+MM-WeA7 DIOS-MS and LC-DIOS-MS for Chemical Analysis***, Z. Shen, C. Fish,* University of California, San Diego*; G. Siuzdak, M.G. Finn,* The Scripps Research Institute*; **J.E. Crowell**,* University of California, San Diego

Desorption/Ionization On Silicon Mass Spectrometry (DIOS-MS) is a new mass spectrometry strategy based on pulsed laser desorption/ionization from a porous silicon surface. DIOS-MS is similar to matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) in that it utilizes the same instrument; however, in DIOS-MS, porous silicon is used to trap analytes deposited on the surface and laser radiation is used to vaporize and ionize these molecules, without the presence of any matrix material. We have shown that DIOS-MS can be used for a wide range of biomolecules, organic molecules, and metal-containing compounds at the femtomole and attomole level with little or no fragmentation. DIOS-MS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. We will discuss the coupling of liquid chromatography separation with DIOS-MS for protein identification and peptide sequencing, and the use of chemical and surface modification for tailored analysis.

4:20pm **HS+MM-WeA8 A Novel Chemical Detector Using Cermet Sensors and Pattern Recognition Methods***, **S.L. Rose-Pehrsson**,* Naval Research Laboratory*; J. Ziegler,* General Atomics*; M.H. Hammond,* Naval Research Laboratory*; D. Gary, K. Caudy,* General Atomics

Smart microsensor arrays are being developed by combining cermet electrochemical sensors, intelligent firmware and software to drive the sensors and analyze the data. The chemical microsensors offer a small size, light weight, low power and low cost alternative to conventional electrochemical sensors. The chemical microsensor architecture may be modified for detection selectivity of a variety of chemical species including chemical agents and combustible or corrosive gases. The microsensor arrays have potential application for monitoring hazardous chemicals in the part-per-million to part-per-billion range in a variety of internal and external environments. The arrays sense analytes using pattern recognition techniques to determine the presence of vapors of interest. General Atomics and the Naval Research Laboratory are developing this technology for the detection of chemical warfare agents and toxic industrial compounds (TICs). A test demonstrator has been developed with a three-sensor array, readout electronics, and system control software. The three-sensor array was exposed to 15 test vapors. The 15-analyte sources, including 2 blood agents, 10 TICs and 3 simulants were generated at 5 different concentrations in humid air. The cermet sensor array provided unique responses for the various analytes tested. Similar analyte types produced similar results. The sensitivity is sufficient to detect all the analytes at their respective exposure limits. Two different pattern recognition methods were developed to identify the analytes.

4:40pm **HS+MM-WeA9 Chemical Warfare Agent Detection Using Random Networks of Single-Wall Carbon Nanotubes***, **E.S. Snow**, J.P. Novak, E.J. Houser,* Naval Research Laboratory

Single-wall carbon nanotubes (SWCNT) are unique structures in that they are composed entirely of surface atoms while exhibiting transport properties superior to single crystalline Si. These features make them an ideal candidate for a new class of molecular sensors. We report the use of random networks of SWCNTs as a sensor for chemical warfare agents. Random networks of SWCNTs are used to provide high-yield sensor fabrication using conventional microlithographic techniques. Molecular adsorption of chemical agents onto the nanotube networks results in a charge transfer that manifests itself as a change in the network conductance. In such devices sub-part-per-billion sensitivity to agent simulants is easily achieved. We discuss these results and our approach to functionalizing the networks to provide additional sensitivity, selectivity against potential interferents, and a high degree of chemical specificity. Arrays of such functionalized devices should provide highly sensitive and specific electronic detection of a wide range of chemical warfare agents and other toxic chemicals.

5:00pm **HS+MM-WeA10 Carbon Nanotubes for Molecular Sensors and Electronic Circuit Elements***, **M.J. Bronikowski**, D.S. Choi, M.E. Hoenk, B.D. Hunt, R.S. Kowalczyk, E.W. Wong, A.M. Fisher,* Jet Propulsion Laboratory/California Institute of Technology*; B. Rogers, J.D. Adams,* University of Nevada, Reno*; J. Xu,* Brown University*; J.F. Davis, L.W. Epp, D.J. Hoppe,* Jet Propulsion Laboratory/California Institute of Technology

This talk will focus on recent efforts at JPL's Microdevices Laboratory in developing several different types of nano-scale electronic devices based on carbon nanotubes (CNT). CNT exhibit a coupling between electronic structure and mechanical deformations: mechanical stress or deformation can result in charge injection into the nanotube, or likewise, charging of a nanotube can result in mechanical deformations. This electromechanical coupling can form the basis for nanotube-based oscillators, signal processors, and RF rectifiers. Nanotube electronic properties, specifically their resistance and current-voltage characteristic, can also change when various molecules bind to their surfaces. This property can form the basis for CNT-based chemical and molecular sensors. For both types of device, CNT are grown directly on silicon substrates in pre-patterned device structures: nanotubes grow by CVD from patterned arrays of particles of catalytic metals, with the pattern of the catalyst determining the pattern of CNT. Of key importance to producing devices by this means is controlled placement of catalyst on the substrate: several methods for generating catalyst patterns on surfaces and devices will be demonstrated and discussed.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI+TF-WeA

Magnetic Thin Films

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

2:00pm **MI+TF-WeA1 Electrodeposition of Epitaxially Grown Fe Films on n-type GaAs***, C. Scheck, **Y.-K. Liu**,* The University of Alabama*; G. Zangari,* University of Virginia*; R. Schad,* The University of Alabama

Epitaxial growth of Fe thin films on both n-type GaAs(001) and n-type GaAs(011) substrates have been demonstrated using Molecular Beam Epitaxy (MBE) in the past. Indeed, Fe and GaAs lattice constants match very well leading to easy epitaxial growth. However, special surface preparation or growth at elevated temperature were needed to obtain good quality films. Also diffusion and segregation of substrate material (As) at the surface, characteristic of intermixing at the interface, were observed on MBE grown films. Electrodeposition (ECD) technique on the contrary is an equilibrium process which thus releases much less energy per absorbed atom than other deposition techniques (MBE). This allows preparation of chemically sharp interfaces (i.e. no intermixing) which otherwise show a high degree of reactivity and interdiffusion. We reported for the first time the epitaxial growth of high quality Fe thin films on both n-type GaAs(001) and n-type GaAs(011) substrates using ECD. Two different electrolytes FeSO4 and FeC§¤2 solutions 0.1M were used at pH 2.5. Results from X-Ray Diffraction (XRD) show Fe(001)[110]//GaAs(001)[110] and Fe(011)[100]//GaAs(011)[100] as the primary epitaxial relations similarly to Fe films grown by MBE. These films' in-plane magnetic anisotropy is related to the crystalline structure. Their coercivity Hc is around 30-100 Oe.

2:20pm **MI+TF-WeA2 Epitaxial Growth of Ferromagnetic Fe Overlayers on CH@sub 3@CSNH@sub 2@ - Passivated GaAs(100)-S(2x1) Reconstruction***, **E.D. Lu**, H.T. Johnson-Steigelman, P.F. Lyman,* University of Wisconsin, Milwaukee

Epitaxial growth of ferromagnetic metallic Fe overlayers on thioacetamide (CH@sub 3@CSNH@sub 2@)-passivated GaAs(100)-S(2x1) reconstructed surfaces at room temperature (RT) has been investigated by low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Prior to Fe deposition, GaAs(100) wafers were passivated by CH@sub 3@CSNH@sub 2@ solution then annealed between 320°C and 450°C under UHV. A clear (2x1) reconstructed LEED pattern with around 1 monolayer (ML) sulfur coverage resulted. Upon deposition of Fe at RT, epitaxial bcc(100) Fe overlayers could be grown from 3 to 40 ML. XPS and AES have revealed that only an initial interface reaction (<4ML) takes place between the evaporated Fe overlayer and GaS sulfide passivation layers. Upon annealing, the Fe/S-GaAs(100) heterostructure appears stable up to 320°C; solid state reaction and/or interdiffusion of the layers starts at higher annealing temperatures, becoming severe by 450°C. Nonetheless, a LEED pattern is observed even after intermixing. These results indicate that the S passivation layer may inhibit Ga and As outdiffusion at modest substrate temperatures, and may thus suppress or reduce the formation of an anti-ferromagnetic Fe@sub 2@As dead layer or other unfavorable Fe@sub 3@Ga@Sub 2-x@As@sub x@ phases.

2:40pm **MI+TF-WeA3 On the Magnetic Properties of Ultra Thin Epitaxial Fe Films on GaAs(001)***, S.A. Morton,* Lawrence Livermore National Laboratory*; J.R. Neal, M. Spangenberg, T.-H. Shen,* University of Salford, UK*; A.E.R. Malins, E.A. Seddon,* CLRC Daresbury Laboratory, UK*; D. Greig,* University of Leeds, UK*; J.A.D. Matthew,* University of York, UK*; **G.D. Waddill**,* University of Missouri, Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory

The magnetic properties of epitaxial Fe films on GaAs have attracted considerable interest in recent years because of their potential for use as spin injection sources for spintronic devices; however, previous studies have been unable to demonstrate a magnetic signature in films with thicknesses below approximately 5 ML. A number of possible explanations for this observation have been proposed such as the presence of a magnetically dead interfacial layer of Fe2As. However, by measuring the thickness and temperature dependence of the Fe 3p core level magnetic linear dichroism signal we have shown that such films are indeed ferromagnetic but that their Curie temperature is substantially below room temperature. For instance a Tc of approximately 240K was measured for thin films with a nominal thickness of 0.9 nm. Furthermore the values of the Curie temperature in this thickness regime have been shown to be extremely sensitive both to initial substrate conditions and to the overall film thickness; an increase in the thickness of 0.35nm results in a Curie temperature above room temperature. These measurements have been complemented with spin resolved and angle resolved measurements of the Fe/GaAs valence band and core levels; together with ex-situ XRD and SPM studies of sample growth. The origins of the evolving magnetic behavior of Fe films on GaAs(001) from 1-50ML is discussed in terms of the spin dependent electronic band structure and the stoichiometry and growth morphology.

3:00pm **MI+TF-WeA4 Correlated Structural and Magnetization Reversal Studies on Epitaxial Ni Films Grown with MBE and with Sputtering***, Z. Zhang*[1]*, R.A. Lukaszew,* University of Toledo*; A. Zambano,* Michigan State University*; C. Cionca,* University of Michigan, Ann Arbor*; D. Walko,* Argonne National Laboratory*; E. Dufresne,* University of Michigan, Ann Arbor*; M. Yeadon,* National University of Singapore, Singapore*; R. Clarke,* University of Michigan, Ann Arbor

The study of epitaxial magnetic thin films is important to understand structure-property correlations. We have studied the correlation between film structure and azimuthal dependence of the magnetization reversal on (001) epitaxial Ni films grown on MgO substrates with two different deposition techniques: molecular beam epitaxy (MBE) and DC magnetron sputtering . The films were grown and annealed in-situ under identical conditions. The magnetization reversal was investigated using MOKE. The coercive field in the sputtered films exhibits 4-fold symmetry as expected for a crystal of good epitaxial quality. The MBE grown films exhibit an additional uniaxial symmetry superimposed to the four-fold symmetry. We note that films of the same thickness made with these two deposition techniques, exhibited the same average coercivity. We performed high-resolution XRD at the Advanced Photon Source (ANL) in order to establish similarities and differences in the structure of the films. Both types of films exhibit epitaxial growth and very good crystalline quality with no indication of strain, and don't exhibit fundamental structural differences. The main difference between the films was the surface morphology. STM images of the surface of the MBE grown films indicated self-assembled periodic stripe nano-patterning, while STM images of the sputtered films didn't exhibit any regular patterning of the surface. Cross sectional TEM studies performed on the films will be correlated with the surface morphology and with the magnetic anisotropy.

3:20pm **MI+TF-WeA5 Adsorption-induced Giant Stress and Surface Relaxation in Ni/W(110)***, **H.L. Meyerheim**, D. Sander, R. Popescu,* Max-Planck-Institut f. Mikrostrukturphysik, Germany*; O. Robach, S. Ferrer,* ESRF, France*; J. Kirschner,* Max-Planck-Institut f. Mikrostrukturphysik, Germany

Surface stress has been recognized as a decisive factor, which determines a variety of phenomena like self-assembled pattern formation on the nano-scale, shape evolution of nano-objects and surface reconstruction. Our work reveals an important aspect of adsorbate-induced stress which might be of key importance for the general understanding of stress-strain relations in the monolayer range. We identify an intimate correlation between structure and stress from an in-situ combination of surface x-ray diffraction and stress measurements. We show that one atomic layer of Ni induces substantial lateral shifts of the top W-atoms of up to 0.5 Å. At this coverage we measure an anisotropic change of the surface stress induced by Ni. The experiments were carried out at the ESRF in Grenoble (France). Surface stress was measured by the crystal curvature technique.@footnote 1@ From earlier experiments@footnote 2@ it is known that Ni forms a c(1x7) superstructure on W(110) at a coverage above 0.8 monolayers (ML, 1ML=1.41x10@super15@ atoms/cm@super2@). Up to 0.8 ML the stress measurements indicate compressive stress along [001] and tensile stress along [1-10]. The emergence of the c(1x7)-structure coincides with the formation of compressive stress along [1-10]. The x-ray analysis shows that the Ni-atoms form a distorted densely packed hexagonal adlayer. However, the most important and astonishing aspect is the pronounced shifts (up to 0.5 Å) of the first layer W-atoms out of their bulk positions along [1-10]. The structure consists of alternating Ni-W-Ni-chains running along [1-11]. In conclusion we have measured a substantial adsorbate-induced relaxation in a system, which is generally considered to be structurally inert upon adsorbate deposition. There is a striking correlation between the onset of lateral shifts of atomic positions and compressive surface stress. @FootnoteText@@footnote 1@D. Sander et al. Rev. Sci. Instr. 66, 4734 (1995); @footnote 2@D. Sander et al. Phys. Rev. B57, 1406 (1998).

3:40pm **MI+TF-WeA6 Ion Deposited Co and DLC Films Generated from Laser Excitation***, **F.J. Cadieu**, L. Chen,* Queens College of CUNY

A modified pulsed laser deposition system has been used to deposit films from ions generated due to the impact of 248 nm excimer laser pulses. A synchronously pulsed magnetic field coil with a wide entrance throat and a tapered bore in conjunction with a set of permanent magnets has been used to capture and concentrate the ion and electron beam flux under vacuum conditions onto the substrates. Co and other films such as diamond like carbon, DLC, are strongly adherent when deposited onto even room temperature substrates. The ion collection and concentration factor is such that Co films deposited on glass to an optical density of 3.0, approximately 7 nm thickness, with coil pulsing and magnets only exhibited an optical density of 0.10 without coil pulsing and magnets for the same number of laser pulses. Films have been characterized by x-ray reflectivity, x-ray diffraction, scanning electron microscopy, SEM, and magnetoresistivity measurements when combined with other magnetic layers. Over an order of magnitude intensity modulation has been observed in x-ray reflectivity measurements for Co films, 7-15 nm thickness, deposited onto R-plane sapphire substrates and onto Si (111) substrates. In contrast to this Co films simultaneously deposited onto A-plane sapphire substrates hardly exhibited x-ray reflectivity fringes indicating a large surface roughness. Similarly DLC films deposited onto (111) Si substrates exhibited order of magnitude intensity modulations indicating a very small surface roughness. X-ray reflectivity measurements of DLC, Co layers on (111) Si are used to show the conditions necessary to make smooth and hence insulating DLC films onto the metallic layer. SEM measurements indicated smooth films were obtained with no discernible particulates. X-ray pole figures are used to characterize single crystal films versus polycrystalline growth modes.

4:00pm **MI+TF-WeA7 Ultrathin Magnetic Layers Electrodeposited on Au(111)and Related Technological Substrates***, **P. Allongue**, F. Maroun,* CNRS, France*; J.E. Schmidt, A. Gundel,* UFRGS*; M.L. Munford,* UFSC*; T. Devolder,* IEF, France **INVITED**

Magnetic properties such as interface perpendicular anisotropy (PMA) is strongly depending on the coupling between the substrate, generally a noble metal, and the ultrathin ferromagnetic layer. Both the film and interface structures are also critically influencing the strength of PMA. We recently showed that electrodeposited Cu/Co/Au(111) structures exhibit strong PMA due to an excellent 2D epitaxial growth of cobalt and some residual elastic stress at the interface. This talk will be divided into two parts. In the first one, I will present in situ structural and magnetic characterizations of M / Au(111) ultrathin layers, with M = Co, Ni and Fe using STM, EXAFS and real time in situ magnetic characterizations (AGFM and PMOKE) with sub-monolayer sensitivity. It will be shown that the latter measurements, performed in the electrolytic environment, yield new information regarding the relationship between the deposition conditions (potential, pH etc.) and the magnetic state of layers. While Co and Fe layers are ferromagnetic at submonolayer coverages, results show that Ni layers become ferromagnetic only after the deposition of 5-6 monolayers. By proper adjustment of the deposition condition, so as to avoid dramatic H-incorporation, ultrathin ferromagnetic Ni layers may however be prepared. The strength of PMA at Co/Au(111) layers will be discussed in details. The second part of the talk will address the deposition of cobalt on epitaxial Au(111) layers on vicinal H-Si(111) surfaces. We are able to prepare ultraflat Au films or Au films consisting in nm-sized dots aligned along the step edges. As a consequence, we may prepare Co/Au/Si films with quite different magnetic properties. For instance, in the case of Au dots in plane anisotropy is obtained and it is possible to vary the coupling between lines of Co dots by changing the Si miscut. These results will be discussed in details at the conference.

4:40pm **MI+TF-WeA9 The Effect of Interlayer Coupling to the Magnetic Phase Transition of Thin Films***, **C. Won**, Y.Z. Wu,* University of California at Berkeley*; A. Scholl, A. Doran,* Lawrence Berkeley National Laboratory*; N. Kurahashi, H.W. Zhao, Z.Q. Qiu,* University of California at Berkeley

Magnetic phase transition of two-dimensional systems is one of the intensively studied topic in condensed matter physics. One of the basic questions on this subject is how the addition of the interlayer coupling changes the magnetic phase transition. The coupled magnetic sandwiches of Co/Fe/Ni/Cu(100) and Co/Cu/Ni/Cu(100) were investigated by photoemission electron microscopy(PEEM). Element-specific magnetic domain images were taken at room temperature to reveal the critical thickness at which the magnetic phase transition occurs. The phase diagrams with thickness of each magnetic film were constructed under a few selected coupling conditions. The results shows three different types of

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[1] **Falicov Student Award Finalist**

magnetic phase transitions depending on the relative ferromagnetic film thickness. If the magnetic orders of two magnetic films are similar, both films undergo magnetic phase transition simultaneously. This means the lost of magnetic order of one film can be compensated by the interlayer coupling with the other magnetic film and two magnetic films are highly correlated each other in the interlayer coupling strength. Other two phase-transitions happened when one film is coupled with the other film that is too thin to have magnetism even with the help of coupling or that is ferromagnetic already by its own magnetic order. The difference of the critical thickness for these two cases shows that interlayer coupling increases Curie temperature. The strength and sign of coupling was changed to see how the coupling strength changes this behavior and we found that not the sign but the coupling strength has main role in the phase transition. And Monte-Carlo simulations based on 2 dimensional Ising model were performed to explain this experimental results.

5:00pm **MI+TF-WeA10 Biased Target Ion Beam Deposition of GMR Multilayers***, H.N.G. Wadley,* ***X.W. Zhou****, J.J. Quan, S. Subha,* University of Virginia*; T. Hylton, D. Baldwin,* 4Wave, Inc.

Detailed atomistic simulations have identified the preferred deposition conditions for growing the ideal atomic structures that maximize the performance of giant magneto resistive (GMR) multilayers. They reveal that increasing the velocity (energy) of condensing atoms or assisting ion fluxes flattens interfaces, but promotes atomic interlayer mixing. The maximum magneto resistance is believed to occur for the lowest combination of interfacial roughness and interlayer mixing. Low values of this metric have been predicted to occur using a constant intermediate energy of a few electron volts throughout the growth process. However, the lowest values of the metric have been predicted to occur when a modulation of the energy during deposition of each material layer is used. It is difficult to implement such processes in a conventional PVD or ion beam system. We have developed a biased target ion beam deposition system to overcome these difficulties and report its design and the characteristics of the spintronic devices grown with it.

Nanometer Structures
Room 308 - Session NS-WeA
Nanotribology

Moderator: R.W. Carpick, University of Wisconsin - Madison

2:00pm **NS-WeA1 MEMS Tribological Coatings and Wear Debris Analysis***,* ***S.A. Smallwood****,* Air Force Research Laboratory*; K.C. Eapen,* University of Dayton Research Institute*; J.S. Zabinski,* Air Force Research Laboratory

Among the most significant challenges to developing reliable MEMS that have mechanical components are stiction, friction, and wear. One potential solution to this problem is to protect the devices with coatings, such as monolayers and hard self-lubricating materials. An essential aspect to developing these materials is to understand how surface chemistry, surface forces, wear, and MEMS performance are interrelated. Due to the small size and complex structure of MEMS, it is difficult to develop a fundamental understanding of these phenomena. Wear debris often has dimensions of < 1 mm and it may be hidden under the MEMS structures. In addition, few surface analytical techniques are available to precisely determine tribochemistry and wear mechanisms on MEMS structures. To combat tribological problems, perfluorinated ethers, esters, and mono- and di-alcohols were deposited on MEMS and their chemical/physical properties were studied and related to MEMS performance. AES, microRaman spectroscopy, and IR spectroscopy were used to probe surface chemistry. SPM and surface force measurement systems were used to understand forces at the MEMS scale. A technique to adequately coat complex MEMS structures will be discussed along with the mechanisms responsible for increasing MEMS electrostatic output motor lifetimes by up to three orders of magnitude.

2:20pm **NS-WeA2 Nanotribological Properties of Ultrananocrystalline Diamond***,* ***D.S. Grierson****, A.V. Sumant,* University of Wisconsin-Madison*; J.E. Gerbi, J.A. Carlisle, O. Auciello,* Argonne National Laboratory*; R.W. Carpick,* University of Wisconsin-Madison

There is an increasing demand for materials applicable to rolling and sliding contacts in MEMS technology. Ultrananocrystalline diamond (UNCD) films have unique mechanical and tribological properties that exhibit great potential for increasing the reliability of micro and nanoscale devices. Fabrication of MEMS components with UNCD has already been successfully demonstrated, but a detailed understanding of the nanotribological behavior of UNCD surfaces has not yet been established. This study is aimed at probing both the top â€œas-grownâ€� surface and the back surface (exposed by etching the substrate) of UNCD films. We will explore the effects of hydrogen termination on both surfaces by examining the morphological, adhesive, and frictional properties of the H-terminated vs. untreated UNCD films as a function of load, sliding speed, and relative humidity. Atomic force microscopy is used to examine the nanotribological properties of these surfaces, and XPS, AES, and SEM are used to characterize the surface structure and chemistry. We will discuss the relationships between nanotribological behavior, surface morphology, and surface chemistry of UNCD. These studies could also be of interest for bio-sensing applications involving H-terminated diamond surfaces.

2:40pm **NS-WeA3 Effect of Electric Fields on Nanoscale Friction Properties of Self-assembled Monolayers: Towards Active Friction Control of Interfaces***,* ***S. Sundararajan****, K.K. Kanaga Subramanian, P. Hattan,* Iowa State University

The ability to actively control friction properties of an interface is of great interest to both nanotechnology and macroscale applications. We present our investigations on the effect of an external electric field on the micro/nanotribological properties of selected self-assembled monolayers (SAMs) using scanning probe microscopy (SPM). It is theorized that an external field would affect the structure of the SAMs, thereby affecting their tribological behavior. The SAMs studied include -CH@Sub3@,-COOH and oligo (ethylene glycol) terminated alkanethiols, and amino terminated silane on Au/Mica due to their well known structures and tribological properties. Micro/nanoscale friction and adhesive forces between the SAMs and a Si@sub3@N@sub4@ tip are studied as a function of applied external AC and DC fields to identify switchable friction states of the SAMs. This study would provide a better understanding of lubrication mechanisms at the molecular level and direct us to realize surfaces for active friction control.

3:00pm **NS-WeA4 Impact of Atomic Corrugation on Sliding Friction as Probed by QCM***,* ***T. Coffey****,* North Carolina State University*; S.M. Winder,* University of South Carolina*; J. Krim,* North Carolina State University

At the atomic scale, friction is believed to originate primarily via sliding induced excitation of phonons.@footnote 1@ Theoretical predictions of the magnitude of phononic dissipation have been related to the atomic corrugation of the adsorbate/substrate potential.@footnote 2@ Using the Quartz Crystal Microbalance (QCM), we have measured the sliding friction of xenon adsorbed at 77 K onto three different surfaces. From lowest to highest atomic corrugation of the adsorbate/substrate potential, the surfaces are: Ag(111), Cu(111), and Ni(111). The QCM probe of sliding friction is the sliptime, which measures the slippage of the adsorbate atop the oscillating surface of the QCM.@footnote 3@ For monolayer coverages, we observed the following sliptimes: 2 ns for Xe/Ag(111), 1 ns for Xe/Cu(111), and 0.5 ns for Xe/Ni(111). We compare our sliptime results to published values of the atomic corrugation for these systems. We also discuss theoretical predictions for the impact of atomic corrugation on sliding friction. @FootnoteText@ @footnote 1@ Fundamentals of Friction; Macroscopic and Microscopic Processes, ed. I.L. Singer and H.M. Pollock, Kluwer, Dordrecht (1992).@footnote 2@ M. Cieplak, E.D. Smith, and M.O. Robbins, Science 265, 1209 (1994)@footnote 3@ J. Krim and A. Widom, Phys. Rev. B 38, 12184 (1986).

3:20pm **NS-WeA5 Wear Structures on the Nanometer Scale***,* ***R. Bennewitz****, E. Gnecco, A. Socoliuc, E. Meyer,* University of Basel, Switzerland

Friction force microscopy has been used to study the onset of wear. Abrasive wear could be detected down to single atomic layers at surfaces of ionic crystals. The wear debris was found to perfectly recrystallize in registry with the underlying surface. Furthermore, we have found a characteristic formation of nanometer-scale ripples perpendicular to the direction of scratching. These ripples are built in an interplay between strain-induced erosion, transport by the action of the tip, and diffusion. In a second part, we will present recent results of atomic friction experiments. The relation between atomic stick-slip instabilities and energy dissipation will be discussed based on experiments which exhibit very little dissipation.

3:40pm **NS-WeA6 Tribological Investigation of AlNiCo Decagonal Quasicrystals by UHV AFM/STM***,* ***J.Y. Park****, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; C.J. Jenks, P.A. Thiel,* Iowa State University

Tribological properties of the 10-fold and 2-fold surfaces of AlNiCo decagonal quasicrystals have been investigated in ultra-high vacuum using an atomic force microscope with WC-coated conducting tips. Using stiff cantilevers either tunnel current (STM mode) or force (AFM mode) can be used for feedback. The quasicrystal surfaces were cleaned by sputtering and annealing in UHV and characterized with low enerey electron diffraction (LEED) and Auger electron spectroscopy (AES). Adhesion and friction of decagonal quasicrystal surface were measured by using contact mode AFM. From force-distance measurements we found that tip-sample adhesion on the clean 2-fold surface is two order of magnitude higher than that of the air-oxidized surface. Because of this high adhesion, STM contrast was used to image surface morphology. The effects of in situ oxidation and carbon passivation on quasicrystal friction and adhesion will also be discussed.

4:00pm **NS-WeA7 The One-Two Punch: Combining Chemical and Mechanical Stimuli at the Nanometer Size Scale***, **J.T. Dickinson,*** Washington State University **INVITED**

Bond breaking at surfaces due to stimuli such as exposure of materials to electrons, ions, photons, mechanical stress, or chemical agents are well established. We discuss in general the role of multiple stimuli (the "one-two punch") in the degradation and modification of materials and solid surfaces. We then show the nanometer scale consequences of combining localized mechanical stress (due to sliding contact with a scanning force microscope--SFM tip) and exposure to aqueous solutions. These nanotribological methods offer a top-down approach to controlled surface modification. Emphasis will be on results concerning tip induced material removal, recrystallization (at small normal forces), and unique patterning produced by scanning in super-saturated aqueous solutions. We also present results on the influence of an SFM tip in contact with polymers immersed in organic solvents. We show a new method for introducing very small amounts of highly localized patches of chemicals into a polymer surface. Finally, we show new evidence of a "1-2-3 punch", where we introduce radiation as a third stimulus on inorganic crystalline surfaces. The results shown have possible applications in sensors, nanofluidics, and optoelectronics. Models will be presented to explain the observed nanometer scale surface modifications.

4:40pm **NS-WeA9 The Wear of NaCl in Humid and Anhydrous Environments***, P.E. Sheehan, **L.J. Whitman,*** Naval Research Laboratory

A recent report on the mechanism of dip pen nanolithography (DPN)@footnote 1@ indicated that wear on NaCl reveals the presence of a residual meniscus even under dry nitrogen. We have studied the wear of a NaCl single crystal by an AFM tip as a function of environmental humidity. In an anhydrous nitrogen environment, we find that the wear mechanism was not meniscus-based but rather mechanical, with the wear rate well-described by a thermal-activation model. By examining the wear track while varying both the temperature and the load, the activation volume and the activation energy could be measured. Introducing a slight amount of water into the anhydrous system dramatically changed the wear mechanism. In this case, salt dissolution and reformation occur, creating islands that are several atomic layers thick with clearly-observable step edges. Interestingly, the morphology of the islands indicates that they are fluid while in contact with the AFM tip and presumably its water meniscus; however, when the AFM tip is quickly removed, the islands solidify and can be imaged by a rapidly moving tip. This observation may lead to a method of patterning NaCl on the nanometer-scale. @FootnoteText@@footnote 1@ Rozhok, S.; Piner, R.; Mirkin, C. A.; J. Phys. Chem. B. (2003) 107 751-757.

5:00pm **NS-WeA10 Nanotribology - Tribochemical Wear of Muscovite Mica in Aqueous Solution***, **J.M. Helt,*** The City University of New York College of Staten Island and the Graduate Center*; J.D. Batteas,* National Institute of Standards and Technology

Part I: Atomic force microscopy (AFM) is used to probe defect nucleation, prior to gross wear, of muscovite mica under aqueous environments. Nucleation is found to present itself initially as surface charging due to stress-induced tribochemical scission of the terminating surface bonds. As the surface bonds are continually cleaved, an ensemble of defects contribute to the ~5.2 Å to ~ 3 Å crystal lattice reconstruction observed in AFM topography and frictional force micrographs. Following lattice restructuring, abstraction of mica surface materials ensues, yielding visible wear scars ranging from ~ 2 - 10 Å in depth. Environmental [OH-] profoundly affects the efficacy of wear events, which is illustrated by the acceleration or inhibition of wear with adjustment of pH under identical load and scan conditions. Part II: In AFM wear trials the area scanned is defined by the length of the slow (L@sub sscan@) and fast scan axis. The ratio of L@sub sscan@ to image resolution (res, lines/image) defines the magnitude of the line step (LS = L@sub sscan@/res) . A contact radius - LS relationship indicates that overlap of successive scans will result if the contact radius - line step ratio (CRLS) is < 1/2. Consequently, the history associated with a single image scan is not equivalent at various loads due to the contact radius being proportional to the load@super 1/3@. Theoretical & experimental analysis on muscovite mica with a Si@sub 3@N@sub 4@ tip illustrate the effects of scan overlap. The CRLS model, derived from the Hertz contact mechanics theory, shows that scan overlap is considerable. AFM wear trials on mica under pH 5 conditions legitimize this development, with CRLS readily predicting the additional scan history from scan overlap for the mild wear regime. CRLS theory, however, consistently underestimates severe wear trends, which is to be expected in light of Hertzian principles employed.

Nanotubes
Room 317 - Session NT-WeA
Properties of Carbon Nanotubes

Moderator: J. Randall, Zyvex Corporation

2:00pm **NT-WeA1 Photoemission Spectromicroscopy and Spectroscopy of Carbon Nanotubes***, **S. Suzuki**, Y. Watanabe, T. Ogino, Y. Homma,* NTT Basic Research Laboratories, NTT Corporation, Japan*; S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova,* Sincrotrone Trieste, Italy*; W. Zhu,* Bell Laboratories, Lucent Technologies*; C. Bower, O. Zhou,* University of North Carolina at Chapel Hill **INVITED**

Investigating the electronic structure of carbon nanotubes, especially their tips, is important for understanding the electron-field-emission properties of nanotubes. A specific electronic structure is expected at the hemispherical tips of nanotubes, where the graphene cylinders are believed to be closed by insertion of the five-member rings in the graphene network. The localized states in the vicinity of the Fermi level would largely contribute to the field emission properties for close-end nanotubes. For open-end nanotubes or nanotubes having imperfect structures, dangling bond states may significantly contribute to the field-emission properties. Moreover, the edge state, which is a characteristic electronic structure formed at a zigzag-type graphene edge, and has a large density of states at the Fermi level, may also play a key role. By means of scanning photoemission spectromicroscopy, we studied the local electronic structure at the tips of aligned multi-walled carbon nanotubes grown using microwave plasma-enhanced chemical vapor deposition. The valence band and the C 1s spectra, measured systematically from spatially selected regions along the tube axes, were the fingerprint for lateral variations in the electron density of states and in the band bending, respectively. The spatially selected photoemission spectra revealed that the tips have a larger density of states in a binding energy range of 0 to about 1 eV, whereas band bending, which would explain such a spectral difference, was not observed. It is suggested that the different density of states near the Fermi level is due to a larger dangling bond density at the tips. We also studied the electronic structure and work function of alkali-metal-doped carbon nanotubes. Drastic change in the electronic structure caused by the doping will also be presented.

2:40pm **NT-WeA3 Preparation and Field Emission Studies of Carbon Based Nanostructured Materials***, **X. Xiao**,* Argonne National Laboratory, U.S.*; O. Auciello, J.E. Gerbi, J. Wang, J. Birrell, J.A. Carlisle,* Argonne National Laboratory*; V.I. Merkulov, H. Cui, D.H. Lowndes,* Oak Ridge National Laboratory*; Y. Wang,* North Carolina State University

Four types of carbon based nanostructured materials were prepared, including nitrogen doped ultrananocrystalline diamond (UNCD) films, UNCD on vertically aligned carbon nanofibers (VACNFs), carbon nanotubes (CNTs), and nanocomposite of UNCD/CNTs. Different methods were employed to characterize the nanostructures, such as scanning electron microscopy, Raman spectroscopy, high-resolution transmission electron microscopy and quadrupole mass spectrometry. The field electron emission properties of these carbon nanostructured materials in different ambients (O@sub 2@, Ar, N@sub 2@) were extensively studied and compared with each other. The experimental results show that the UNCD/VACNFs composite is a good field emitter with low threshold value for electron emission, good stability and long lifetime. The excellent field emission property of the composite is believed to be due to the combined effect from the negative electron affinity of UNCD and high aspect ratio of carbon nanofibers. CNTs, especially vertically aligned CNTs, can not stand long-time ion bombardment from the residual gas in the field emission process, and distortion of CNTs has been observed subsequently to electron emission measurements. Possible damage mechanism is discussed. We acknowledge support from the US Department of Energy, Office of Science / Basic Energy Science-Materials Science, under Contract W-31-109-ENG-38.

3:00pm **NT-WeA4 Infrared Stimulated Emission and Optical Gain in Isolated Single-Walled Carbon Nanotubes*, M.S. Arnold*,** *J.E. Sharping, S.I. Stupp, P. Kumar, M.C. Hersam,* Northwestern University

Bandgap fluorescence from single-walled carbon nanotubes (SWNTs) isolated in surfactant micelles has recently been reported.@footnote 1@ Since semiconducting SWNTs possess electronic bandgaps in the near infrared region of the optical spectrum, these nanomaterials have potential application in fiber optic communication and infrared medical imaging. In this talk, we will discuss experimental results characterizing stimulated emission of infrared radiation from SWNTs isolated in aqueous micellar suspensions. Solutions of nanotubes are optically pumped at the E@sub 22@ transition for a particular (n, m) chirality, and stimulated emission is probed at the corresponding E@sub 11@ transition. The stimulated emission in isolated SWNT solutions is observed to be more than 122 times larger than in a control sample of aggregated SWNTs. Pump and probe power, wavelength, and polarization; path length; and concentration dependencies have been characterized. For small probe intensities, the stimulated emission intensity increases linearly with probe intensity, while sub-linear behavior is observed for large probe intensities; and gain and stimulated emission are maximized for co-linear-polarization of pump and probe. Currently, measurements are underway to quantify the gain coefficient and carrier lifetimes using delayed pulsed pump-probe spectroscopy. These results suggest the conditions under which tunable infrared optical amplification devices may be realized with SWNTs. @FootnoteText@ @footnote 1@ M. J. O'Connell et al., Science, 291, 2002.

3:20pm **NT-WeA5 Defective Carbon Nanotube Channel Single Electron Transistor with Ultra-High Coulomb Energy of 5000K and its Applications*, K. Matsumoto,*** Osaka University, Japan **INVITED**

Coulomb diamond characteristics with Signal/Noise ratio of 10000 and drain current level of ~10@mu@A was attained even at room temperature in the single electron transistor (SET) using the segmented carbon nanotube (CNT) of 1~2nm diameter as multi-isla nds for the SET. The position and direction of the carbon nanotube for the channel of the SET is controlled by the patterned chemical catalysts of 3nm thick iron (Fe) and applied field between them. Using methane gas in the CVD process, the single wall c a rbon nanotube was grown between two patterned catalysts on the Si0@sub2@/Si substrate. Most important technology is the introduction of defects into the carbon nanotube channel using the chemical process. The defects make the carbon nanotube to the segmen ted structure of 1~2nm diameter, which is used as multi-islands for the SET. The electrical property of the defective carbon nanotube channel single electron transistor was measured all at room temperature. The drain current shows the Coulomb gap of ~80 0mV, which corresponds to the Coulomb energy of 400meV and Coulomb temperature of 5000K. The drain current shows the Coulomb oscillation characteristics with the modulation ratio of as large as 96~99%. The effective island size is as small as ~1nm es tima ted from the electrical property. Coulomb diamond structures were observed even at room temperature. By improving the ohmic contact resistance, the drain current becomes of the order of ~10@mu@A and there is no noise observed in the Coulomb diamond characteristics. The signal/noise ratio becomes as high as 10000. This SET has a high sensitivity to the one electron because of the small gate capacitance of 1E-19~1E-20F, and is applicable to the single electron sensor at room temperature.

4:00pm **NT-WeA7 The Highly Robust Electrical Interconnects and Ultrasensitive Biosensors Based on Embedded Carbon Nanotube Arrays*, J. Li,*** NASA Ames Res. Center*; A.M. Cassell,* NASA Ames Res. Center / Eloret Corp.*; J. Koehne,* NASA Ames Res. Center*; H. Chen, H.T. Ng, Q. Ye, R. Stevens, J. Han,* NASA Ames Res. Center / Eloret Corp.*; M. Meyyappan,* NASA Ames Res. Center **INVITED**

We report on our recent breakthroughs in two different applications using well-aligned carbon nanotube (CNT) arrays on Si chips, including (1) a novel processing solution for highly robust electrical interconnects in integrated circuit manufacturing,@footnote 1@ and (2) the development of ultrasensitive electrochemical DNA sensors.@footnote 2@ Both of them rely on the invention of a bottom-up fabrication scheme which includes six steps, including: (a) lithographic patterning, (b) depositing bottom conducting contacts, (c) depositing metal catalysts, (d) CNT growth by plasma enhanced chemical vapor deposition (PECVD), (e) dielectric gap-filling, and (f) chemical mechanical polishing (CMP). Such processes produce a stable planarized surface with only the open end of CNTs exposed, which can be further processed or modified for different applications. By depositing patterned top contacts, the CNT can serve as vertical interconnects between the two conducting layers. This method is fundamentally different from current damascene processes and avoids problems associated with etching and filling of high aspect ratio holes at nanoscales. In addition, multiwalled CNTs (MWCNTs) are highly robust and can carry a current density of 109 A/cm2 without degradation. It has great potential to help extending the current Si technology. The embedded MWCNT array without the top contact layer can be also used as a nanoelectrode array in electrochemical biosensors. The cell time-constant and sensitivity can be dramatically improved. By functionalizing the tube ends with specific oligonucleotide probes, specific DNA targets can be detected with electrochemical methods down to subattomoles. @FootnoteText@@footnote 1@J. Li, Q. L. Ye Q, A. M. Cassell, H.T. Ng, R. Stevens, J. Han, M. Meyyappan, Appl. Phys. Lett., 82 (15), 2491 (2003). @footnote 2@J. Li, H. T. Ng, A. Cassell, W. Fan, H. Chen, Q. Ye, J. Koehne, J. Han, M. Meyyappan, Nanoletters, in press.

4:40pm **NT-WeA9 Photocurrents in Nanotube Junctions***, D.A. Stewart,* ***F. Léonard,*** Sandia National Laboratories

Carbon nanotubes have demonstrated great promise for future nano-electronic devices. However, their potential for opto-electronic applications has received much less attention, despite their seemingly ideal properties, such as a direct band-gap, quasi-one-dimensional density of states, low defect density and a high surface-to-volume ratio. In this talk, we present calculations of photocurrents in nanotube junctions using a non-equilibrium quantum transport theory. The dependence of the short-circuit photocurrent on incoming photon energy shows many fatures, due to band-to-band transitions and photon-assisted tunneling. The operation of such devices in the ballistic transport regime leads to unusual size effects.

5:00pm **NT-WeA10 Gas Adsorption on Multi-walled Carbon Nanotubes: An Experimental and Theoretical Study*, S. Picozzi*,** *L. Lozzi, C. Cantalini,* University of L'Aquila, Italy*; L. Valentini, I. Armentano, J.M. Kenny,* Universita di Perugia, Italy*; S. Santucci,* University of L'Aquila, Italy

The effects of environment gases (such as O2, NO2, NH3) on the electronic and transport properties of carbon nanotubes have recently attracted great interests.@footnote 1@ In this work a combined experimental and theoretical study on CNT-based system for gas sensing applications is reported. Carbon nanotubes thin films have been deposited by plasma enhanced chemical vapor deposition on Si3N4/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM and Raman spectroscopy highlight the growth of defective tubular carbon structures. CNTs show a p-type response with decreasing electrical resistance upon exposure to NO2 gas (100 ppb) and the highest sensitivity at 165° C working temperature. No response has been found by exposing the film to CO gas in the temperature range between 25 and 250° C. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+CO and CNT+NO2 systems.@footnote 2@ Our spin-unrestricted density functional calculations show that NO2 retains its spin-polarized state upon adsorption. Both CO and NO2 molecules adsorb weakly on the tube wall, with essentially no charge transfer between the tube and the molecules. The electronic properties of CNTs are sensitive to the adsorption of NO2, due to an acceptor-like peak close to the tube valence band maximum, while they are insensitive to the CO adsorption. According to the experimental findings, our theoretical results suggest that gas-induced modification of the density of states close to the Fermi level might significantly affect the transport properties of nanotubes. @FootnoteText@@footnote 1@ J. Kong, N.R. Franklin, C. Zhou, M.G.Chapline, S. Peng, K. Cho and H. Dai, Science 287, 622 (2000).@footnote 2@ B. Delley, J. Chem. Phys. 113, 7756 (2000).

Plasma Science and Technology
Room 314 - Session PS1-WeA

Mechanisms in Plasma-Surface Interactions

Moderator: E. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS1-WeA1 PECVD of Thin Films: The Study of the Plasma-surface Interaction by Means of In Situ Plasma and Film Diagnostics***, **M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands **INVITED**

Plasma enhanced chemical vapor deposition (PECVD) is now a well established technique to obtain various high quality films for e.g. micro-electronic, photovoltaic, scratch resistant or abrasive applications. Although widely applied in industry, fundamental knowledge on the actual plasma deposition mechanism is to a large extent unknown. The reason is the complexity of the problem: to unravel the deposition mechanism requires a simultaneous investigation of the plasma phase, the plasma-surface interaction and the film properties using in situ plasma and film diagnostics. The need to understand the mechanism is evident since the development and design of new functional materials and up scaling of the technique to large areas involves detailed and generic knowledge of the plasma-surface interaction. In this talk I will discuss the approach our group has undertaken to investigate the deposition mechanism of a limited number of model systems: the fast plasma deposition of hydrogenated amorphous silicon, carbon and silicone films utilizing a remotely expanding thermal plasma. I will discuss the measurement of radical and ion densities using sensitive plasma diagnostics such as cavity ring down spectroscopy and (modulated beam) appearance potential mass spectrometry. From measurements using the time-resolved version of these diagnostics, taken in the afterglow of a small perturbation of the plasma, plasma and surface reaction probabilities of selected radicals are determined. The results are compared with molecular dynamics simulations of the plasma-surface interaction and are discussed in relation to in situ characterizations of the chemical and structural composition of the film surface of the growing film.

2:40pm **PS1-WeA3 Plasma Nitriding and Reactive Deposition in Electron Beam Generated Plasmas****, **C. Muratore**, D. Leonhardt, S.G. Walton, D.D. Blackwell, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

A molecular gas based electron beam generated plasma provides a significantly higher atomic ion flux than molecular ion flux. Additionally, the well-defined geometry of the electron beam gives rise to a high spatial dependency of the plasma specie flux due to gas phase reactions between the beam edge and surface to be modified. To investigate the utility of the unique features associated with electron beam generated plasmas for materials processes, planar electron beams were used for plasma assisted nitriding and reactive sputter deposition. Stainless steel and other metals were exposed to electron beam generated plasmas containing mixtures of nitrogen and other gases at appropriate treatment temperatures to produce nitrided surface layers. The activation energy for nitriding was determined for stainless steel and other metals, and found to be lower than values associated with other plasma assisted nitriding processes. Thin films were reactively sputtered at equivalent total ion fluxes with variations in only plasma chemistry (e.g., N@super +@/N@sub 2@@super +@ flux ratios). All materials were characterized using standard techniques including atomic force microscopy, X-ray diffractrometry, electron microscopy and nanoindentation. Observed trends in microstructural features and materials properties correlate well to the measured plasma characteristics. @FootnoteText@ @footnote *@This work is supported by the Office of Naval Research. Muratore, C., NRL/ASEE Postdoctoral Research Fellow; Blackwell, D.D., SFA Inc., Largo, MD 20744.

3:00pm **PS1-WeA4 Angular Dependence of SiO@sub 2@, Si and Si@sub 3@N@sub 4@ Etch Yield in Fluorocarbon Gas Chemistries by using Plasma Beam***, **K. Kurihara**, A. Egami, M. Nakamura,* ASET, Japan

A plasma-beam irradiation apparatus, which can control plasma parameters independently, such as ion energy, radical/ion composition and incident angle of ions, is very useful to examine the plasma-surface interactions under a real etching environment for constructing a process simulator without experiments of trial and error. We measured etch yield dependence on the incident angle of ions for Si, SiO@sub 2@, and Si@sub 3@N@sub 4@ substrates under the three conditions of Ar gas and two different fluorocarbon gas chemistries. One provides low selectivity of SiO@sub 2@ to Si using CF@sub 4@/Ar gas mixture (low selective mode), and the other provides high selectivity of that using CF@sub 4@/C@sub 4@F@sub 8@/Ar gas mixture (high selective mode). As for physical sputtering using Ar plasma, the etch yield at incident angle of 60 ° (oblique incidence) was about 4 times larger than that at incident angle of 0 ° (normal incidence) for all substrates at the ion energy of 530 eV, and this tendency was kept at the low ion energy of 120 eV. On the other hand for the case of CF@sub 4@/Ar gas chemistry, the etch yield of the oblique incidence was about 1.4 times larger than that of the normal incidence at the ion energy of 530 eV, but at that of 120 eV the etch yield did not increase with the increase in incident angle. In the case of etching reaction proceeded chemically by fluorocarbon gases, the angular dependence on the etch yield was influenced by the ion energy. The gas chemistry also affected the angular dependence on the etch yield. The etch yield of Si@sub 3@N@sub 4@ weakly depended on the incident angle in the case of the low selective mode, but that strongly depended on the incident angle in the case of the high selective mode. Concerning Si and SiO@sub 2@ substrates the angular dependence has no difference under above two modes. We will discuss the relation between composition of surface reaction layer and the etch yield. This work was funded by NEDO.

3:20pm **PS1-WeA5 Reduction Mechanism of VUV Radiation Damages in Pulse-Time-Modulated Plasma Processes***, **Y. Ishikawa**, M. Okigawa,* Tohoku University, Japan*; S. Yamasaki,* National institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

In plasma processing using high-density plasma, vacuum-ultraviolet (VUV) radiation damage is one of the most serious problems. The electrical characteristics of dielectrics directly exposed to plasma are affected by plasma-emitted VUV radiation. VUV radiation with a higher photon energy than the SiO@sub 2@ band gap energy (8.8 eV) can generate electron-hole pairs in the irradiated dielectric films. The generation of electron-hole pair increases the charge densities trapped in the SiO@sub 2@ bulk and SiO@sub 2@/Si interface, affecting the conductivity of the SiO@sub 2@ layer. This results in dielectric breakdown, shorter lifetime of minority carriers, and a flat band voltage shift in transistors. Thus, reducing the VUV radiation damage is important for improving the reliability of semiconductor devices. To realize these requirements, we proposed a pulse-time-modulated plasma (pulsed plasma). In this paper, to understand the reduction mechanism of VUV radiation damages using pulsed plasma, we investigated the time dependence of defects (E' center) generation in the SiO@sub 2@ film by altering the pulse-on and off time. We found that the E' center was increased during the pulse-on-time and was also reduced during the pulse-off time. It is speculated that the generation and loss of E' center was progressed at the time constant of µmseconds. As a result, the pulsed plasma could drastically reduce the generation of E' center in the SiO@sub 2@ film and could eliminate VUV radiation damages in comparison with the continuous plasma.

3:40pm **PS1-WeA6 IRIS Investigations of Gas Phase Species in Fluorocarbon Plasmas***, **I.T. Martin**, E.R. Fisher,* Colorado State University

Fluorocarbon (FC) plasmas are widely used for FC film deposition and the etching of Si-based materials. Investigating a specific molecule during plasma processing of a substrate can yield information on its role in the chemistry occuring at the plasma surface interface. CF@sub 2@ is a particularly interesting species in FC plasmas because its role differs in various plasma systems. CF@sub x@ and C@sub x@F@sub y@ radicals have been cited as FC film deposition precursors, while other work has shown cases where CF@sub 2@ is not a deposition precursor.@footnote 1,2,3@ We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF@sub 2@ radicals with Si substrates during plasma processing. CF@sub 2@ surface loss coefficients determined for 25-200W C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas show relatively high levels of scattering, which indicates that CF@sub 2@ radicals are produced at the surface in these systems. One advantage of the IRIS system is our ability to collect data for multiple molecules in a single plasma system. Experimental excitation spectra have verified the presence of CF in our FC systems and have been used to determine the rotational temperatures (@theta@@sub R@) of CF in the plasmas. Trends in @theta@@sub R@ are discussed as a function of plasma input power and source gas. Surface reactivity studies will determine if CF contributes to CF@sub 2@ scatter in these systems. Preliminary investigations of SiF@sub 2@(g) formation at the surface will also be presented. @FootnoteText@ @footnote 1@ R. d'Agostino, et al., in Plasma Deposition, Treatment, and Etching of Fluorocarbons, edited by R. d'Agostino (Academic Press, Inc., San Diego, 1990) p.95-143.@footnote 2@ S. Samukawa, AIP Conference Proceedings 636, 95-107 (2002).@footnote 3@ K. Sasaki, et al., Thin Solid Films 374(2), 249-255 (2000).

4:00pm **PS1-WeA7 Fluorocarbon-based Plasma Etching: The Role of the Energy Distribution of Bombarding Ions***, R. Silapunt, S. Williams,* ***A.E. Wendt,*** University of Wisconsin, Madison*; K.H.R. Kirmse, L. Losey,* Texas Instruments

In fluorocarbon-based plasma etching of dielectrics, an overlying thin fluorocarbon film, deposited on the substrate during etching, strongly affects etch rate and etch selectivity.@footnote 1@ Here we report on recent results that suggest that the energy distribution of bombarding ions (IED) has a significant effect on the thickness of this polymer layer, subsequently affecting etch rate and selectivity as well. Specifically, we have narrowed the IED while keeping other process conditions unchanged by tailoring the shape of the RF voltage waveform used for substrate bias. Significant improvements in etch selectivity for SiO@sub2@ over silicon, SiO@sub2@ over photoresist and organosilicate glass (OSG) over silicon nitride and silicon carbide have been obtained by using a narrow IED compared to the broad IED resulting from a sinusoidal bias waveform. X-ray photoelectron spectroscopy (XPS) has been used to determine the thickness of the overlying fluorocarbon film as a function of bias voltage for both narrow and broad IEDs. The results show a strong inverse correlation between film thickness and etch rate, suggesting that the sensitivity of this polymer film to the IED is the key to observed improvements in selectivity.@footnote 2@@FootnoteText@@footnote 1@ G. S. Oehrlein et al., JVST A 15, 1881 (1997)@footnote 2@ Supported by SRC (TI custom funding) .

4:20pm **PS1-WeA8 Investigating the Fundamental Mechanism of Surface Smoothening of Plasma-Deposited Amorphous Silicon Thin Films through Atomistic Simulations***,* ***S. Sriraman****, S. Agarwal, E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. Nevertheless, the deposition mechanism of a-Si:H films and the fundamental surface processes that determine the surface morphology during deposition are still not well understood. Under conditions of low SiH@sub 4@ dissociation in the plasma, the dominant precursor for deposition is the SiH@sub 3@ radical. The remarkable smoothness of the a-Si:H films grown under these conditions has been used to conclude that the deposition precursor is very mobile and that it can fill surface valleys after adsorbing onto the film. Using molecular-dynamics (MD), molecular-statics, and Monte Carlo methods, we studied the growth of a-Si:H on initially H-terminated Si(001)-(2x1) surfaces; the films were grown through MD simulations of repeated impingement of SiH@sub 3@ precursor. The relationship between the structure, H coverage, morphology, and reactivity of plasma deposited a-Si:H film surfaces was investigated. Surfaces of a-Si:H films grown with SiH@sub 3@ as the sole deposition precursor were found to be remarkably smooth due to a valley-filling mechanism where mobile precursors, such as SiH@sub 3@ and Si@sub 2@H@sub 6@, diffuse and react with dangling bonds present in surface valleys. Surface transport of these adsorbed species may be driven by the surface Si-Si bond strain distribution, as well as the surface reactivity and morphology. Mobility of the surface species maybe mediated through the formation of over-coordination defects as weakly chemisorbed SiH@sub 3@ diffuse on the surface. Our analysis of the mechanism of SiH@sub 3@ precursor diffusion on the c-Si and a-Si:H surfaces will be presented. In particular, we emphasize the role of Si-Si bond strains in mediating the valley-filling mechanism leading to smooth film surfaces and the identity of the mobile precursor state.

4:40pm **PS1-WeA9 Study of SiO@sub 2@ Plasma Etching with Off-normal Mass-analyzed CF@sub x@@super +@ Ion Beam Irradiation***,* ***K. Yanai****, K. Karahashi, K. Ishikawa, M. Nakamura,* Association of Super-Advanced Electronics Technologies, Japan

To clarify the elementary surface reactions in the fluorocarbon plasma etching, the mass-analyzed CF@sub x@@super +@ (x = 1-3) ion beam was irradiated on the SiO@sub 2@ surface at various incident angles. The noble gas ions, such as Ne@super +@, Ar@super +@, Kr@super +@, and Xe@super +@, were also irradiated to compare chemically active CF@sub x@@super +@ ions. The angular dependence of the etch yield depends on the kind of CF@sub x@@super +@ ion. In the case of CF@sub 3@@super +@ ion irradiated at 1 keV, the etch yield increases little with the incident angle below 60°, and decrease rapidly due to the reflection of the ion at the surface over 60°. The ratio of the etch yield at 60° to that of 0° is about 1.2. On the other hand, in the case of CF@sub 1@@super +@ ion at 1 keV, the etch yield increases rapidly with the incident angle below 60°. The ratio of the etch yield at 60° to that of 0° is about 2.3. In the case of the noble gas ions, the angular dependence of the etch yield does not depend on the species, indicating cos@super -2@@theta@ below 60°. The etch yields of CF@sub x@@super +@ ions were analyzed on the basis of an etching model, involving two components originated from different removal mechanisms. The chemical component, due to the thermally desorbed molecules generated through the chemical reactions between incident species and substrate materials, is constant with the incident angles. The physical component, due to the atoms sputtered away from the substrate by the momentum transfer through collision cascade, depends on the incident angle like cos@super -2@@theta@. This model can explain the angular dependence of the etch yields of CF@sub x@@super +@ ions at 1 keV very well. The chemical component of each CF@sub x@@super +@ ion is proportional to the number of the fluorine atoms in the ion with the coefficient of 1/2, consistent with the observation that SiF@sub 2@ is the main desorbed product. This work was funded by NEDO.

5:00pm **PS1-WeA10 Reactive Surface Coefficients for Radicals in a Vacuum Beam System***,* ***Y. Kimura****, J. Coburn, D. Fraser, H. Winters, D.B. Graves,* University of California, Berkeley

We present direct measurements of reactive surface coefficients for various radicals on a range of surfaces. The reactive surface coefficients are determined using the Radical- and Ion-Surface Interaction Analysis System (RISIAS). RISIAS is equipped with two external radical sources and an external ion beam source, all of which can be simultaneously trained on a surface. A threshold ionization quadrupole mass spectrometer (TIQMS) is aligned with one of the radical beamâ€™s line of sight to measure radical flux in the beam. After measuring the radical flux, the TIQMS is vertically translated to allow insertion of a sample surface into the beam path via a load lock. With the sample surface in place, reflected radicals are measured with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and reflected components. Experiments conducted with a temperature-controlled quartz crystal microbalance allow measurements of net deposition or etching with various beam components on a range of surfaces. The beam-to-background ratio of the radical beam in the TIQMS is measured to be 15 for the direct line of sight, and about 1 for reflected radicals. RISIAS can measure reactive surface coefficients from ~ 0.01-1. Measurements of CF@sub 3@, CF@sub 2@, CF, NH, NH@sub 2@, F and O radicals reacting with stainless steel, silicon, silicon dioxide, hydrocarbon and fluorocarbon surfaces will be presented.

Plasma Science and Technology
Room 315 - Session PS2-WeA

Atmospheric Plasmas & Micro Discharges

Moderator: G. Selwyn, Los Alamos National Laboratory

2:00pm **PS2-WeA1 Electrical Characterization and Time-resolved Emission Spectroscopic Studies of Dielectric-barrier Controlled Atmospheric-pressure Glow Discharges in Helium***,* ***J. Shin****, P.L. Varghese, L.L. Raja,* The University of Texas at Austin

We report experimental studies of a dielectric-barrier controlled atmospheric-pressure glow (APG) discharge. The study is aimed at providing fundamental understanding APG discharge phenomena in high-purity helium. Electrical characteristics and time-resolved emission spectroscopic diagnostics are used. Dielectric barrier controlled APG discharge phenomena is characterized by a single or multiple current pulse during each half cycle of voltage input to the discharge. We study discharge phenomena under a variety of conditions such as varying gap sizes, operating frequencies and dielectric placement. Significant and random scattering as well as random asymmetries in current pulse shape are observed. We correlate these discharge peculiarities with the time-resolved emission spectroscopic results. In particular, we report spectroscopic observations of discharge condition just prior to glow-to-arc transitions.

2:20pm **PS2-WeA2 Measurement of the Fluorine Atom Concentration in a Carbon Tetrafluoride and Helium Atmospheric-Pressure Plasma***,* ***X. Yang,*** *S.E. Babayan, G.R. Nowling, M. Moravej, R.F. Hicks,* University of California, Los Angeles

A titration technique has been developed to measure the fluorine atom concentration in the downstream region of a low-temperature, atmospheric pressure plasma fed with helium and carbon tetrafluoride. The fluorine atoms were titrated with H@sub 2@ molecules, and the HF reaction product was detected by infrared spectroscopy. The radio-frequency gas discharge produced 1.2x10@super 15@ cm@super -3@ of F atoms, which was about two orders of magnitude higher than that found in low-pressure plasmas. The average electron density and temperature in the plasma was estimated to be 6.1x10@super 11@ cm@super -3@ and 2.5 eV. A numerical model of the plasma indicated that most of the fluorine atoms were generated by the reaction of CF@sub 4@ with metastable helium atoms. The results of the experiments and the model will be presented at the meeting.

2:40pm **PS2-WeA3 Generation Mechanism of the Atmospheric Glow in a DBD Configuration***, **E. Aldea,*** Eindhoven University of Technology, The Netherlands*; C.P.G. Schrauwen,* TNO-TPD , The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Conventional wisdom attributes the generation of atmospheric glow plasmas to gas pre-ionization, which is related to ions or to electron generation by metastable-metastable and metastable-surface collisions . However there is not yet unambiguous experimental evidence, which can prove the validity of either of the proposed mechanisms. Beside that this pre-ionization mechanisms can not explain either how the glow to arc transition a notorious instability of atmospheric plasmas is avoided. Therefore to our opinion the physical basis of the atmospheric glow remains an open and challenging issue. In this contribution we analyze the basic conditions needed for uniform glow plasma generation. A simple analysis of the glow generation indicates that it is extremely improbable that the metastables or ions can have a significant contribution to glow generation via a pre-ionization mechanism. The low diffusion rate of ions and metastables excludes any mechanism of streamers or electron avalanches superposition. The preionization mechanism based on ions or metastables cannot also explain why the standard breakdown mechanism of atmospheric plasma streamer breakdown does not occur. Besides these theoretical arguments no evidence was found in the experimental current-voltage characteristics, plasma emission or breakdown voltage suggesting a significant pre-ionization or even the presence of a large amount of metastables. We conclude that the major problem in generation of atmospheric glow plasma is glow to arc transition. In this respect metastables are rather the problem for a stable plasma generation because their presence enhance the probability of stepwise ionization and glow to arc transition. The experimental data suggests that the surface of the dielectrics plays a major role in uniform and stable atmospheric glow plasma generation. The surface effect is probably due to a high secondary emission at the surface.

3:00pm **PS2-WeA4 Ultraviolet Emission Spectroscopy and Absorption Spectroscopy of CF@sub 2@ Radical in Chemical Vaporization Machining (CVM) Plasma Generated with High Speed Rotating Cylindrical Electrode***, **Y. Oshikane**, S. Sato, A. Nagao, K. Yamamura, K. Endo, Y. Mori,* Osaka University, Japan

Optical emission spectroscopy and broad-band absorption spectroscopy in UV region have been applied for determining CF@sub 2@ radical density in the chemical vaporization machining (CVM) plasma, which is generated in below 1 mm gap between the side of rotating cylindrical electrode (alumina) and flat substrate (silicon, quartz) by VHF at 150 MHz. By using a grating spectrograph consists of imaging aspheric mirrors coupled with cooled CCD camera, a spatially resolved UV spectrum has been recorded for CF and CF@sub 2@ radicals. Relative changes in CF@sub 2@ density in He/CF@sub 4@/O@sub 2@ plasma were monitored. The experiments cover a wide range of pressure, composition, rotation speed, and power deposition conditions (10@super 3@-10@super 5@ Pa, 0.01-1% CF@sub 2@, 0.01-1% O@sub 2@, 0-2000 rpm, 15-100 W). Increasing the pressure from 10@super 3@ to 10@super 5@ Pa showed large changes in CF@sub 2@ band spectrum. Both emission and absorption spectrum of a 10@super 3@ Pa He/CF@sub 4@/O@sub 2@ plasma showed the A(0,v,0)-X(0,0,0) (v=0 to 13) transition of the CF@sub 2@ molecule from 230 to 270 nm. But the spectrum shifts to longer wavelengths and showed the A(0,0,0)-X(0,v,0) (v=0 to 10) transition spectrum from 260 to 340 nm at atmospheric pressure. The spatially resolved absorption spectrum showed the absorption peaks near the side of electrode and substrate surface.

3:20pm **PS2-WeA5 A Simulation Study of the Role of Surface Phenomena in Dielectric-barrier Atmospheric-pressure Glow Discharges***, **X. Yuan**, L.L. Raja,* The University of Texas at Austin

Atmospheric-pressure glow (APG) discharges controlled by dielectric barriers can be used for a variety of new applications such as etching and deposition of thin films, surface modification, and plasma sterilization, without need for vacuum chambers. Dielectric-barrier controlled APG discharges exhibit a variety of interesting phenomena that are determined by plasma dynamics, volumetric chemistry, and dielectric surface effects. A clear understanding of these interactions is often difficult to unravel through purely experimental means and first principles simulation approaches can play an important role. In this talk, we will present detailed one-dimensional simulation results for a dielectric-barrier APG discharges in high-purity helium. Simulation results will be used to explain several experimentally observed dielectric-barrier APG characteristics such as large scatter in peak current values, asymmetry in current pulses, and parametric dependence of peak current pulse values on different discharge operating conditions. Our modeling results present convincing evidence that run-to-run variations in surface conditions (such as secondary electron emission coefficients) control the experimental observations such as scattered and asymmetric current pulses.

3:40pm **PS2-WeA6 Miniature Microwave Plasma Torch Applicators and Characteristics***, **T.A. Grotjohn,*** Michigan State University and Fraunhofer Center for Coatings and Laser Applications*; K. Hemawan, S. Zuo,* Michigan State University*; J. Asmussen,* Michigan State University and Fraunhofer Center for Coatings and Laser Applications

The experimental evaluation of two miniature microwave plasma torch applicators that have potential use in materials synthesis and surface treatment are described. The first applicator employs an open ended coaxial structure with the discharge located at the tip of the center conductor. The discharge is formed at atmospheric or slightly below atmospheric pressure where the feed gas flows through the center conductor of the applicator. The second applicator is similar to a microstripline coupling structure described earlier.@footnote 1@ This applicator couples microwave energy to a surface wave discharge formed in an open ended tube placed between and perpendicular to the strip transmission lines. The feed gases are fed directly through the surface wave discharge and flow out to a pressure controlled environment ranging from approximately 10 Torr to atmospheric pressure. Both microwave plasma torches are experimentally evaluated over a range of input power and a variety of feed gas mixtures including argon, mixtures of argon with hydrogen and selected hydrocarbon gases, nitrogen, and air. These torches operate from 10's to 100's of watts of input power and are able to maintain discharges over a wide range of flows from diffusional flow of radicals for gentle surface processing to high velocity flows approaching supersonic velocities. Objectives of this work are to create compact microwave plasma torch designs that operate from below atmospheric pressure to one atmosphere pressure with processing spot sizes ranging from several mm down to less than 0.25 mm. The numerous applications of these microplasma torches include cutting, welding, cleaning and other surface treatments. @FootnoteText@ @footnote 1@ T. A. Grotjohn, et.al., "Characteristics of Miniature Microwave Excited Plasma Discharges," AVS Symposium, Denver, 2002.

4:00pm **PS2-WeA7 Microplasma Surface Modification of the Inner Surface of Small Diameter Polyethylene Tubing for Improved Hematocompatibility***, **J.L. Lauer**, J.L. Shohet, C. Pratoomtong, R.D. Bathke, R.M. Albrecht, S. Esnault, J.S. Malter,* University of Wisconsin, Madison*; S.B. Shohet,* University of California, San Francisco*; U. von Andrian,* Harvard Medical School

Microplasma surface modification was used to modify the inner surface of small diameter (280 and 800 µm and up to 1 meter in length) polyethylene (PE) tubing. Polyethylene glycol was grafted to the lumenal surface using an oxygen plasma and then cross-linked with an argon plasma. The plasma was created by placing hollow cathodes electrodes, in vacuum, at the ends of the PE tubing. The electrodes were powered by a 15 kV pulsed a.c. supply. Since feedstock gases and reaction products must pass along the length of the tubing, the resulting pressure drop has the potential to cause nonuniform plasma chemistry and thus a nonuniform treatment along the tubing. Emitted light from the plasma was analyzed with a monochromator, that was moved along the length of the tubing, giving insight on plasma uniformity. Treatment effectiveness on the lumenal surface was evaluated using a capillary rise method, which can be directly related to the contact angle. Uniformity of the atomic surface composition along the length of the inner surface of the PE tubing was analyzed by XPS. To test for hematocompatibility, a loop, powered by a peristaltic pump, circulated heparinized human blood for times up to one hour at flow rates of the order of 1 ml/minute at 37 C. After the flow test, the tubing was rinsed with phosphate buffer solution (PBS) for 10 minutes (with the same flow rate as the blood). The cells were fixed for 30 minutes with 1.25% by volume glutaraldehyde and 0.5% by weight tannic acid dissolved in PBS. After the fixation, the tubing was rinsed with PBS for another 10 minutes. It was then dehydrated with two-minute exposures to ethanol of increasing concentration from 50% to 95%. Plasma-treated and untreated tubing were then evaluated by studying the morphology of adhering platelets along the tubing with SEM. By suitably modifying the plasma parameters, the degree of uniformity as a function of distance along the tubing and proximity to the peristaltic pump can be optimized.

4:20pm **PS2-WeA8 Microdischarge Plasma in Supercritical Fluid***, **K. Terashima**,* The University of Tokyo, Japan **INVITED**

We have performed the study of microscale/nanoscale plasma science and technology.@footnote 1@ In this talk, our recent work on microdischarge plasma in supercritical fluid (SCF), particularly near the critical point (CP), for CO@sub 2@ (CP:7.38MPa,304K)and H@sub 2@O (CP:22.1MPa,674K), are presented. SCF,which is an intermediate state of matter between liquid and gas, has attracted much interest in scientific and enginering fields due to abnormal characteristics, such as high solubility. In particular, near CP, large density fluctuation results in drastic change of the properties. From a microscopic viewpoint, the SCF consistes of various sized clusters. Therefore, it is highly anticipated that the ionized state, such as the plasma state, in SCF may exhibit unique characteristics and reactions, that are distimct from those of the normal plasma state in gas. In addition to the first generation@footnote 2@ of plasma in SCF, abnormal features of breakdown voltages (V@sub B@) as a function of environmental pressure are demonstrated. For CO@sub 2@, measurements of V@sub B@as a function of pressure for high-pressure CO@sub 2@ up to SCF conditions of various temperatures have been performed using a 1-µm-gap coplanar film electrode. The curve of the V@sub B@ exhibits an inflection at around 3 MPa and a drastic decrease near CP. The V@sub B@ in pressure environments higher than the inflection at around 3 MPa can be analyzed using the Townsend theory and density fluctuations, which typical indicates clustering, and the drastic decrease of V@sub B@ near CP was shown by a scaling function. The same features were also observed for H@sub 2@O. Finally, as an example of an application, the preparation of carbon-cluster systems, such as nanopolyhedra and nanotubes, using SCF-CO@sub 2@ plasma is also presented. @FootnoteText@ @footnote 1@ K.Terashima, L.Howald, H.Haefke and H.J.Güntherodt, Thin Solid Films 282(1996)634. @footnote 2@ T.Ito and K.Terashima, Appl.Phys.Lett.80(2002)2854.

5:00pm **PS2-WeA10 Two-dimensional Simulation of dc Microdischarge Phenomena***, **P.S. Kothnur**, L.L. Raja,* The University of Texas at Austin

Microdischarges have gained much attention in the plasma process community for a variety of applications. Proposed applications range from generation of intense UV radiation to maskless etching of thin films. Recently, arrays of microhollow cathode discharges are being investigated for applications such as sources of flat panel light sources or electron sources. While some estimates of properties of micro hollow cathode discharges are available, a detailed understanding of the plasma dynamics and chemistry is lacking. Further, it is not fully clear as to what conditions influence the existence of the hollow cathode effect in microdischarge geometries. This talk presents results from a self-consistent, two-dimensional computational study of the glow-like phenomena in microdischarges. The model includes a description of multi-species transport and chemistry, electric field, electron and heavy species energy distributions in the microdischarge. The talk explores conditions under which the hollow cathode effect occurs in microdischarge geometries, and presents a fundamental understanding of the overall microdischarge phenomena. Further, we explore thermal heating effects in dc microdischarges in the presence of bulk flow inside the discharge. This aspect of the study is motivated by our proposed use of microdischarges in space thruster applications.

Surface Science
Room 328 - Session SS+NS-WeA
Perspectives and New Opportunities

Moderator: R.A. Bartynski, Rutgers University

2:00pm **SS+NS-WeA1 The Birth and Evolution of Surface Science: Key Role of AVS***, **C.B. Duke**,* Xerox Wilson Center for R&T **INVITED**

This presentation consists of a description of the birth and evolution of surface science as an interdisciplinary research area. It provides an overview of the themes developed in the Surface Science section of the AVS 50th anniversary issue of The Journal of Vacuum Science and Technology (JVST). The history of Surface science can be traced in terms of four waves of innovation [see e.g., C. B. Duke, Proc. Nat. Acad. Sci. 100, 3858 (2003)]. It was born in the mid 1960s based on the combination of ultra high vacuum technology, the recognition that "low energy" (500 eV) electrons exhibit inelastic collision mean free paths of atomic dimensions, and the commercial availability of single-crystal samples. The founding in 1964 of JVST and Surface Science marks this event. During the 1970s through the turn of the century the evolution surface science was strongly influenced by the microelectronics revolution that in turn was profoundly impacted by the evolving surface analytical capabilities. In the 1980s scanning probe microscopy was invented. It blossomed in the 1990s, launching a new era of digital imaging in surface science. Today, the frontiers of surface science are increasingly in its applications to characterize complex systems, including solid-liquid interfaces and fragile biological systems. Descriptions of these are taken from C. B. Duke and E. Ward Plummer, eds. "Frontiers in Surface and Interface Science", Surf. Sci. 500 (2002). In this presentation I trace the evolution of surface science through these four eras of its evolution with emphasis on how AVS has been instrumental in shaping each era.

2:40pm **SS+NS-WeA3 STM Single Atom/Molecule Manipulation: A New Dimension for Nanoscience and Technology***, **S.-W. Hla**,* Ohio University **INVITED**

The fascinating advances in single atom/molecule manipulations with the STM-tip allow scientists to fabricate artificial atomic scale structures, to study local quantum phenomena or to probe physical and chemical properties of matter at single atom and molecule level on crystal surfaces.@footnote 1-4@ The STM-tip is not only used as an imaging tool but also as a manipulating and even, as an engineering tool in these experiments. In this presentation, our recent results of single atom/molecule manipulation experiments conducted by using a low temperature UHV-STM on metallic surfaces will be presented. A variety of cutting-edge STM single atom/molecule manipulation procedures, in combination with complementary tunneling spectroscopy and imaging, are systematically used to develop robust and innovative experimental schemes. Using these schemes, we examine the mechanical stability, electronic properties and chemical reactivity of single molecules at the spatial limit. The presentation will include vibrational spectroscopy/microscopy of single sexi-phenyl molecules, electronic spectroscopy examinations of single Ag atoms/vacancies and self-assembled molecular films. Determination of mechanical strengths and internal conformational changes of large single molecules using tip-molecule interaction forces will be shown. Detail single atom movement mechanisms during quantum corral constructions with the STM-tip will be demonstrated. The extraction of single atoms from the native substrate and construction of various atomic scale structures on an atom-by-atom basis using the STM-tip will be presented by showing STM movies. @FootnoteText@@footnote 1@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330 (2003). @footnote 2@H.C. Manoharan, C.P. Lutz, D.M. Eigler, Nature 403, 512-515 (2000). @footnote 3@B.C. Stipe, M.A. Rezaei, W. Ho, Science 280, 1732-1735 (1998). @footnote 4@C. Joachim, K. Gimzewski, A.Aviram, Nature 408, 541-548 (2000).

3:20pm **SS+NS-WeA5 Stark-Effect and Two-Electron Photon Emission in Scanning Tunnelling Spectroscopy***, R. Berndt, G. Hoffmann, L. Limot, T. Maroutian,* University of Kiel, Germany*; P. Johansson,* University of Ã–rebro, Sweden*; **J. Kroeger**,* University of Kiel, Germany **INVITED**

We report a quantitative low-temperature scanning tunnelling spectroscopy (STS) study on the Ag(111) surface state over an unprecedented range of currents (50 pA to 6uA) through which we can tune the electric field in the tunnel junction of the microscope. We show that in STS a sizeable Stark effect causes a shift of the surface state binding energy E@sub S@ , even at very low currents. Data taken are reproduced by a one-dimensional potential model calculation, and are found to yield a Stark-free energy E@sub S@ in agreement with recent state-of-the-art photoemission spectroscopy measurements. Next, unusual emission of visible light is observed in scanning tunnelling microscopy of the quantum well system Na on Cu(111). Photons are emitted at energies exceeding the energy of the tunneling electrons. Model calculations of two-electron processes which lead to quantum well transitions reproduce the experimental fluorescence spectra, the quantum yield, and the power-law variation of the intensity with the excitation current.

4:00pm **SS+NS-WeA7 Electrostatic Potential Profile within a Biased Molecular Electronics Device: a Cavity QED Approach***, **J.W. Gadzuk**,* National Institute of Standards and Technology

The fundamental principle behind a molecular electronics (MoleE) device is similar to that driving many resonant electron scattering or transmission processes; initial insertion of an electron into a resonance state, propagation in some manner (coherent, incoherent, or diffusive) that is a controllable characteristic of the resonance-supporting system, and final extraction of the selectively transmitted electron. The stages of a MoleE system responsible for the three-step conduction are often referred to as donor, bridge, and acceptor. The scattering or resonance properties depend amongst other things, upon the electrostatic potential profile along the bridge or molecular wire. Since the molecular wires are packed together within a self-assembled monolayer in real MoleE devices, the present study focuses on the electrostatics and dynamics of such structures, here formulated as a problem in cavity QED of a structured, polarizable continuum film of the bridge material inserted between parallel metallic plates rather than as one in conventional quantum chemistry. The plates (electrodes) and the molecular film are each characterized by their dielectric response functions and the donor/acceptor-electrode interactions by charge redistribution required to satisfy the appropriate electrodynamic boundary conditions. This approach provides fresh insights into the overall features of the electrostatic potential profile and select atomic-scale properties such as electrode-induced shifts in the resonance (aka HOMO and/or LUMO) energies within the molecules which in turn are crucial in determining the current-voltage characteristics of the MoleE device, as will be demonstrated.

4:20pm **SS+NS-WeA8 Quantum Size Effect Induced Modification of CO Chemisorption on Cu/fccFe/Cu(100)***, **A.G. Danese**, R.A. Bartynski,* Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. The quantum confinement of electrons due to high reflectivity scattering at the film's interfaces forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. We have studied the role of MQW states in the chemisorption of CO on n ML Cu/fccFe/Cu(100) where ~2 < n < ~14 using inverse photoemission (IPE) and temperature programmed desorption (TPD). IPE results show the unoccupied MQW states in the Cu overlayer increasing in energy as a function of increasing Cu thickness with MQW states crossing the Fermi energy (E@sub F@) at 5 ML Cu and 11 ML Cu in both the bare and CO covered system. Accordingly the IPE intensity at E@sub F@ oscillates as a function of Cu well thickness and temperature programmed desorption (TPD) performed on the CO covered Cu films exhibits modulations in the CO peak desorption temperature (T@sub des@) which are correlated with these IPE modulations. The MQW states are quasi 2 dimensional (2-d) and we attribute this chemisorption QSE to the bottom of a 2-d subband that crosses E@sub F@ every time a MQW is observed to cross E@sub F@. This increases the density of states at E@sub F@ available for the CO-Cu bond, thus strengthing the bond as observed by two T@sub des@ maxima at 5 ML Cu and 11 ML Cu. Between these E@sub F@ crossings, the DOS as measured by IPE intensity decreases and we observe that the two quantities oscillate together.

4:40pm **SS+NS-WeA9 Manipulating Single Metal Atoms with the Scanning Tunnelling Microscope***, **K.-F. Braun**, K.H. Rieder,* Freie Universit@um a@t Berlin, Germany*; K. Flipse,* Eindhoven University of Technology, The Netherlands*; S.-W. Hla,* Ohio University

Scanning tunnelling microscopy has been used to manipulate single atoms, small molecules as well as larger molecules and parts of it. Lateral manipulation can be applied to position atoms for the construction of artificial assemblies on desired atomic sites. Although manipulation techniques have been used on a variety of systems only little is known about the interaction forces between microscope tip and adparticle. Here we present a detailed study of the lateral manipulation of Au and Ag atoms on Ag(111) and Ni(111) surfaces. We describe a complete picture of how single Ag atoms move on the various potential energy landscapes of a Ag(111) surface during a quantum corral construction by using an STM tip at 6 K. The threshold tunnelling resistance and tip-height to move the Ag atom across the surface are experimentally measured as 210 ï,± 19 kï—and 1.3 ï,± 0.2 Ã…. The experimental atom manipulation signals reveal remarkably detailed atom movement behaviour dependent on the surface crystallographic orientation and offer atomic-level tribology information.@footnote 1@ Manipulation experiments with Au atoms on the same Ag(111) surface show a voltage dependent threshold resistance above ï,±100 mV. Possible current and field effects will be discussed. Measurements on Au atoms on a Ni(111) surface display even a long-ranged repulsive interaction for voltages below -300 mV. The influence of the electronic surface structure on the manipulation will be discussed. Electrons injected in the antibonding levels of the atom-surface system can weaken the bond to allow lateral manipulation at high voltages as well as desorb the atom.@footnote 2@ @FootnoteText@@footnote 1@S.W. Hla, K.-F. Braun, K.H. Rieder, Phys. Rev. B, Rapid Comm., accepted (2003). @footnote 2@K.-F. Braun, K. Flipse, K.H. Rieder, in preparation (2003).

5:00pm **SS+NS-WeA10 Adsorption and Deprotonation of Dichlorothiophenol on Cu(111): STM-Based Hydrogen Abstraction and Thiolate Formation***, B.V. Rao, K.-Y. Kwon, J. Zhang, A. Liu, **L. Bartels**,* University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial steps of the adsorption of di-chloro-thio-phenol (DCTP), an aromatic thiol, on Cu(111). Upon adsorption of ultra-low coverages at 15 K individual molecules can be found on Cu(111) terraces which appear as large, flower-shaped protrusion in STM images. This is caused by the rotation of the molecule around the sulfur atom which rests at an on-top site of the substrate. Deprotonation to the thiolate may be caused by annealing to nitrogen temperatures or attachment/removal of electrons to/out of the molecule at a bias exceeding 300 mV. Following deprotonation, the sulfur atom shifts to a higher-coordinated substrate site and the molecules is fixed in place. STM-based vibrational spectroscopy reveals a pronounced S-H stretch mode at 320 meV before deprotonation, which is absent from spectra taken after deprotonation. The STM based hydrogen abstraction process can be accomplished reliably at -500mV with a first-order dependence on the current. Perfect selectivity for the sulfur bound hydrogen is achieved even if the excitation current targets the benzene ring. Adsorption of 1 L of DCTP at nitrogen followed by annealing to ambient temperatures leads to the formation of an ordered structure comprised of pairs of DCTPs of opposite chirality in the adsorbed state. Further increasing the adsorbate coverage, more and more of the molecules do not lie flat on the surface but have the benzene ring pointing up.

Surface Science
Room 327 - Session SS+OF-WeA
Growth and Characterization of Organic Films

Moderator: L.A. Baker, Naval Research Laboratory

2:00pm **SS+OF-WeA1 Electronic and Geometric Structures of Pentacene Molecules Grown on Au(100)***, **Y.J. Song**, K. Lee, J. Yu, Y. Kuk,* Seoul National University, Korea

A pentacene molecule has attracted much interest for its possible application to organic-based electronic devices with its interesting electronic properties. Despite reported semiconducting property of the bulk crystal, it is hard to grow the high-quality film. Here, we report our scanning tunneling microscopy studies on the geometric and electronic structures of pentacene molecular layers on a Au(100) surface. Because of the high diffusivity of the molecule at room temperature, the STM studies were done at low temperature. At submonolayer coverage, the molecules are confined to the troughs of the reconstructed Au(100)-(5x20), forming a chain structure perpendicular to the reconstrcted ridges. We resolved the HOMO and LUMO states of pentacene molecules on a Au(100) surface with atomic resolution. The DFT (density functional theory) results of the molecular layer reveal good agreement with the observed gerometric and electronic structures. The electronic levels of pentacene molecules are shifted in the presence of metallic substrate. This result can be valuable when one makes metal-pentacene junctions for device applications. The electronic levels are also shifted with pentacene-pentacene interactions. At the coverages higher than 2 monolayers, a single phase was observed. The pentacene-pentacene interaction plays a important roll to the growth structures. The 5 pentacene molecules work as a base unit for the multilayer film. The correlation between the growth structure and the transport property will be discussed.

2:20pm **SS+OF-WeA2 Pentacene Thin Films on Clean and Chemically Modified Si(001) Surfaces***, **K.P. Weidkamp**, L. Fang, R.J. Hamers,* University of Wisconsin-Madison

We have investigated the microstructural, chemical and electronic properties of pentacene thin films formed on Si(001) surfaces. Using FTIR and valence-band photoemission spectroscopy, we find that the initial pentacene molecules deposited onto the surface undergo a transition from sp@super 2@ to sp@super 3@ bonding and partial dissociation, all indicating the formation of covalent C-Si bonds that inhibit diffusion and thereby result in poor pentacene crystal formation. In contrast films prepared by deposition on to Si(001) surfaces that were initially modified with a monolayer of pentacene molecules show no evidence for dissociation and exhibit highly reversible adsorption and desorption, demonstrating that the pentacene molecules do not form covalent bonds with the underlying organic-modified surface. In order to understand how the molecular structure of the interfacial organic layer affects that structure and electronic properties of the pentacene thin films, we have investigated pentacene thin films deposited onto silicon surfaces that were modified with several different organic molecules including cycopentene, dodecene, and phenanthrenequinone. These three molecules are expected to differ significantly in thickness, molecular rigidity, and effective molecular conductivity. AFM images show that the each organic molecular layer induces specific changes in the microstructure of the pentacene films deposited on top. Measurements of the electrical properties through the films will also be presented.

2:40pm **SS+OF-WeA3 Spectroscopic Measurements on Ultra Thin Highly Ordered Films of Organic Semiconductors***, **T. Fritz,*** TU Dresden, Germany **INVITED**

Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. High quality samples, precise structural data, and a detailed understanding of the physical properties are essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, and therefore displaying well defined physical properties. In order to investigate those physical properties deeply, spectroscopy methods are required which allow to characterize films with film thicknesses down to even submonolayers. In our contribution two different spectroscopy methods will be discussed in detail. By the first one, called Scanning Tunneling Spectroscopy (STS), one can determine the energetic positions of both filled and empty states of a molecular layer on an inorganic substrate in a single measurement. Due to the high special resolution small domains with different ordering can be electronically distinguished. Despite electron spectroscopies, optical spectroscopy on organic materials is a very powerful tool and can even provide structural information. Given the fact that exciton confinement effects in quasi-one-dimensional organic crystals will become apparent only if the layer is sufficiently thin (usually less than 4 monolayers), a method is required which will allow to measure the optical absorption down to submonolayers coverage with a sufficient signal-to-noise ratio. The method of choice is the Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy), carried out in situ, i.e., during the actual film growth.

3:20pm **SS+OF-WeA5 Epitaxial Growth of Pentacene on Bi/Si(111) Films***, **G.E. Thayer,*** IBM T.J. Watson Research Center*; J.T. Sadowski,* Tohoku University, Japan*; R.M. Tromp,* IBM T.J. Waston Research Center

Electrical contacts between organics and metals have been known to limit charge injection in organic electronic devices. Thus it is not surprising that there is a considerable amount of current work modifying metal surfaces and interfaces in an effort to align conduction with organic molecular levels. The solution to this problem begins with understanding the fundamental mechanisms that control both the morphology and electronic structure at the interface between metal and organic materials. Although the interfaces of organic films grown on many clean substrates (semiconductors, insulators, and metals) are found to be poorly ordered, our work has revealed that pentacene grows epitaxially on Bismuth (a semimetal). Using LEEM, PEEM, LEED, AFM, and STM our efforts have focused on understanding how pentacene molecules order in Pn/Bi/Si(111) thin films (1ML-10MLs). In contrast to the frequently used Pn/Au system, in the first ML of Pn/Bi the pentacene molecules stand up and are highly ordered as seen by the sharp LEED patterns that we observe. Our LEED analysis finds that the structure of Pn/Bi/Si(111) thin films is similar to the bulk structure of Pentacene with lateral 2D cell dimensions of a=7.8Å, b=6.2Å, and @gamma@=84.9°. In one dimension, this structure is 1:1 commensurate in the sqrt(3) direction of the underlying hexagonal Bi surface structure. However, in the other direction it is rotated by a small angle and is incommensurate with the Bi lattice. Control of Pn crystal orientation on metal electrodes will enable the fabrication of organic FFT's whose electrical characteristics are not degraded by large angle grain boundaries at the source and drain junctions.

3:40pm **SS+OF-WeA6 AFM Study of Carboxylic-Acid Functionalized Pentathiophenes on Mica Surfaces***, **J. Chen,*** Lawrence Berkeley National Laboratory*; A.R. Murphy,* University of California*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; J.M.J. Frechet,* Lawrence Berkeley National Laboratory and University of California

We studied SAM films of the oligothiophene derivative (D5TBA @footnote 1@) with AFM to determine its growth and structure and its response to mechanical excitations. We found that self-assembled films formed on mica substrates from hydrophilic (THF) and hydrophobic (chloroform) solutions were totally different in their structure and mechanical properties. In one case methyl groups were exposed while in the other carboxylic groups (COOH) were exposed, resulting in very different friction properties. Friction anisotropy was observed between domains of different orientations. Scanning polarization force microscopy (SPFM) was used to obtain contact potential maps (Kelvin Probe mode) to confirm film structures deduced from contact mode imaging. Generally, deposition from THF solutions produced stable monolayer aggregates with exposed methyl groups. Multilayer regions were sometimes observed, with alternate methyl and carbonxyl group terminations. During contact AFM imaging the third and higher layers could be progressively peeled off by increasing the load applied to the tip, however the second layer was found to incorporate into the first layer in a densification process. Deposition from chloroform solutions usually produced unstable multilayer films with methyl groups contacting the mica surface. @FootnoteText@ @footnote 1@ D5TBA, or 4-(5''''-Decyl-[2,2';5', 2''; 5'', 2'''; 5''', 2''''] pentathiophen-5-yl)-butyric acid, was prepared by Stille cross-coupling methods using functionalized thiophene monomers.

4:00pm **SS+OF-WeA7 Surface Polymerization by Ion Assisted Deposition for Polythiophene Film Growth***, **S. Tepavcevic**, Y. Choi, L. Hanley,* University of Illinois at Chicago

Cationic polymerization is induced at the gas-solid interface by hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers.@footnote 1@ This process, termed surface polymerization by ion assisted deposition (SPIAD), produces films that maintain the chemical structure of the monomer.@footnote 2@ A polythiophene film is produced here by SPIAD with 100 eV thiophene ions and terthiophene monomers coincident on Si and indium tin oxide (ITO) substrates held under vacuum. X-ray photoelectron spectroscopy observes enhancement in film growth for SPIAD compared with either thiophene ion or terthiophene exposure alone. Polythiophene films grown by both mass-selected@footnote 1@ and non-mass-selected ions@footnote 3@ with coincident terthiophene dosing both display similar fluorescence intensity at two wavelengths characteristic of emission from films of the terthiophene monomer. Raman spectra of films from non-mass-selected ions display several vibrations also observed in terthiophene films. Ions therefore play a critical role in film growth from non-mass-selected ions, in addition to any radical or photochemically driven processes that may also occur. @FootnoteText@ @footnote 1@L. Hanley and S.B. Sinnott, Surf. Sci. 500 (2002) 500. @footnote 2@S. Tepavcevic, Y. Choi, and L. Hanley, J. Amer. Chem. Soc. 125 (2003) 2396.@footnote 3@L. Hanley, Y. Choi, E.R. Fuoco, F.A. Akin, M.B.J. Wijesundara, M. Li, A. Tikhonov, and M. Schlossman, Nucl. Instr. Meth. Phys. Res. B 203C (2003) 116.

4:40pm **SS+OF-WeA9 Molecular Dynamics Simulation Study of Continuous C@sub 3@F@sub 5@@super +@ and CF@sub 3@@super +@ Ion Depositions on Polystyrene Surfaces***, **I. Jang**, S.B. Sinnott,* University of Florida

Fluorocarbon plasma treatment is widely studied and used to change surface properties and to grow thin polymer films. However, it is difficult to determine the detailed mechanisms responsible for the surface reactions that lead to thin film growth due to the complexity of plasma systems. Computer simulations of the deposition of mass selected fluorocarbon ions have been used to isolate the effects of polyatomic ions in low energy plasma deposition of thin films. In this study, the continuous deposition of a beam of polyatomic fluorocarbon ions (C@sub 3@F@sub 5@@super +@ and CF@sub 3@@super +@) on polystyrene surfaces is performed using classical molecular dynamics simulations. The forces are determined using the reactive empirical bond order method for short-range interaction and Lennard-Jones potential for long-range van der Waals interaction. The incident energy of the ions is 50 eV/ion and they are deposited normal to polystyrene surface. The simulations allow us to determine the mechanisms responsible for thin-film growth and surface modification by the ion beam deposition. Specifically, they show how fluorocarbon polymer precursors are formed and react with one another. Overall, the simulations predict that CF@sub 3@@super +@ depositions are more effective in fluorination of polystyrene surface than C@sub 3@F@sub 5@@super +@ depositions. This work is supported by the NSF under grant CHE-0200838.

5:00pm **SS+OF-WeA10 Exploring the Reactivity of Atomic Oxygen with Organic Surfaces*, G.M. Wolfe*,** *A.J. Wagner, J. Torres, C.C. Perry, D.H. Fairbrother,* Johns Hopkins University

Atomic oxygen is a major component in oxygen and air-based plasmas and also plays a major role in the erosion and degradation of polymeric coatings in spacecrafts as they pass through Low Earth Orbit (LEO). Through the use of self-assembled monolayers and well-defined polymeric substrates an understanding of the fundamental molecular level surface reactions of atomic oxygen with organic surfaces can be determined. Our work explores the interactions of O radicals, with a series of self-assembled monolayers (SAMs), employed as models for polymer surfaces. In situ X-ray photoelectron spectroscopy (XPS) is used to elucidate the mechanism of radical reactions occurring with dodecane, hexadecane, and X-ray modified hexadecane SAMs, as well as a semi-fluorinated SAM (CF-SAM). In the hydrocarbon SAMs, the reaction with atomic O progresses through three stages. Initially, reactions at the vacuum/film interface generate a steady state concentration of C-O, C=O and O-C=O groups. Sustained atomic oxygen exposure on hydrocarbon-based SAMs promotes the formation of volatile oxygen-containing carbon species, e.g. CO@sub 2@, leading to the development of a steady state etch front. Ultimately, oxygen penetrates to the film/substrate interface to form sulfonate and Au@sub 2@O@sub 3@ species. Experiments on the CF-SAM reveal an induction period of ~90 minutes prior to oxygen incorporation, an effect ascribed to the inertness of C-F and C-C bonds towards atomic oxygen and the well-ordered structure of the CF-SAM. In contrast to the hydrocarbon SAMs, reactivity within the CF-SAMs are initiated by O atom reactions at the film/substrate interface leading to desorption of intact adsorbate chains. Results on the interaction of atomic O with phosphorous ion-implanted poly(ethylene) will also be presented.

Thin Films
Room 326 - Session TF+MM-WeA
Sensors, Smart Films and Functional Materials

Moderator: C.H. Stoessel, Consultant

2:00pm **TF+MM-WeA1 CMOS-Based Microsensors*, O. Brand*,** Georgia Institute of Technology **INVITED**

CMOS-based microsensors combine, on a single chip, the necessary transducer elements and integrated circuits. This way, the microsensors benefit from well-established fabrication technologies and the possibility of on-chip circuitry. Besides sensor biasing and signal conditioning, added on-chip functionality, such as calibration, self-testing, and digital interfaces, can be implemented. A number of microsensors, including magnetic field and temperature sensors, are completely fabricated within the regular CMOS process sequence. A far larger number of microsystems can be realized by combining CMOS or BiCMOS technology with compatible micromachining and thin film deposition steps. These additional fabrication steps are performed either before, in-between, or after the regular CMOS process sequence. Commercially available examples include pressure sensors, accelerometers, gyroscopes, humidity sensors, mass flow sensors, and imaging devices. In the first part, the paper summarizes major technological approaches to CMOS-based sensors. In the second part, a packaged CMOS-based chemical microsystem, developed at ETH Zurich, Switzerland for the detection of volatile organic compounds in air is highlighted. On a single chip, the microsystem combines a sensor array featuring three different sensing principles with circuitry for sensor biasing, signal read-out, analog-to-digital conversion, and digital interfacing. The chemical microsystem is fabricated using an industrial CMOS technology in combination with post-processing bulk-micromachining to release the micromechanical sensor structures. After packaging the microsystem using flip-chip technology, the three sensor structures are coated with chemically sensitive polymer films. Absorption of volatile organic compounds in the polymer films results in a change of the (physical) film properties, such as the mass, dielectric constant, or temperature, which is then recorded by the underlying sensor structure.

2:40pm **TF+MM-WeA3 Behavior of Thin Ionic Liquid Films Studied with Atomic Force Microscopy*, J.J. Nainaparampil*,** *B.S. Phillips,* AFRL/MLBT*; K.C. Eapen,* University of Dayton Research Institute*; J.S. Zabinski,* AFRL/MLBT

Ionic liquids (IL's) represent a new class of solvents having the character of molten salts. They have no detectable vapor pressure, are moisture, air and temperature stable and therefore are excellent solvents. Most of these IL's consists of cations such as different alkyl imidazolium or alkyl pyridinium ions and anions such as BF@sub 4@, PF@sub 6@, N (CF@sub 3@SO@sub 2@)@sub 2@, CF@sub 3@SO@sub 3@. In this work, crystals of alkyl imidazolium+ PF@sub 6@ are dissolved in water or acetonitrile to form 0.2% to 0.5% solutions and deposited on Si surface to form thin films. Atomic force microscope working in non-contact mode capable of providing biased tip lithography is used to characterize these films. It is observed that scanned films give rise to certain geometrical structures that are repeated in recrystallized surfaces. A biased AFM tip is used to mobilize these structures to form other complex structures. It is noted that the same solution, when used as a lubricant in sliding contacts gives rise to drastic friction reduction compared to other lubricants. These IL's were used to lubricate a micro electro mechanical system (MEMS) electro static output motor. Results from MEMS endurance tests and an interface model that is based on the AFM study will be presented. Electro-migration of crystallites and adhesion of transfer films affect the friction and durability significantly.

3:00pm **TF+MM-WeA4 Bilayer Transition-edge Sensors for X-ray Calorimeter and Infrared Bolometer Arrays*, J.N. Ullom*,** *J.A. Beall,* National Institute of Standards and Technology*; J. Beyer,* PTB, Guest Researcher NIST*; S. Deiker, W.B. Doriese, G.C. Hilton, K.D. Irwin, C.D. Reintsema, L.R. Vale,* National Institute of Standards and Technology **INVITED**

Microcalorimeters and bolometers made from thin superconducting films cooled to temperatures near 100 mK have made dramatic progress in recent years. These devices provide an order of magnitude improvement in energy resolution over existing semiconductor x-ray sensors and are likely to be used in upcoming astronomical instruments spanning the spectrum from x-ray to millimeter wavelengths. The sensitivity of these devices is derived from the low heat capacities and thermal conductivities possible near 100 mK and from the strong dependence of resistance on temperature in the superconducting-to-normal transition. Our devices are made from bilayers of a normal metal and a superconductor. Use of a bilayer allows the transition temperature and resistivity of the sensors to be precisely controlled. In this talk, we describe recent progress towards kilopixel sensor arrays using multiplexed SQUID readout. We are building arrays of x-ray microcalorimeters for two applications: energy-dispersive x-ray spectroscopy on scanning electron microscopes and for the upcoming NASA satellite Constellation-X. We are building arrays of submillimeter bolometers for the SCUBA-2 camera on the James-Clerk Maxwell Telescope on Mauna Kea. At this time, the measured noise in both microcalorimeters and bolometers approaches but does not equal the value predicted from simple thermodynamics. We will present measurements of this excess noise and describe recent mitigation efforts.

Thin Films
Room 329- - Session TF1-WeA
Thin Film - Based Combinatorial Methods

Moderator: J. Kidder, Vermont Technical College

3:40pm **TF1-WeA6 Combinatorial Approach to Functional Thin Film Materials*, I. Takeuchi*,** University of Maryland **INVITED**

In this talk, I will describe the combinatorial materials research methodology we have developed using thin film techniques targeting a variety of functional materials. The basic idea of combinatorial thin film deposition systems is to create controlled compositional variation across given chips. Versatile compact combinatorial pulsed laser deposition systems are used for pursuing metal oxide systems. For studying metallic alloys, an UHV co-sputtering system is used to fabricate natural composition spreads. In this system, three magnetron guns are placed in a parallel geometry in order to maximize the coverage of ternary compositional phase space on three inch wafers. The spreads are primarily used for rapidly exploring novel phase space of magnetic materials. Various high-throughput characterization tools are used for rapid characterization of thin film combinatorial libraries and composition spreads. They include quantitative scanning microwave microscopes for studying dielectric/ferroelectric and resistive materials, scanning SQUID microscopes for mapping of magnetic properties and a scanning X-ray diffractometer for structural characterization. We also implement micromachined device libraries such as arrays of cantilevers for investigation of smart materials. Our studies have led to identification of novel compositional regions of ferromagnetic shape memory alloys.

4:20pm **TF1-WeA8 Preparation of Ternary Alloy Libraries for High-throughput Screening of Material Properties by Means of Thick Film Deposition and Interdiffusion: Benefits and Limitations***, **A. Rar**,* Oak Ridge National Laboratory and The University of Tennessee*; E.D. Specht,* Oak Ridge National Laboratory*; E.P. George, G.M. Pharr,* Oak Ridge National Laboratory and The University of Tennessee

Numerous techniques have been developed for making ternary alloy libraries for combinatorial materials development. Two popular approaches for synthesizing films are: (i) co-deposition from 3 different pure element sources and (ii) preparation of multilayer thin films with thickness gradients in different directions for each component, followed by annealing of the films to achieve local alloying. However, both methods have limitations. In the first, the elemental distribution is non-linear, the film thickness is not constant, and regions with low concentrations of one or more elements are difficult to achieve. In the second approach, synthesis of thick films may be a problem because of the large numbers of layers required. One possible solution is to deposit a single relatively thick layer for each element, followed by annealing to achieve alloying. This approach was examined for the Ni-Fe-Cr ternary system. Spatially resolved alloy properties were compared with well known structural properties by means of rapid XRD mapping with synchrotron radiation. Specimens were prepared by depositing films onto sapphire substrates with an e-beam evaporation system. After deposition, the layers were interdiffused by annealing in different environments. The quality of the resulting specimens was examined using cross sectional SEM, electron microprobe analysis, angular resolved x-ray fluorescence, and XRD. The main problems were encountered during annealing. Selection of annealing temperatures and times that could be used to produce good interlayer diffusion without Cr evaporation or Kirkendall voiding proved difficult. In addition, there was a tendency to form chromium oxide at the surface. Despite these problems, an isothermal section of the ternary phase diagram was reasonably well reproduced.

4:40pm **TF1-WeA9 Combinatorial Pulsed Laser Deposition for Investigation of Metal Oxide Systems***, **K.S. Chang**,* University of Maryland, College Park

Pulsed laser deposition (PLD) is an efficient technique for fabrication of a variety of thin film materials especially metal oxides. We have developed a compact combinatorial PLD system. The heart of the system is contained in a portable combinatorial thin film deposition flange which can be fitted into any physical vapor deposition system. The eight-inch flange features an automated two-dimensional shutter/mask system and a rotatable substrate heater which can go up to 800 ÂºC. Spatially selective shadow depositions are carried out by controlling the motion of the shutter/masks which glide over a mounted substrate during and in between depositions. Different designs of discrete combinatorial libraries and continuous composition spreads can be achieved by cutting different apertures on the replaceable masks made of stainless steel sheets. SnO2 based semiconductor gas sensor libraries consisting of 16 discrete compositions have been fabricated, and their operation as electronic noses were successfully tested. By monitoring the number of laser pulses, one can control the deposition of materials at atomic layer level. This layer-by-layer technique can be used for epitaxial growth of continuous composition spreads with controlled compositional variation across chips. Some of the materials we have looked at include ferroelectric BaTiO3-SrTiO3 composition spreads where continuous change in microwave properties were studied and MgO-ZnO composition spreads which can be used for construction of solar blind multi-channel UV detector arrays.

5:00pm **TF1-WeA10 Gadolinium-doped Yttrium Aluminum Garnet Ultraviolet Emitting Materials Deposited by rf Reactive Magnetron Sputtering***, **Y. Deng**, J.D. Fowlkes,* University of Tennessee*; J.M. Fitz-Gerald,* The University of Virginia*; P.D. Rack,* University of Tennessee

Gadolinium is known to radiate in the ultra-violet region at ~ 312nm and 275nm due to intra-band 4f transitions when suitably doped in oxide host materials. To investigate the ultraviolet Gd emission, thin films of gadolinium-doped with yttrium aluminum garnet (YAG:Gd) have been deposited by rf reactive magnetron sputtering. The parameters in this work include RF power, substrate temperature, O2 partial pressure ratio and annealing temperature. An optimized combinatorial process has been obtained by statistical analysis on a factorial design of experiment. The structure and composition of the films have been characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystallinity of the films has been investigated by X-ray diffraction (XRD). The effect of Gd doping level on the cathodoluminescent (CL) properties of the films has also been studied and has been correlated to the chemical and microstructural properties of the films.

Thin Films
Room 329 - Session TF2-WeA
Optical Thin Films and Photovoltaics II

Moderator: R. Sargent, OCLI

2:00pm **TF2-WeA1 Magnetron Sputtering for II-VI Semiconductor PV Materials***, **A.D. Compaan**,* University of Toledo **INVITED**

The deposition of polycrystalline, thin-film, II-VI semiconductors such as CdTe is possible by many different techniques, but the use of a plasma-based method such as magnetron sputtering can have significant advantages. In this paper we review recent advances in the fabrication of CdS/CdTe cells using rf planar magnetron sputtering and discuss some of the advantages that accrue from the use of sputtering in this class of materials. Some of these advantages take on increased relevance as the polycrystalline thin-film community begins to address issues related to the challenges of fabricating high efficiency tandem cells with efficiencies over 25%. Recently we have achieved improved sputtered cell performance (Voc= 814 mV, Jsc=23.5 mA/cm2, fill factor = 73.25, and efficiency = 14.0%) from superstrate cells based on window layers with sputtered ZnO:Al. In addition we have used reactive sputtering for the deposition of nitrogen-doped layers of p-ZnTe for possible use in transparent back contacts to CdTe. We shall also discuss recent results in the sputtering of wider and narrower bandgap alloys of CdTe with Zn, Mn, and Hg, and in the fabrication of cells with very thin CdTe layers having relatively little loss in performance and stability. Finally, the use of magnetron sputtering permits the fabrication of flexible thin-film cells on temperature-sensitive substrates such as polyimides. Work supported by the National Renewable Energy Lab and the U.S. Air Force.

2:40pm **TF2-WeA3 The Effects of Cu and Cl at the Device Junction on the Performance of CdTe-CdS Photovoltaic Cells***, **T.J. Bukowski**, D. Albin, J. Pankow, S.E. Asher,* National Renewable Energy Laboratory

Current CdTe photovoltaic device design utilizes processing steps that incorporate both Cu and Cl into the cell structure. Such treatments produce an enhancement in the initial device efficiencies. However, there has been concern that Cu and Cl at the CdTe-CdS interface may have an effect on the stability of the device. In the unstressed state, CdTe devices are known to have significant amounts of both Cu and Cl at the interface. In addition, Cu placed at the back contact has been proven to diffuse toward the interface as the device is stressed, increasing the amount of Cu at the junction. There is thought to be a correlation between the amounts of Cu diffused to the interface from the back-contact and the resulting observed degradation in performance, the origin of which has yet to be determined. We have begun experiments studying how direct incorporation of Cu and Cl at the interface affects device performance. In this study, we detail the correlation observed between CuCl vapor-deposited at the CdS/CdTe interface prior to CdTe deposition with resulting device performance. X-ray diffraction, x-ray photoelectron spectroscopy, SIMS, Raman spectroscopy and optical absorption techniques are used to characterize the resulting change in the CdS films as a result of incorporating Cu and Cl. It is shown that at treatments below 250°C a CuCl layer forms on the surface of the CdS. Above 250°C, additional compounds begin to appear such as Cu@sub x@S. Absorption data shows that the band edge of the CdS shifts from 2.61eV down to 2.41eV as the CuCl treatment temperature increases. Devices are then made from the treated CdS films and their J-V data compared with data from both untreated controls and degraded devices. Device performance results are then correlated with the amounts of CuCl deposited at the interface.

3:00pm **TF2-WeA4 Cu Diffusion from Back Contacts in CdS/CdTe PV Devices***, **S.E. Asher**, T.A. Gessert, C. Narayanswamy, D. Albin, R. Dhere,* National Renewable Energy Laboratory*; C. Ferekides,* University of South Florida*; M.R. Young,* National Renewable Energy Laboratory

It has been shown that for nearly all polycrystalline CdS/CdTe photovoltaic (PV) devices, the presence of Cu within the back contact is linked to both significant improvements in device performance as well as potential long-term device instability. There have been several studies of Cu distributions in devices performed using secondary ion mass spectrometry (SIMS), and in most depth profiles the Cu appears to segregate to the CdS layer in the device. Taken with the knowledge that grain sizes in the CdS are smaller, this has suggested that Cu is distributed primarily along grain boundaries. However, artifacts in the SIMS measurements may distort the profile and lead to erroneous conclusions if differences in sputter rate and corrections for ion yield are not made. In this study we use ion implanted standards of Cu into CdTe and CdS to quantify the levels of Cu in CdTe/CdS devices before, and after, one of three different back contact processes are applied. Our results show that while Cu does increase in the CdS layer of the device, the level prior to contacting is usually lower than in the CdTe. We also show that the CdCl@sub2@ process typically performed prior to application of the back contact can introduce significant levels of Cu into the device. Device characteristics are also compared with the SIMS diffusion profiles.

3:40pm **TF2-WeA6 Electron Cyclotron Resonance Plasma Sputtering Deposition of Highly Textured LiNbO@sub 3@ Thin Films on Si Substrates and Their Electro-Optic Properties***, **H. Akazawa**, S. Masaru,* NTT Microsystem Integration Laboratories, Japan

*Electron cyclotron resonance plasma sputtering provides high-quality thin film growth in the spontaneously generated electric field as well as the plasma stream, which carries kinetic energies of 10-30 eV. This technique has been used to grow textured LiNbO@sub 3@ (LN) thin films on Si substrates with a LiNbO@sub 3@ target. Smooth, crack-free films more than 1.2 µmm thick, were obtained. The x-ray diffraction pattern of films grown under optimized conditions revealed a single LiNbO@sub 3@ phase with its direction preferentially oriented along the substrate normal. The LiNb@sub 3@O@sub 8@ phase developed under excess O@sub 2@ gas ambient because of the enhanced re-evaporation of Li@sub 2@O molecules. ICP atomic emission spectroscopy confirmed that the composition is mainly affected by the oxygen partial pressure, but little affected by the growth temperature. Cross-sectional TEM images revealed columnar grains extending from the interface, and the volume fraction of the c-axis oriented domains was about 30%. Double inter-layers, 3-5 nm thick, (possibly a-SiO@sub 2@ and a-LN) were seen between the crystalline LN film and the Si substrate. The refractive index of the LN film was similar to the value of bulk crystal, indicating that the film was densely packed. The current-voltage characteristic was reversible up to the electric coercive force of bulk LN without destroying the insulating property, and the resistance was of the order of 10@super -11@ @ohm@cm below the applied voltage of 2 eV. The electro-optic effect was investigated by spectroscopic ellipsometry. We could detect a @delta@n value in the 10@super -4@ range, which corresponds to 30-20% of the Pockels constant of bulk crystal.

4:00pm **TF2-WeA7 Infrared Electroluminescent Zinc Sulfide: Rare Earth Doped Thin Film Devices***, **A.S. Kale**, W. Glass, N. Shepherd, M.R. Davidson, P.H. Holloway,* University of Florida

ZnS doped rare earth fluoride thin films have been fabricated by RF magnetron sputtering in the conventional metal-insulator-semiconductor-metal electroluminescence (EL) configuration as a novel source for IR radiation. These ACTFEL (alternating current thin film electroluminescent) devices have promise for applications in fiber optic communication and industrial gas sensors as well as consumer electronic devices. ZnS thin films, typically 1µm thick, doped with ErF@sub 3@ and NdF@sub 3@ have been studied for their IR versus visible emissions. Electroluminescence has been investigated after different annealing temperatures (as deposited to 475°C) at a fixed time (60min) to study the influence of annealing on the IR brightness. An extremely sharp temperature dependence has been found in the IR emission, where anneals at 425°C sharply increase the emission intensity, while temperatures 25°C higher or lower result in sharply attenuated emission. The origin of this effect will be discussed. Emission spectra and efficiency from 0.35 to 1.55µm will be reported. For Er doped films, there is no shift in 4f-4f emission wavelengths versus annealing temperature, but shifts of up to 10 nm are seen for Nd doped ZnS thin films. This shift in wavelengths in Nd has been attributed to crystal field effects on the mixed 5d-4f as well as the 4f-4f transitions. Room as well as low temperature time resolved decay measurements are presented to compare the nature of specific energy transitions and energy transfer mechanisms as function of device temperature.

4:40pm **TF2-WeA9 Dual-Color UV/IR Photodiodes Based on AlGaN Grown on Si and SOS for Advanced Fire/Flame Detectors***, **D. Starikov**, C. Boney, N. Medelci, R. Pillai, A. Bensaoula,* University of Houston

Rugged and reliable fire/flame detector arrays can be developed through integration of mature Si-based photodetectors with the newer UV wide band gap semiconductor photodetector technology. A GaN/InGaN/GaN double heterostructure grown on Si is photosensitive in the range from near UV to near IR. The UV range provided by the nitride layers (235-365 nm) is extended into visible and IR regions (365-1100 nm) by a Si p-n junction formed during the growth of the AlN buffer on the Si substrate. Schottky barrier photodiodes based on AlGaN layers grown on Si (detector 1) and sapphire (detector 2) can further extend the UV range of the above described structure and will be the focus of this paper. The AlGaN structures were grown using RFMBE and were processed by Cl-based reactive ion etching in order to expose each layer in the multilayer structure, deposit ohmic and Schottky barrier contacts, and investigate the electrical and photovoltaic properties of each interface. The results from detector 1 indicate high responsivity in short UV wavelengths down to 275nm, confirming the 35% Al concentration as determined by independent transmittance measurements, and in 550nm and longer range. Measurements from the detector 2 show a response limited to the UV range with a cutoff of between 290nm and 300nm indicative of an aver age Al content of ~25%. The above results are currently being implemented in the development of UV/IR sensitive tandem structures fabricated on silicon-on-sapphire (SOS) substrates. Results on the SOS-based photodetector fabrication, testing, as well as optimization of the UV to IR ratio by modeling of the component pixel structure will be presented.

5:00pm **TF2-WeA10 Gadolinium Doped Yttrium Oxide Thin Films Deposited by Radio-frequency Magnetron Sputtering; Film Quality and Cathodoluminescence Properties***, **J.D. Fowlkes**, P.D. Rack, Y. Deng,* The University of Tennessee, Knoxville*; J.M. Fitz-Gerald, R.K. Bansal,* The University of Virginia

Miniaturized ultraviolet (250 - 350 nm) emitting solid - state sources are required as components for proposed device structures such as non-line-of-sight communication transceivers and receivers and bioparticle detection units. Rare - earth doped, yttrium oxide thin films emit ultraviolet light over this proposed frequency range. Yttrium oxide thin films were deposited by radio - frequency magnetron sputtering in a reactive oxygen atmosphere. The films were deposited on Si (001) substrates and were polycrystalline with a preferred (222) pole orientation along the substrate normal that became more prominent at high temperature. In addition to texture, crystal size and crystal quality were determined, using x-ray diffraction, for a host of sputtering conditions. Yttrium oxide was doped with gadolinium which emits in the ultraviolet via an interband 4f-4f transition. The films emit at 314 - 315 nm with optimum intensity at ~ 10 at% Gd. Correlations have been made between thin film orientation, crystallite size, residual stress, and cathodoluminescence (CL) studies. CL excitation was optimized per sample by proper voltage, current, and temperature selection. In addition, CL data will be presented that reflects the characteristics of the Gd optical transition. Specific information regarding the phonon assisted transition and thermal and concentration quenching will be discussed.

Vacuum Technology
Room 323 - Session VT-WeA

Outgassing and Large Vacuum Systems

Moderator: L. Westerberg, Uppsala University, Sweden

2:00pm **VT-WeA1 How to Control Hydrogen Outgassing from Gauges and Materials***, **F. Watanabe**,* Vaclab Inc., Japan **INVITED**

The most important point for XHV technology is control of hydrogen emitted from the bulk. If we generate XHV, which is denoted by a hydrogen equivalent pressure below P=10@super -10@(H@sub 2@)Pa in a vacuum chamber, from the equation P=Q/S at the ultimate pressure, the limiting level of total outgassing should be below Q=PS=~10@super -11@Pa(H@sub 2@)m@super 3@/s when the pumping speed is e.g. S=~0.1m@super 3@/s. Here, we need three technologies for XHV, a minimum amount of a chamber, a pump and a gauge, in order to check the generated vacuum. However, if there is a large hydrogen outgassing from any component, the ultimate pressure is limited by that total value. That is, Q@sub total@(material)= Q@sub c@(chamber)+Q@sub g@(gauge)+Q@sub p@(pump) In the case of the chamber, a surface area of A=~0.5m@super 2@ is typical for a laboratory, therefore, the hydrogen outgassing rate from the material should be below q=Q/A=~2×10@super -11@Pa(H@sub 2@)m/s. To meet this situation, we have obtained an outgassing of Q=~10@super -12@Pa(H@sub 2@)m@super 3@/s for a hot-cathode ionization gauge and the extremely low outgassing rate of q=~10@super -14@Pa(H@sub 2@)m/s in the material of a 0.2% beryllium copper alloy. Therefore, we can easily obtain XHV in a laboratory using a pump of only a few liters/second. At the session, the process of development up to the present will be reviewed with the following program: (1) the importance of low emissivity material, (2) the unavailability of cold emitters for a gauge, (3) the concept of the heated-grid gauge/RGA, (4) the importance of copper alloy materials, (5) a comparison of recently-published ultra-low hydrogen outgassing materials, and (6) my conclusion for hydrogen outgassing reduction.

2:40pm **VT-WeA3 Outgassing Characteristics of a TiN-coated SUS-316 Vacuum Chamber Developed for XHV***, **M. Hirata**, H. Akimichi, A. Kurokawa, S. Ichimura,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; H. Yamakawa,* ULVAC Technologies, Inc.

The control of outgas from a vacuum chamber is the key issue to achieve XHV condition, since any pump has a limited pumping speed usually determined by effective connection area of the pump to the chamber. We have developed a new chamber accordingly, aiming at reducing outgas from the chamber wall as low as possible, and studied outgassing characteristic of the chamber. The chamber is made of vacuum melted stainless steel (SUS 316L) to minimize hydrogen outgassing, and treated by electrolytical polishing followed by pre-baking in vacuum and TiN coating. The outgassing rate of the chamber was measured by a throughput method after each treatment. The results are 4x10@super -9@Pa m/s, 3x10@super -12@Pa m/s and 1x10@super -13@Pa m/s, respectively.@footnote 1@ However, the ultimate pressure of the chamber (1x10@super -9@Pa) evacuated by a pump (1000 L/s) was quite higher than the pressure of 2x10@super -13@Pa estimated from the lowest value of the rate and the chamber inner area. In order to clarify the difference, the rate of the TiN coated chamber was measured by pressure rise method using an ionization (extractor) gauge and a spinning rotor gauge for several months. The results were 3x10@super -10@Pa m/s by the ionization gauge and 2x10@super -13@ to 3x10@super -12@Pa m/s by the spinning rotor gauge, respectively. The lowest value measured by the spinning rotor gauge was roughly equal to the value obtained by throughput method. These results suggest that outgas from the ionization gauge could not be ignored, and that the measured pressure of 1x10@super -9@Pa could be mainly attributed to outgas from the ionization gauge. A new method for XHV pressure measurement is inevitable. @FootnoteText@@footnote 1@S.Ichimura et. al.: Vacuum 53 (1999) 291.

3:00pm **VT-WeA4 Residual Gas in the LIGO Beam Tubes: Science, Arts and Recipes***, **R. Weiss**,* Massachusetts Institute of Technology **INVITED**

The LIGO (Laser Interferometer Gravitational-wave Observatory) has remote sites at Hanford, Washington and Livingston Louisiana. At these sites laser beams traverse 4km long 1.2 meter diameter beamtubes in vacuum to make the gravitational wave detection. The vacuum requirements are pressures less than 10^-8 torr of hydrogen and smaller pressures for heavier and more polarizable gases. The talk will describe the science and techniques developed, including: outgassing models, outgassing measurements, optical properties, material preparation, surface cleaning, bakeout and leak detection.

3:40pm **VT-WeA6 RHIC Pressure Rise with High Intensity Beam****, P. He, **H.C. Hseuh**, L.A. Smart, D. Weiss, S.Y. Zhang,* Brookhaven National Laboratory

RHIC is a superconducting heavy ion collider with two rings of 3.8 km circumference designed for nuclear physics research. With increasing ion beam intensity during recent RHIC operations, pressure rises of several decades within a few seconds were observed at a few room temperature vacuum sections. There are two distinct types of pressure rises, one occurs at injection and the other during acceleration. The first type has been associated with electron multi-pacting, electron stimulated desorption and ion desorption. The second type is coupled with beam halo scraping and desorption, with desorption rates of up to 10e+7 molecules per incident ion. Improvements to the RHIC vacuum systems have been evaluated, and some implemented, including extensive in-situ bakes, additional UHV pumping with lumped pumps and NEG coating, electron detectors and beam tube solenoids. The effectiveness of these measures in reducing the beam induced pressure bumps and increasing the vacuum system reliability are discussed and summarized. *Work performed under Contract Number DE-AC02-98CH10886 with the auspicious of the U.S. Department of Energy.

4:00pm **VT-WeA7 The Effect of Purge Pressure on Desorbing Water Removal Rate***, **L.D. Hinkle**,* Falmouth Public Schools

The need for high purity gas supply for vacuum systems and related processing equipment has driven the requirements for the design and operation of components in gas delivery subsystems. Water has been widely regarded as a major contaminant species in such subsystems. For designs that follow generally accepted practices for construction, sealing, and layout, the primary cause of water contamination is associated with ambient atmospheric exposure during maintenance or repair. The subsequent removal of this adsorbed water, and in particular, how this process can be accelerated has been the subject of much interest. While the enhancement of molecular desorption through various methods has received considerable attention, the effective removal of water vapor after desorption is also worthy of attention. This is especially true when considering the typical geometry of gas distribution and delivery subsystems. It is shown that at typical purge pressures a water molecule desorbing from a surface is likely to be adsorbed again. Thus, desorption may be required multiple times for the molecule to be removed from the subsystem. However, if the purge flow is operated at modest vacuum, a desorbing molecule remains in the purge stream considerably longer and travels farther downstream before being re-adsorbed, thus improving the removal rate. The primary focus of this investigation is to understand the dependence of the rate of water removal on the pressure of an inert gas purge. In most cases, the implementation of lower pressure purge may be accomplished with little or no change to existing equipment. In addition to the obvious savings and convenience resulting from a time reduction, considerably less purge gas is consumed.

4:20pm **VT-WeA8 Vacuum Analysis and Improvement for the Jefferson Lab Photo-Electron Guns***, **M.L. Stutzman**, P.A. Adderley, G.R. Myneni, B.M. Poelker,* Thomas Jefferson National Accelerator Facility

The 100 keV photo-electron guns at Jefferson Lab have demanding vacuum requirements since the photo-cathode lifetime is decreased by residual gas ionization and photocathode ion back-bombardment. The gun vacuum in the vicinity of the cathode/anode gap is ~ 1x10@super -11@ Torr. Improved vacuum would enhance the operating lifetime of the photo-electron guns. Measurements on vacuum test stands have been undertaken to better understand the vacuum limitations of the Jefferson Lab photo-electron guns. The measurements include a comparison of vacuum chamber material outgassing rates, preliminary investigations into coatings to reduce outgassing rates, and NEG pump speed measurements under various activation conditions. The results of these studies will be presented together with recommendations for improving photo-electron gun vacuum. @FootnoteText@ This work was supported by U.S. Department of Energy Contract No. DE-AC05-84-ER40150.

4:40pm **VT-WeA9 Status of the SNS Accumulator Ring Vacuum Systems****, P. He, **H.C. Hseuh**, M. Mapes, L.A. Smart, R. Todd, D. Weiss,* Brookhaven National Laboratory

The 2 MW US Spallation Neutron Source (SNS) consists of a 1 GeV linac, a 248m accumulator ring, two beam transport lines, and a mercury target. Brookhaven is undertaking the design, construction and commissioning of the accumulator ring and the beam transport lines for SNS. To this date, over 80% of the ring and transport line vacuum components have been fabricated and assembled. More than 50% of the ring vacuum chambers have been coated with TiN. The physics objective and the design of SNS will be briefly described. The status of the vacuum systems will be presented. Technical developments and challenges encountered, such as remote flange assemblies and conductive coating of large ceramic chambers, will be summarized. *Work performed under Contract Number DE-AC05-00OR22725 with the auspicious of the U.S. Department of Energy.

5:00pm **VT-WeA10 High Vacuum Applications of Silicon-Based Depositions on Stainless Steel***, **D.A. Smith**,* Restek Corporation*; B.R.F. Kendall,* Elvac Associates

Continuing tests of stainless steel components with a silicon-based deposition have shown progressively lower outgassing rates. Evolution of the coating process has led to significantly lower outgassing rates over a wide range of operating conditions when compared with untreated stainless steel and stainless steel surfaces cleaned via a combination of ultrasonic, heat and vacuum techniques. Experimentation was developed for comparing otherwise identical samples having various surface treatments and/or coating types. The samples are heated and cooled in turn while the outgassing rates are recorded at temperatures up to 250 degrees C. Base pressures ranged from 10@super -7@ Torr to 1.2 x 10@super -10@ Torr. The coatings are resilient, inert and capable of withstanding temperatures above 400 degrees C. Other surface aspects have been evaluated, including electronic characteristics and anti-galling traits. As well as the obvious potential for reducing outgassing rates in vacuum chambers thereby allowing shorter pump-down times with smaller vacuum pump systems, these coatings have proved useful in minimizing errors due to thermal desorption in experimental metal-envelope ionization gauges operating down to the low 10@super -10@ Torr range.

Thursday Morning, November 6, 2003

Applied Surface Science
Room 324/325 - Session AS-ThM

Electron Spectroscopy

Moderator: B.R. Rogers, Vanderbilt University

8:20am **AS-ThM1 Role of Vacuum Technology and Other Drivers in the Development of Surface Analysis***, **C.J. Powell**,* National Institute of Standards and Technology **INVITED**

A perspective will be given on the development and use of surface analysis, primarily by AES and XPS, for solving scientific and technological problems. Some of the early approaches for AES and XPS analyses will be described together with major developments (e.g., the availability of demountable flanges and suitable pressure gauges) in instrumental capabilities. Information will be presented on growth and trends in instrumental measurements with reduced uncertainties, knowledge of surface sensitivity, and knowledge and effects of sample morphology. Finally, an overview will be given of analytical resources now available for AES, XPS, and SIMS.

9:00am **AS-ThM3 Valence-band X-ray Photoelectron Spectroscopic Studies of Phosphorus Oxides and Phosphates***, K.J. Gaskell, M.M. Smith, **P.M.A. Sherwood**,* Kansas State University

Valence band X-ray photoemission can be used to identify subtle chemical differences in surface chemistry. Phosphorus oxides are known in a number of different crystalline forms, and a very large number of phosphates are known some of which contain one phosphorus atom, and others contain condensed phosphates with a number of phosphorus atoms in chains, rings and three dimensional structures. The phosphorus oxides can be distinguished from the many phosphate species by valence band X-ray photoelectron spectroscopy (XPS), which is also able to distinguish between different crystalline forms of the oxides. The paper will give an overview of the phosphorus/oxygen valence band spectra, with the spectra interpreted by spectra predicted by band structure and cluster calculations. The paper will also describe how oxide free thin (less than 100@Ao@) films of phosphate species can be formed on metal surfaces, with the phosphate composition altered by changing the pH of the solution used to generate the films, and by changing the type of phosphorus acid used . The work provides an example of how valence band XPS can be especially valuable in the characterization of surface films when it is important to identify small chemical differences. This material was based upon work supported by the National Science Foundation under Grant No. CHE-0137502.

9:20am **AS-ThM4 Application of Electron Based Spectroscopies Combined with Chemical Derivatization for the Characterization of Black Carbon Surfaces***, **L.A. Langley**, T.H. Nguyen, W.P. Ball, D.H. Fairbrother,* Johns Hopkins University

Black carbon (BC) is derived from charred plant materials and soot from combustion processes and is ubiquitous in the environment. It is now recognized that remarkably small concentrations of BC can have strong effects on the sorption of hydrophobic organic chemicals (HOCs). Despite the ubiquity of such BC particulates and the importance of sorption to contaminant fate and treatment, little is known about the physical and chemical variability of BC materials or the manner in which their properties can impact the sorption of HOCs in aquatic environments. The surfaces of soots and chars are best described as extended graphene sheets decorated at the edges by various surface oxides. The nature and composition of these surface oxides is believed to play a critical role in determining the sorption properties of BCs towards HOCs. Although X-ray Photoelectron Spectroscopy (XPS) can provide information on the elemental composition of the surface and detect changes in the O/C ratio of different BCs, quantification of the distribution of surface oxides by analysis of the C(1s) and O(1s) lineshapes alone is very difficult. To circumvent this problem XPS augmented by chemical derivatization has been employed in order to provide quantitative information on the distribution of oxide functional groups on the surface of BC. We will also present results on the potential application of bromine as a chemical derivatizing agent capable of titrating the degree of aromatic character in BCs. Additionally, synthetic chars generated from the pyrolysis of wood samples will be characterized as a function of their formation conditions. Results from XPS and chemical derivatization studies of natural chars and synthetic chars will be presented. These results are complemented by sorption studies, where different trends in sorption can be rationalized based on the surface characterization of the BC sorbents.

9:40am **AS-ThM5 Comparison of X-ray and Electron Beam Induced Damage Rates***, **A.S. Lea**, M.H. Engelhard, D.R. Baer,* Pacific Northwest National Laboratory

While many people are aware of the effects of damaging electrons during Auger electron spectroscopy or electron microscopy, x-ray induced changes in specimens frequently occur and may be more common than often recognized or noted in the literature. Although electrons interact strongly with samples with a high damage cross-section and x-rays of similar energies interact less strongly and penetrate deeper into a material, the mechanisms of damage are often very similar. In an effort to efficiently take advantage of the variety of damage rates reported in the literature to obtain estimates for possible thresholds for different system, we have examined the rates of both electron induced and x-ray induced damage for a variety of materials. Based on the data, an approach is developed to compare x-ray damage rates reported for different systems and an approximate method for comparing electron beam and x-ray damage is reported. The electron beam damage is done using a 10 kV electron beam in a Phi 680 system while the x-ray damage is done in a Phi Quantum 2000. For at least some materials (e.g., poly(vinyl chloride) and poly(acrylonitrile)), the ratio of electron and x-ray damage rates are essentially identical even when the absolute rates differ by a factor of 10.

10:00am **AS-ThM6 Charge Referencing in XPS Analysis of Self-assembled Nano-phase Particle (SNAP) Surface Treatments***, **L.S. Kasten**,* University of Dayton Research Institute*; V.N. Balbyshev,* Universal Technology Corporation*; M.S. Donley,* Air Force Research Laboratory (AFRL/MLBT)

To investigate the surface chemistry of Self-assembled NAno-phase Particle (SNAP) SNAP films, X-ray photoelectron spectroscopy (XPS) was utilized to obtain detailed chemical state information on the coating constituents. SNAP coatings were created by forming nanosized siloxane structures comprised of hydrolyzed tetramethoxysilane (TMOS) and glycidoxypropyltrimethoxysilane (GPTMS) in aqueous solution and then crosslinking them upon application to form thin, dense protective organic surface treatment coatings on Al aerospace alloys. A charge referencing method from which accurate and reliable photoelectron peak binding energies could be determined was developed. In order to gain further insight into the chemical composition of the SNAP coatings, data from three related research efforts involving TOF-SIMS analysis of SNAP coatings, studies of the SNAP solution chemistry, and studies involving modeling of the SNAP oligomer formation process enabled some key assumptions to be made about the structure of the SNAP coatings. Based on these studies, an internal standard was chosen which enabled the spectra to be charge referenced, and the referenced data allowed accurate identification of chemical bonding states in the SNAP coatings. Results show that the Si bonds present in the SNAP film are a combination of the bonds in the individual precursors TMOS and GPTMS. The SNAP coatings retain the siloxane character of the of the GPTMS and TMOS precursors. These data support the concept that the nanosized siloxane macromolecules are retained through the coating application process and comprise the film. This was further verified by the use of a silicon chemical state plot, including the use of the modified Auger parameter. The SNAP film's Auger parameter value fell between the precursors' Auger parameter values. These surface analytical data are both self-consistent and consistent with the observations and assumptions of the model.

10:20am **AS-ThM7 Quantitative Depth Profiling of Silicon Oxynitride Films by Electron Spectroscopy***, **P. Mrozek**, D.F. Allgeyer, B. Carlson,* Micron Technology Inc.

Detailed surface analysis was performed using X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (XAES) on silicon oxynitride (SiON) films grown on silicon (Si). Results of conventional XPS depth profiling of SiON at shallow angles demonstrated high depth resolution with fine details of N and O distributions. Si Auger parameter analysis supplemented XPS by showing the extent of nitridization as a function of depth. Angle-resolved data were analyzed using QUASES-ARXPS software. Results are discussed in terms of possible growth mechanisms of SiON.

10:40am **AS-ThM8 Characterization of Silicon-Oxynitride Dielectric Thin Films using Grazing Incidence X-Ray Photoelectron Spectroscopy***, **E. Landree**, T. Jach,* National Institute of Standards and Technology

The evolution of gate dielectric film thickness outlined in the 2002 International Technology Roadmap for Semiconductors (ITRS) is continually driving the need for new techniques sensitive to variations in spatial composition and thickness on the order of sub-nanometers. One of the promising techniques for characterizing ultrathin films is grazing incidence x-ray photoelectron spectroscopy (GIXPS).@footnote 1@ GIXPS utilizes the dependence on the material properties of the film, and the incident angle of the x-rays to control the electric field penetration in the sample. Varying the angle of incidence from zero to some value slightly greater than the angle for total x-ray external reflection, it is possible to probe nondestructively the chemical nature of the film at different depths. Physical properties such as depth profile, density and thickness, are extracted by comparing the calculated photoemission spectrum of a constructing model of the film structure and the measured angle dependent photoemission spectrum. The measured dielectric thin film thickness and chemical depth profile from a diverse group of silicon oxynitride samples in the range of 2 - 5 nm will be discussed. In addition, challenges associated with the dependence of the technique upon various fundamental materials parameters will be addressed. @FootnoteText@ @footnote 1@ T. Jach and E. Landree. Journal of Surface Analysis. 9, 3 (2002).

11:00am **AS-ThM9 XPS Study of Ultrathin Ferroelectric Films*, L. Vanzetti,* *M. Bersani, M. Barozzi, M. Anderle,* ITC-irst, Italy*; V. Nagarajan, T. Zhao, R. Ramesh,* University of Maryland

Lead zirconate titanate (PZT) thin films have been extensively studied for potential application in nonvolatile memory devices, infrared sensors, and microelectromechanichal systems. In addition to compositional and structural factors, the impact of the thickness of the ferroelectric layer, and the interface quality have to be considered in understanding the structure-property relationship in PZT thin films. In this work we show results of our investigation on ultrathin ferroelectric films by XPS and SIMS. PbZr@sub 0.2@Ti@sub 0.8@O@sub 3@ films of varying thickness were deposited by pulsed laser deposition on SrRuO@sub 3@ buffered SrTiO@sub 3@ substrates. Ferroelectric measurements show that the switchable polarization drastically decreased as the PZT thickness is scaled down from 15 to 4 nm. XPS measurements on the two representative samples, 4 and 15nm thick, show that the composition of both films is the same. Moreover, the surface does not show rutenium segregation from the buffer layer. This result proves that the drop in the polarization is not due to a change in the film composition. In addition, we also show SIMS depth profiling for both films.

11:20am **AS-ThM10 Auger Spectra Line Shape Study in Iron-Aluminum-Oxygen Reaction System*, S. Nayak,*** University of Tennessee, Knoxville*; H.M. Meyer, III,* Oak Ridge National Laboratory*; N.B. Dahotre,* University of Tennessee, Knoxville

Normalized intensity-kinetic energy Auger electron spectra were collected for different state of iron and aluminum. The standards and the samples were ion-sputtered and monitored until they attained a stable spectrum. The line-shape of spectra corresponding to iron in standard pure iron, iron oxides (Feo, Fe@sub 2@O@sub 3@ and Fe@sub 3@O@sub 4@) and Fe@sub 3@Al were compared. The spectra non-metallic irons exhibit distinctly different line shape than that of metallic iron. This change in line shape was also accompanied by shift in peak. Similarly, spectra corresponding to aluminum were collected for pure aluminum, Al@sub 2@O@sub 3@ and Fe@sub 3@Al. There is a distinct change in shape of line both in the case of aluminum and iron. The information was used to study the non-equilibrium two phenomena: (1) laser-induced reaction coating of iron oxide on aluminum alloys and (2) mechanical alloying of iron oxides and aluminum. In laser coating, the high rate of heating and cooling freeze-in the reaction between iron oxides and aluminum. Elemental mapping using the shift in peak position provides information about reaction mechanism. The spectra obtained from laser coating sample has a shape intermediate between purely metallic and oxidized iron and aluminum. The mechanically alloyed powder exhibited spectra line-shape commensurate with the extent of reaction. By choosing the window of kinetic energy, it was possible to map Fe and Al in combined and metallic state distinctly. Al@sub 2@O@sub 3@ and Fe@sub 3@Al were formed during the reaction between iron oxide and Al. The intermediate (frozen-in) reaction products showed gradual change of peak position and line shape from metallic to oxidized state for Fe and Al. The concept of line shape and peak shift was used to successfully study the reaction and its mechanism.

11:40am **AS-ThM11 The Dispersion of Quantum Well States in Cu/Co/Cu(001)*, Y.Z. Wu,*** *C. Won,* University of California, Berkeley*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; H.W. Zhao,* University of California, Berkeley*; N.V. Smith,* Lawrence Berkeley National Laboratory*; Z.Q. Qiu,* University of California, Berkeley

Electrons inside a metallic thin film experience confinement in the normal direction of the film to form quantum well states (QWS) which plays a key role in a number of important properties in metallic thin films such as the oscillatory interlayer coupling, the magnetic anisotropy, the stability of magic thickness, etc. We will report the QWS study using angle resolved photoemission spectroscopy (ARPES) for Cu/Co/Cu(100) system. QWS in the normal direction were studied for both the lower and upper bands relative to the vacuum level. The QWS in both bands can be described as a whole by the phase accumulation method (PAM). The phase shift at the interface can be obtained experimentally. The experimental value of the phase shift deviates away from the value calculated by PAM. The dispersion of QWS with different in-plane momentum was studied near the normal direction. We found that the QWS dispersion depends on the Cu film thicknessï¼Œ and that the quantized perpendicular momentum changes with the in-plane momentum. The latter has a dramatic effect in obtaining the in-plane effective mass of the electron. The in-plane effective mass of Cu increases with the energy.

Technology for Sustainability
Room 320 - Session AT-ThM

Development and Implementation of Sustainable Processes

Moderator: R.L. Bersin, Emergent Technologies Corporation

9:00am **AT-ThM3 Development and Implementation of Green Processes for Manufacturing***, D.A. Dornfeld, **N. Krishnan,*** University of California, Berkeley **INVITED**

Environmental and health issues associated with manufacturing (specially semiconductor manufacturing) are growing in importance and offer strong incentives to reduce resource use and minimize waste. The large flows of materials and energy throughout the economy lead to a wide range of upstream environmental impacts. A strategy for a comprehensive design for environment (DFE) tool to assess the environmental and health impacts of semiconductor manufacturing and to feed this information back into semiconductor equipment and process development cycles is presented. This work builds upon previous research at Berkeley such as environmental value analysis system (EnV-S). A comprehensive approach including (i) scope considering upstream life cycle impacts and facilitating integration into downstream environmental assessments and (ii) metrics supporting a wide range of local and global environmental and health metrics, is proposed. Ideally, feedback loops from DFE tools can inform designers of equipment and processes and aid environmental decision making by regulators, industry suppliers, utilities, etc. A further goal is to promote the broader use of this tool to support industrial ecology. The tool can also have a strong educational component if used in a classroom environment to support the teaching of environmentally conscious manufacturing and industrial ecology. There are several significant intellectual hurdles: what level of detail is required, how can we link upstream life cycle impacts and facilitate downstream environmental assessments of electronics, what local and global environmental metrics are needed (e.g. for health hazard issues), and can the tool be an effective policy planning instrument? The paper will address these issues based on our experience so far with a much reduced scope of effort in EnV-S. The results of this work should establish the feasibility of real, effective design and manufacturing for reduced environmental impact.

9:40am **AT-ThM5 Environmental Accounting of Air Biofiltration using an Energy-based Life-cycle Assessment Approach***, **D.R. Tilley**, P. Ganeshan,* University of Maryland, College Park

Biofilters are shown to remove gaseous pollutants such as volatile organic compounds, hydrogen sulfide, nitric oxide and carbon monoxide from industrial waste emissions. Biofiltration integrates one of nature's most free services into a sustainable technology that has environmental advantages not shared with competitive technologies. To account for the free services of nature used in biofiltration, life-cycle assessment (LCA) was integrated with the solar emergy methodology (emergy is the total amount of energy of one form required directly and indirectly to make a product or provide a service). Our evaluation demonstrates the ability of emergy-based LCA to quantify, and place into perspective, the importance of natural processes in ameliorating industrial wastes. It also quantifies the life-cycle advantages that biofiltration possesses over other treatment technologies.

10:00am **AT-ThM6 Living Machines Out of Control: Experiments in Autonomous Ecological Engineering**, ***P. Kangas**, D. Blersch, D. Callahan, M. Walsh,* University of Maryland

Ecological engineering is a new field that utilizes ecosystems for environmental problem-solving. One application of ecological engineering has been termed living machines because of the close coupling of ecosystem with its technological interface. Most living machine designs have been multipurpose, aquatic systems with an emphasis on wastewater treatment. In this presentation experiments for making living machines autonomous, or self controlling, are described. Three working prototypes are presented to illustrate the path towards living machine autonomy. First, a solar-powered, floating system that improves water quality of a pond or lagoon is described. Second, a wetland soil microcosm that alternatively feeds itself carbon or nitrogen based on a redox sensor is described. Third, a home-scale wastewater treatment and recycling system that is interfaced through the internet is described. These kinds of systems with increasing degrees of autonomy represent a new approach to bioremediation where by living machines work on environmental improvement tasks independently of direct human control. These systems can be thought of as being "out of control" (in the same way as Rodney Brooks' new generation of robots), because they are designed to have their own independent agendas and power sources. Future directions in autonomous living machines are discussed for wastewater treatment and for other biologically-based processes.

10:20am **AT-ThM7 Enhanced Safety, Reliability and Cost Control with Integrated Gas Control Packages**, *N.A. Downie,* Air Products and Chemicals, UK; *J.J. Hart,* Air Products and Chemicals, Inc.; *J. Irven,* Air Products and Chemicals, UK; *R.E. Parise, **R.M. Pearlstein**, J. VanOmmeren,* Air Products and Chemicals, Inc.

The high-pressure gas cylinder is a reliable package for containing and transporting a wide variety of specialty gases used in semiconductor processing operations. These packages are typically used in gas cabinets that feed the delivery lines leading to the point of use. We found it to be advantageous to move some of the functions that control the pressure, flow and purity of the gas away from the gas cabinet panels, where they are conventionally found, by integrating them directly onto the gas cylinder package itself. In this paper, we will outline a number of these integrated functions, and demonstrate how they can lead to improved safety and product quality while also lowering the users' cost of ownership (COO). For example, by integrating a fixed, sub-atmospheric pressure regulator into the cylinder valve, gas will only be dispensed when the suction of the process equipment is applied. As a result, the risk of a hazardous gas release to the atmosphere can be substantially controlled. Further, these integrated delivery systems can permit a greater filling density of the process gas compared to dilute mixtures or low-pressure adsorbent systems. The increased gas inventory significantly reduces the cost of ownership of the system by reducing down-time for cylinder replacements while still effectively mitigating the high pressure risks.

10:40am **AT-ThM8 Responsible Care(r): Protecting our Industry**, ***J. Henninger**,* Air Products and Chemicals, Inc. **INVITED**

When Responsible Care was launched in the late 1980's, it was a groundbreaking initiative and unique in industry. Its goals were: improve environmental, health and safety performance and allay community concerns about the industry. As a result, the performance of the industry improved significantly as did the relationships with our neighbours but not the general public. The program is being expanded and improved significantly to address the issues of today, e.g., terrorism. The presentation will describe the Responsible Care and how Air Products uses it to protect our people, our customers, our communities, the environment, and our license to operate.

Biomaterial Interfaces
Room 318/319 - Session BI-ThM

Biosensors

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

9:00am **BI-ThM3 Simultaneous Electrochemical and Tapping Mode Imaging of Soft Biological Samples with AFM Tip Integrated Nanoelectrodes and Nanobiosensors**, ***A. Kueng**, C. Kranz,* Georgia Institute of Technology; *A. Lugstein, E. Bertagnolli,* Vienna University of Technology, Austria; *B. Mizaikoff,* Georgia Institute of Technology

Recent developments in combined scanning probe techniques are aiming at complementary, simultaneously mapped information on physical and chemical surface properties with high spatial resolution. The integration of micro and nanoelectrodes into AFM tips using micromachining and focused ion beam (FIB) techniques recently described by our research group@footnote 1,2@ enables to simultaneously obtain laterally resolved electrochemical information at the sample surface during tapping mode AFM imaging. A defined geometry of an electroactive surface integrated above the very end of the original AFM tip allows direct correlation of the current signal and the topographical information. Hence, the functionality of scanning electrochemical microscopy (SECM) can be integrated into AFM. The presented technology enables integration of potentiometric electrodes or micro-/nanobiosensors providing simultaneous in-situ information on bioactive processes at the sample surface during AFM imaging. Due to the achieved current-independent positioning of the integrated electrode, biosensor functionality can be realized by modification of the electrode surface with an enzyme receptor, such as peroxidase or glucoseoxidase. Furthermore, bifunctional probes are applied to simultaneously image topographical and electrochemical properties of biologically active sample surfaces in AFM tapping mode. The activity of an oxidoreductase immobilized into a periodic micro-pattern of a soft polymer matrix is electrochemically detected during AFM imaging in tapping mode. For the first time specific detection of a molecular product resulting from enzymatic substrate conversion was obtained during AFM imaging. @FootnoteText@ @footnote 1@ C. Kranz, G. Friedbacher, B. Mizaikoff, A. Lugstein, J. Smoliner, E. Bertagnolli, Anal. Chem., 73, 2491-2500 (2001). @footnote 2@ A. Kueng, C. Kranz, B. Mizaikoff, A. Lugstein, E. Bertagnolli, Appl. Phys. Lett., 82, 1592-1594 (2003).

9:20am **BI-ThM4 Simultaneous Atomic Force Microscopy and Fluorescence Imaging of Supported Biomembranes**, ***A.R. Burns**, J.M. Gaudioso,* Sandia National Laboratories

Lateral organization of lipids and proteins in membranes is critical to cellular signaling processes. Separately, fluorescence imaging and atomic force microscopy (AFM) are both effective ways to map structures in supported membranes. However, the ability to correlate information gathered from fluorescence imaging of labeled biomolecules and lipids with detailed lateral structures mapped out with AFM is highly advantageous. We discuss simultaneous AFM and submicron confocal fluorescence imaging of domain structures in model lipid bilayers. Lipids labeled by fluorescent probes either at the headgroups or tailgroups enable domain contrast in fluorescence imaging on the basis of partitioning between gel and disordered liquid phases. However, correlation with AFM topographic information reveals that they do not always faithfully report exact gel domain size or shape. Furthermore, we find that the fluorescence contrast decreases significantly with domain size, such that small domains observed with AFM are not observed in fluorescence images despite adequate optical resolution. Imaging of labeled proteins bound to membrane receptors is also discussed. In all cases, the complete correlation of topographic and fluorescence images provides evidence that gel-phase domains occur across both leaflets of the bilayer. This research was supported in part by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

9:40am **BI-ThM5 Force Spectroscopy Investigation of HIV Envelope Glycoprotein and Dual Antibody Complex using Atomic Force Microscopy**, ***Y. Lam,*** Duke Univ. and Center for Biomolecular and Tissue Eng.; *W.K. Lee,* Duke Univ.; *P. Marszalek,* Duke Univ. and Center for Biomolecular and Tissue Eng.; *M. Alam,* Human Vaccine Institute; *R. Clark,* Duke Univ.; *B. Haynes,* Human Vaccine Institute; *S. Zauscher,* Duke Univ. and Center for Biomolecular and Tissue Eng.

Understanding the structure-function relationships of pathogenic molecules is the key to designing sensitive detection mechanisms, as well as effective inhibitory drugs. Atomic force microscopy (AFM) is an optimal tool for investigation of these molecular scale biomechanics, as it provides high temporal and spatial resolution while maintaining an aqueous testing environment. In this study, we use the AFM to examine a well-characterized model system of Human Immunodeficiency Virus-1 (HIV-1) envelope glycoprotein gp120 and several monoclonal antibodies. Antibodies were screened before AFM experiments using surface plasmon resonance (SPR), and chosen for greatest binding affinities. In the AFM experiment, one antibody, a human T-cell CD4 mimic, is immobilized on the surface, and functions to bind gp120 from solution. The second antibody, a human chemokine receptor mimic, is attached to the AFM tip, and only interacts with the bound gp120-CD4 complex. A large majority of trials registered adhesion events, qualitatively signifying the presence of gp120. Quantitative analysis determined antibody-antigen binding strengths on the order of 100 pN, in agreement with binding forces of other molecular recognition systems. Experiments with poly(ethylene glycol) tethers and variable pulling rates provide force profiles revealing details of attachment and detachment mechanisms. Results from this study show that AFM can be used effectively as a detection as well as characterization method to better understand the pathogenic system.

10:00am **BI-ThM6 Multi-technique Studies of Bio-Interface Processes; QCM-D, (Nanoparticle) SPR, SERS, AFM, Electrical Impedance, and Cell Force Sensor**, ***B. Kasemo,*** Chalmers University of Technology and Goteborg University, Sweden **INVITED**

Title: Multi-technique studies of Bio-Interface kinetics with QCM-D,(nanoparticle) SPR, SERS, AFM, Electrical Impedance, and Cell Force Sensor. Text: Bio-interface sensing is commonly based on immobilization of some sensing molecules on a surface, and detection of how unknown sample molecules bind specifically to them. Techniques for detection include optical, electrical, mechanical and electro-acoustic methods. The first part of this talk describes the preparation of a sensing platform based on functionalized supported phospholipid bilayers, using QCM-D, AFM, SPR and electrical impedance (ac forward transmission factor).@footnote 1, 2@ Sensing applications with this platform are illustrated by several examples;@footnote 3@ DNA immobilization and hybridization, protein-bilayer interactions, and enzymatic reactions. With the QCM-D technique rich information is obtained through frequency and dissipation shift measurements at multiple (overtone) frequencies, additionally strengthened by combining this technique with SPR. The second part describes nano- and micro fabricated structures for sensing, including EBL fabricated Ag arrays for (G)SERS,@footnote 4@ colloidal lithography of nanoparticles for plasmon resonance enhancement,@footnote 5@ and standing cantilever arrays for cell force sensing.@footnote 6@ @FootnoteText@ @footnote 1@ Reimhult, E., et al., Langmuir 19 (2003) 1681-1691. @footnote 2@ Hook, F., et al., Analytical Chemistry 73 (2001) 5796-5804@footnote 3@ Hook, F., et al., Langmuir 17 (2001) 8305-8312. @footnote 4@ Gunnarsson, L., et al., NanoStructured Materials 12 (1999) 783-788.@footnote 5@ Hanarp, P., et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects 214 (2003) 23-26@footnote6@ Petronis, S. et al Journal of Micromechanics and Microengineering (to be published).

10:40am **BI-ThM8 Coupling of his-tagged scFvs to Functionalized Lipid Assemblies for Array Based Sensing**, ***C. Larsson,*** *F. Höök,* Chalmers University of Technology, Sweden

Lipid bilayers containing 5% NTA-lipids supported on SiO@sub 2@ have been used as a template for efficient immobilization of oligohistidine-tag containing single-chained antibody fragments (scFv) directed towards cholera toxin (CT). It was demonstrated that his-tagged scFv:s is equally efficient coupled to the NTA/Ni@super 2+@ containing lipid bilayer from a purified sample and the expression supernatant. Using the latter, time consuming protein purification steps is avoided. Independent on whether the coupling was made from the supernatant or from the purified sample, the template was proven efficient for antigen detection, in this case verified via the quartz crystal microbalance with dissipation monitoring (QCM-D) technique using the antigen CT (Mw ~85 kD). Via a secondary amplification step utilizing G@sub M1@ containing vesicles, i.e. the membrane receptor for CT, sub-nanomolar concentrations of CT was detectable with QCM-D. Furthermore, this coupling strategy was also utilized for creation of protein array templates. The template was, however, based on novel DNA-array design, using streptavidin-based DNA-immobilization on gold spots, surrounded by a pure lipid bilayer on SiO@sub 2@, but with the aim to be used as a protein array rather than a DNA array. The latter was accomplished using DNA-modified lipid vesicles, directed to predefined DNA spots via complementary hybridization, where the protein-array concept was proven utilizing scFv-modified lipid vesicles utilizing NTA/Ni@super 2+@-based coupling for highly sensitive detection of fluorescently labeled CT.

11:00am **BI-ThM9 Real-Time, Quantitative Surface Plasmon Microscopy Measurements of Protein Adsorption**, ***J.S. Shumaker-Parry,*** University of Washington, presently at the Max Planck Institute for Polymer Research, Germany; *M.H. Zareie, C.T. Campbell,* University of Washington

Surface plasmon resonance (SPR) spectroscopy has become a popular technique for measuring biomolecular interactions in real time with high sensitivity and without labels. SPR microscopy provides the same advantages as SPR spectroscopy with the added feature of using a CCD camera to image changes in reflected light intensity across a large area of a sensor surface simultaneously with good spatial resolution (~ 4 µm). Recently we have developed quantitative SPR microscopy methods for measurement of adsorption and desorption processes in real time based on monitoring changes in reflected intensity at a high contrast angle. For a small range of angles in a linear region of a SPR curve, reflectivity changes are proportional to effective refractive index changes near the sensor surface. By fixing the angle of measurement at a high contrast angle in such a linear region, refractive index changes may be monitored in real time by measuring reflectivity changes for pre-selected regions of a sensor surface. By extending methods used to quantitate SPR spectroscopy wavelength and angle shifts to changes in reflectivity measured by SPR microscopy, quantitative, real-time adsorption measurements are possible. We used these methods to measure adsorption of a DNA-binding protein to its DNA-binding site immobilized in a double-stranded DNA (dsDNA) array on a streptavidin linker layer to demonstrate the use of SPR microscopy for parallel, high-throughput array-based analysis. A major advantage of these array-based studies is the ability to use array elements without the DNA-binding site as reference regions to correct for non-specific adsorption and common refractive index changes. The real-time detection limit for fast time resolution measurements is less than ~8 x 10@super 6@ proteins per 200-µm array spot.

11:20am **BI-ThM10 Material and Surface Characterization of Electrodeposited Polysaccharide Chitosan Film as a Platform for Biomolecular Reactions in BioMEMS Systems**, ***C. Pederzolli,*** *L. Lunelli, G. Speranza, R. Canteri, M. Anderle,* ITC-IRST, Italy; *J.J. Park, L.-Q. Wu, H. Yi, R. Ghodssi, W.E. Bentley, G.F. Payne, G.W. Rubloff,* University of Maryland

The polysaccharide chitosan provides a high density of amine sites for biomolecular adsorption and reaction. Exploiting the fact that under mildly acidic conditions (pKa=6.3) chitosan is water soluble with the amine groups positively charged, we have electrodeposited chitosan onto negative electrodes and demonstrated schemes for attachment of fluorophores, proteins and nucleic acids. The chitosan films can be deposited as relatively compact films or hydrogels, depending on process conditions. We have studied film properties by changing to high pH after deposition, rinsing, and drying. Measurements indicate a complex structure with density substantially lower than expected for a closed packed film, consistent with AFM images which reveal a morphology with substantial (50-150 nm) roughness. One may anticipate deprotonation and local enhancement of the pH at the surface during deposition, which could be accompanied by H@sub2@ evolution; localized features observed in AFM images could be consistent with H@sub2@ bubble formation during electrodeposition. Estimates of amine site density made from these observations are in agreement with fluorescence intensity measurements that directly reveal densities in the range 10@super14@-10@super15@ sites/cm@super2@. XPS and ToF-SIMS reveal chemical components of glucosamine (-CH@sub2@-NH@sub2@) and also of N-acetylglucosamine (-NH-(C=O)-) the monomeric residues of chitosan. The extent of cell adhesion on these chitosan films was analyzed using fibroblast-like cells (NIH-3T3, HGF-1), and results indicate that cell adhesion and growth are dependent on deposition parameters and film thickness. These observations of the materials and surface properties are important for our use of electrodeposited chitosan as a platform for biomolecular reactions in bioMEMS systems.

11:40am **BI-ThM11 Infrared and Visible Spectroscopy of Anisotropic Spin-cast Chitosan Films*, W.H. Nosal*,** *S. Sarkar, A. Subramanian, D.W. Thompson, J.A. Woollam,* University of Nebraska, Lincoln

Chemical modification of chitosan is postulated as a way to control thrombosis at the surface of biomedical implants. Recent interest in performing surface modification of biomaterials has led to chitosan as a candidate to improve biocompatibility, due to the relative ease with which the amine groups can be chemically modified. As a way to evaluate surface modification effectiveness, spin-cast films of chitosan on silicon wafers were characterized using both infrared and visible spectroscopic ellipsometry (SE). Infrared SE data was modeled using a set of harmonic oscillators to represent the chemical bonds of the chitosan molecule. Visible SE data was modeled using an anisotropic uniaxial Cauchy dispersion model. In-plane vs. Out-of-plane optical anisotropy was detected in both the Infrared and visible wavelength data. This work shows there is a preferred orientation of the molecule, likely a result of spin casting. Visible ellipsometry surface mapping was used to determine anisotropy as a function of position on the wafer. This work discusses anisotropy and orientation of identified chemical bonds in a biomolecular film by spectroscopic ellipsometry.

Electronic Materials and Devices
Room 321/322 - Session EM-ThM

Materials for Interconnects and Contacts to Semiconductors

Moderator: S.E. Mohney, The Pennsylvania State University

8:20am **EM-ThM1 Self-aligned Silicides for Ohmic Contacts in CMOS Technology: TiSi@sub 2@, CoSi@sub 2@ and NiSi*, S.-L. Zhang*,** KTH, Sweden **INVITED**

Metal silicides have played an indispensable role during the remarkable developments of microelectronics since PtSi was first used to improve the rectifying characteristics of diodes in early 1960's. Along with several other technological innovations, the implementation of the self-aligned silicide (SALICIDE) technology has paved the way for rapid and successful miniaturization of device dimensions for metal-oxide-semiconductor field-effect transistors (MOSFETs) keeping in pace with the Moore's law. The primary use of silicides has also evolved from creating reliable contacts for diodes, to generating high-conductivity current paths for local wiring, and lately to forming low-resistivity electrical contacts for MOSFETs. With respect to the choice of silicides for CMOS technology, a convergence has become clear with the self-alignment technology using only a limited number of silicides, namely TiSi@sub 2@, CoSi@sub 2@ and NiSi. The present work discusses the advantages and limitations of TiSi@sub 2@, CoSi@sub 2@ and NiSi with the development trend of CMOS technology as a measure. Specifically, the reactive diffusion and phase formation of these silicides in the three terminals of a MOSFET, i.e. gate, source and drain, are analyzed. This work ends with a brief discussion about future trends of metal silicides in micro/nanoelectronics with reference to the potential material aspects and device structures outlined in the International Technology Roadmap for Semiconductors.

9:00am **EM-ThM3 Ni-Si Thin Films Reactions at Low Temperatures: Phase Identification and Sequence Characterization*, C. Coia,*** École Polytechnique de Montréal, Canada*; C. Lavoie,* IBM Research*; M. Tremblay,* École Polytechnique de Montréal, Canada*; C. Detavernier, F.M. d'Heurle,* IBM Research*; P. Desjardins,* École Polytechnique de Montréal, Canada

The phase formation sequence upon thermal annealing of 5 to 20-nm-thick Ni layers on Si(001) has been investigated using a combination of in-situ synchrotron x-ray diffraction (XRD), diffuse elastic light scattering, and electrical resistance complemented by post-annealing transmission electron microscopy and XRD analyses. In addition to the generally reported Ni@sub 2@Si, NiSi, and NiSi@sub 2@ phases, we observe the formation of several metal-rich silicide compounds at low temperatures. The complete sequence is identified as Ni-Ni@sub 31@Si@sub 12@-Ni@sub 2@Si-Ni@sub 3@Si@sub 2@-NiSi-NiSi@sub 2@ with the possible brief appearance of Ni@sub 3@Si preceding Ni@sub 31@Si@sub 12@. The sequence observed for Ni reaction with B- and P-doped Si(001) starts at higher temperatures and occurs over a narrower range in temperature than for undoped Si(001), n-doping having a stronger influence thus showing the larger increase in temperature. Quantitative analyses of XRD peak intensities during isothermal anneals are used to determine rate limiting mechanisms and reaction kinetics. In complementary experiments, 200-nm-thick single-phase layers were obtained for each of the stable phases present in the Ni-Si binary phase diagram in order to determine their physical and chemical properties. The phase formation sequence in these thicker layers of fixed composition suggests that the phases still grow sequentially with the first phase being the Ni@sub 31@Si@sub 12@.

9:20am **EM-ThM4 Development of Ohmic Contact Materials for Compound Semiconductors*, M. Murakami*,** *M. Moriyama, S. Tsukimoto,* Kyoto University, Japan **INVITED**

Compound semiconductors have been extensively used in a variety of devices which Si semiconductor cannot function. Although wide gap compound semiconductors are attractive for light emitting diodes, ultra-violet laser diodes, and high frequency and/or high power devices, lack of reliable, low resistance ohmic contact materials for these compound semiconductors hinders development of these devices. Our studies on ohmic contacts for GaAs, SiC, and diamond (although not compound semiconductor) indicated that formation of an intermediate semiconductor layer (ISL) which reduced the barrier height and/or the width of the depletion region (formed at an interface between the contact metal and the semiconductor) was essential to prepare low resistance ohmic contacts. Thus, once key materials for ISL formation was found, reduction of the contact resistance was obtained in these contacts by annealing at an optimum temperature. However, materials to form ISL could not be found for InP, ZnSe, GaN, and InGaN. For these semiconductors, not only search of materials to form ideal ISL's by reacting with these compound semiconductors should be continued, but also another contact formation mechanism should be explored. Our recent activities for ohmic contact formation mechanisms for various compound semiconductors will be reviewed.

10:00am **EM-ThM6 Indium-Based Ohmic Contacts to n-Type Gallium Antimonide*, J.A. Robinson*,** *S.E. Mohney,* The Pennsylvania State University

Antimonide based compound semiconductors are promising for a variety of optoelectronic and electronic devices. For some of these devices, shallow ohmic contacts to n-type GaSb are required. Among the ohmic contacts that have been developed for this semiconductor, indium-bearing contacts have provided the lowest specific contact resistances. These contacts offer the possibility of lowering the bang gap of the semiconductor and the barrier height at the metal/semiconductor interface through the formation of InGaSb near the metal/semiconductor interface. However, no studies have been reported demonstrating indium-bearing contacts that remain very shallow, penetrating only tens of nanometers into the semiconductor. Furthermore, the surface morphology of these contacts can be poor due to In agglomeration. Using Pd and In, we are engineering shallow In-based contacts with improved surface and interfacial morphology. To achieve this goal, we are combining an investigation of the phase equilibria in the relevant multi-component systems and an understanding of the kinetics of reaction at the Pd/GaSb interface. In this presentation, we describe the formation of newly identified ternary phases in the Pd-Ga-Sb system, the kinetics of reaction at the Pd/GaSb interface, and the formation of ohmic contacts containing Pd and In on n-type GaSb (n = 2.8 x 10@super 18@ cm@super -3@). By choosing the proportions of Pd and In with guidance from multi-component phase diagrams and by minimizing the sheet resistance of the metallization itself, we have achieved to date contact resistances as low as .085 ohm-mm and specific contact resistances as low as 2 x 10@super -6@ ohm-cm@super 2@.

10:20am **EM-ThM7 Long and Short Term Thermal Stability of Gate Metallizations on GaN/AlGaN/GaN Heterostructures*, E.D. Readinger*,** *S.E. Mohney,* Penn State University*; R. Therrien,* Nitronex Corp.

The III-nitride family of semiconductors is expected to provide devices for a variety of high power/high temperature applications, but only a few reports have addressed the thermal stability of gate metallizations for high electron mobility transistors (HEMTs) designed for these applications. This study examines two different forms of thermal stability. First, high temperature rapid thermal processing (RTP) commonly used for ohmic contact formation is used to identify candidates for gate metallizations that could be deposited prior to the anneal of source and drain ohmic contacts. Second, long-term anneals at moderate temperatures to accelerate the aging of HEMTs have been performed. A GaN capped Al@sub 0.23@Ga@sub 0.77@N/GaN heterostructure was used; the metallizations Re, Pt, Au, Ni, Ni/Au, Ni/Ga/Ni and Co were tested; and current-voltage curves were evaluated. Aside from Au and Pt which begin degrading above 400°C, the contacts exhibited neither improvement nor degradation after annealing for 60 s at 600°C. All the metallization schemes degrade above 600°C; however, Re showed marked improvement at 800°C for 60 s, returning to the as-deposited condition. The same metals were evaluated for long times at 425°C and 550°C. Although the commonly used Ni/Au contacts did not provide the lowest reverse currents among the metals tested, they do provide great stability at either temperature for at least 4 weeks. Rhenium exhibits improvement with respect to reverse currents after long times at 425°C, whereas most other contacts either degrade or remain stable. Materials characterization of the contacts will also be presented.

10:40am **EM-ThM8 Compositional Shift in Al@sub x@Ga@sub 1-x@N Induced by Reaction with Metallic Thin Films***, **B.A. Hull**, E.D. Readinger, S.E. Mohney,* The Pennsylvania State University*; U. Chowdhury, R.D. Dupuis,* The University of Texas at Austin

The increasing use of AlGaN in group III nitride devices calls for further advances in our understanding of the chemistry of contacts to this alloy semiconductor. Interfacial reactions between the metals Ni, Pd or Au and Al@sub x@Ga@sub 1-x@N (0.15 < x < 0.6) have been studied for annealing temperatures of 250 to 900°C. X-ray photoelectron spectroscopy indicates that the Al to Ga ratio within the Al@sub x@Ga@sub 1-x@N directly beneath the contact metal increases, in some cases dramatically. Elemental profiles across the interfaces of annealed Ni/Al@sub 0.47@Ga@sub 0.53@N samples obtained by scanning transmission electron microscopy confirm the Al-enrichment near the interface. The Al-enrichment is consistent with thermodynamic modeling, which indicates that the AlGaN composition is favored to shift towards the more stable of the two binary nitride components (AlN). Less severe annealing conditions result in smaller compositional shifts; however, a very narrow annealing temperature range (750°C to 825°C) was required to induce extensive compositional shifts (greater than 5% increase in x), regardless of the initial Al@sub x@Ga@sub 1-x@N composition, indicating that extensive reaction is limited by the slow diffusion of Ga and Al within the AlGaN rather than the thermodynamic driving force for reaction. These compositional shifts can be expected to significantly impact the electrical properties of contacts annealed at high temperature due to the strong dependence of the band gap and Schottky barrier height on the AlGaN composition. We have correlated these reactions to the electrical characteristics of annealed ohmic contacts to p-type AlGaN as well as the thermal stability of Schottky contacts to n-type AlGaN.

11:00am **EM-ThM9 Low Temperature Chemical Vapor Deposition and Characterization of Ultra-thin Ruthenium for Copper Diffusion Barriers in ULSI Interconnects***, **Q. Wang**, Y.-M. Sun, D. Gay, J.M. White, J.G. Ekerdt,* University of Texas at Austin

Ultra-thin ruthenium (Ru) films covering Ta were investigated as part of a Cu diffusion barrier with enhanced adhesion of Cu that potentially enables seedless Cu plating on the barrier surface in ULSI interconnect processes. A low temperature thermal chemical vapor deposition (CVD) of ultra-thin Ru films on Ta and SiO@sub 2@ surfaces using ruthenium carbonyl [Ru@sub 3@(CO)@sub 12@] as a precursor was developed. Films deposited at substrate temperatures between 423 and 593 K were characterized using in-situ X-ray photoelectron spectroscopy (XPS), atomic force microscopy and in-situ four-point probe resistance measurements. A pure Ru ultra-thin film with low resistivity of ~50 µ@Ohm@@super .@cm was deposited without any reactive gas at temperatures as low as 423 K. In-situ ion scattering spectrometry and Ta 4f XPS peak attenuation indicated that the minimum thickness to form a continuous Ru film on Ta is ~2.5 nm. The pure Ru film also showed good thermal stability at elevated temperatures (up to 593 K). This Ru film also inhibited oxidation of the Ta film when the sample was exposed to air. Compared with poor wettability of Cu on Ta, only ~0.3 nm of Cu fully covers Ru indicating excellent wetting.

11:20am **EM-ThM10 Evaluating Ruthenium Thin Film Deposited on Silicon as a Directly Plate-able Cu Diffusion Barrier***, **O. Chyan**,* University of North Texas*; T.G. Hurd,* Texas Instruments*; R.M. Wallace, M.J. Kim, R. Chan, T. Arunagiri,* University of North Texas

Tantalum (Ta) and tantalum nitride (TaN) bilayer diffusion barrier is currently used in the fabrication of 130 nm integrated circuits to ensure the electrical integrity of the copper interconnects. Thin Ta/TaN are too resistive to plate Cu effectively, additional Cu-seed layer is deposited on Ta/TaN to carry the required current for copper electrofill. However, the Cu-seed/Ta/TaN tri-layer configuration will encounter severe scaling difficulties at the 45 nm node where ultra-thin barrier is need to minimize effects on interconnect resistivity. In this paper, we explore using ruthenium (Ru) as a new Cu diffusion barrier to afford direct Cu plating without the additional Cu-seed layer. Ru is an air stable transition metal with high melting point (2310 C) and is nearly twice as thermally and electrically conductive as Ta. More importantly Ru, like Ta, shows negligible solid solubility with Cu even at 900 C. The preparation and interfacial characterization of Cu thin film on both Ru metal surface and Ru thin film (<10 nm) sputtered on silicon wafer substrate will be discussed. Both dry (magnetron sputtering) and wet (electrodeposition) preparation routes were employed to deposit Cu on Ru. We will present un-published results that demonstrate efficient Cu plating (over 95% efficiency) was achieved on a ~8 nm an ultra-thin film of Ru metal deposited on silicon wafer. The nucleation and growth of Cu deposited layer on Ru was studied by the current transient techniques. The Cu deposited Ru thin film samples (Cu/Ru) were characterized by XPS, SEM, AFM. XRD and SIMS depth profiling. The observed direct Cu-plating on the ultra thin Ru film with excellent adhesion and the effective barrier performance properties based on SIMS depth-profiling and sheet resistance measurements underscores the potential of Ru as an effective direct plate-able Cu diffusion barrier for the advanced 65 and 45 nm nodes.

11:40am **EM-ThM11 ZrB@sub 2@ Diffusion Barriers: Conformal CVD Below 400 °C***, **E.J. Klein**, D.-Y. Kim, S. Jayaraman, G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are classified as "metallic ceramics" due to their high mechanical hardness, chemical stability, melting temperature > 3000 °C and low electrical resistivity. This combination of properties makes them attractive as diffusion barrier materials for the contact metallization in next-generation microelectronics or to wide bandgap semiconductors. We report the low temperature and fully conformal chemical vapor deposition of ZrB@sub 2@ thin films with essentially bulk properties. The ZrB@sub 2@ films are deposited at substrate temperatures of 200-500 °C using the single-source precursor Zr(BH@sub 4@)@sub 4@ and a concurrent flux of atomic hydrogen produced by a remote hydrogen plasma source. The films have a B/Zr atomic ratio of 2 and electrical resistivity < 40 µm@ohm@-cm; those produced at < 400 °C appear amorphous in X-ray diffraction. By contrast, films grown without the use of atomic hydrogen are B-rich, oxidize rapidly in air, and have high resistivity; these problems were typical of previous attempts to deposit ZrB@sub 2@ films reported in the literature. In this work, we study the diffusion barrier characteristics of ZrB@sub 2@ by annealing a sandwich structure of evaporated Cu (50 nm) / amorphous ZrB@sub 2@ (20 nm) / c-Si(100) [both n- and p-type]. For various annealing temperatures, we report the contact resistivity, stress, and micromorphology. Initial results show that no Cu diffuses into Si during annealing up to 650 °C for 30 minutes; the onset of Cu in-diffusion correlates with the appearance of crystalline X-ray diffraction peaks for ZrB@sub 2@. We will discuss the failure mechanism of the barrier material.

Homeland Security Topical Conference
Room 309 - Session HS-ThM

Detection of Biological Agents and Self-Cleaning of Contaminated Surfaces

Moderators: L.J. Buckley, Defense Sciences Office, DARPA, D.W. Grainger, Colorado State University

8:20am **HS-ThM1 Direct Electrical Detection of Specific Protein Binding at Surfaces***, **T.L. Lasseter**, W. Cai, W. Yang, R.J. Hamers,* University of Wisconsin, Madison

Most biological analyses ultimately rely on optical methods of detection. Here, we show that the binding of proteins to surfaces can be detected electrically in a completely label-free manner using electrochemical impedance spectroscopy. Experiments have been conducted on several different substrates including gold, glassy carbon, and silicon. In each case, we covalently linked biotin to the surface, and then investigated the changes in electrical impedance when the surface was exposed to avidin over the frequency range from 5 mHz to 1 MHz. The changes in impedance are most apparent at low frequencies, < 1 Hz. By using fluorescently-labeled avidin, we also correlated the magnitude of the observed electrical changes with the intensity of the observed fluorescence from the surface. Measurements of the impedance changes as a function of avidin concentration show that the detection limit from these electrical measurements is comparable to or even better than the detection limit observed from fluorescence spectroscopy. Finally, circuit modeling of the interface is being use to relate the electrical changes observed to the physical structure of the interface.

9:00am **HS-ThM3 Autonomous DNA Testing for Bio-Detection*, K. Petersen,*** Cepheid **INVITED**

After 18 months of extensive testing and evaluation, the US Postal Service has made a decision to deploy automatic bio-threat detection systems in mail sorting facilities throughout the United States. A team, including Northrop Grumman, Cepheid, Smiths Detection, and Sceptor has developed this system called BDS (Bio Detection System). The BDS system will be the first and only automated, nationwide bio-threat detection system approved through rigorous testing of stringent systems requirements. The highest possible detection sensitivity is achieved by using the polymerase chain reaction (PCR), which is increasingly becoming the "gold standard" for biological detection and identification; oftentimes better than culturing. The lowest possible false positivity rate is achieved by extensive internal controls and assay validation procedures. Some aspects of the performance of the BDS system actually exceeds that of the US blood banking system for pathogen detection. Yet, all of this sophisticated, state-of-the-art biological processing is performed completely automatically, in a dusty, industrial environment in about 30 minutes. This presentation will describe the advanced fluidic, biological, chemical, and engineering aspects of this revolutionary technology. We will also discuss how a key sub-system of the BDS, the GeneXpert, is being applied to many other biomedical applications such as the detection of infectious diseases and cancer.

9:40am **HS-ThM5 Magnetically Based Microarray Platform for Rapid Handheld Bioassays*, M.C. Tondra,*** NVE Corp.

Biochemically functionalized magnetic beads are being used as labels in the development of rugged, handheld bioassays. These magnetic labels can be adapted for use in both protein and DNA assays. A palm-sized magnetic excitation module has been fabricated and demonstrated with integrated Giant Magnetoresistive (GMR) detector arrays. The arrays have 20 sites, each of which is a GMR magnetic sensor underneath a 200 micron diameter functionalizable assay surface. The sites are functionalized by attaching a reference protein or oligonucleotide to the surface. The assay is typically a sandwich-type assay, though other techniques are possible. The sensitivity of the assay is quite good, with reports of better than 1 femtoMolar detection limits. The integrated detectors can detect a single immobilized magnetic label, and has a dynamic range of better than 10^3. The ultimate performance of a given assay is dependent on microfluidics and sample handling. The magnetic detection scheme has several advantages over common optically based techniques. The excitation device and detector array are both solid state devices and are inherently rugged. Both are amenable to low cost mass- manufacturing techniques. And it is possible, with sophisticated sample handling, that PCR amplification may be unnecessary due the ability to detect a single label. Magnetic forces may also be used to enhance reaction rates and improve specificity. This presentation will address issues related to fabrication and surface modification of the GMR sensor array chip. The most common assay surfaces include silicon nitride, silicon dioxide, aluminum dioxide, and gold. In all cases, the surface quality must be very high to achieve predictable and desirable assay results. With continued development, this magnetic bioassay platform should prove to be ideal for applications where high speed multiplexed sandwich-type assays are done on a disposable platform.

10:00am **HS-ThM6 Microfluidic Approaches to Improving Biosensor Performance*, J.C. Rife,*** *P.E. Sheehan, L.J. Whitman,* Naval Research Laboratory

The sensitivity of a microarray biosensor depends on many factors other than the sensor performance, including sensor area, analyte diffusion, and non-specific binding of target and/or label. However, when the detection system is sensitive enough to detect single labels, the performance will be limited by these factors. We are confronting such limitations in the development of two systems for biowarfare pathogen detection. The Bead ARray Counter (BARC) and the Force Discrimination Biosensor (FDB) systems use biomolecular recognition to bind magnetic microbeads to either a solid or porous substrate. At our current detection limits, we are labeling one analyte molecule per detectable microbead. Under these conditions, the BARC system can detect DNA concentrations as low as 1 fM (10@super 5@ molecules/ml) and FDB can sense protein toxins at concentrations <0.5 pg/ml (10@super 6@ molecules/ml). Further gains in system performance will depend on careful design of the fluidics systems. We will present analytical and finite element calculations aimed at understanding and optimizing the microfluidic delivery of assay reagents to the sensor surfaces. The role of flow profile, fluidic forces, and sensor geometry in maximizing the assay performance will be discussed.

10:20am **HS-ThM7 Comparison of Bioassay Surface Chemistries on Gold and Alumina Films*, S.P. Mulvaney,*** *C.L. Cole, J.C. Rife, K.A. Wahowski, L.J. Whitman,* Naval Research Laboratory

The surface bioaffinity coating is arguably the most critical component of any biosensor based on ligand-receptor capture on a solid substrate. The characteristics of this interface have profound effects on the overall performance of the sensor, affecting the assay sensitivity and selectivity (including background due to non-specific binding), and signal transduction. The physical properties of the sensor surface must be compatible with the detection method employed and chemically suitable for functionalizing with receptor biomolecules such as antibodies or oligonucleotides. The utility of gold films for electrochemical and optical detection schemes has made it one of the most commonly used sensor surfaces. One common approach to functionalizing gold is to first conjugate the desired biomolecules to a mercaptan functional group which can then immobilized on the surface via a Au-S bond. Alternatively, thiolated self-assembled monolayers (SAMs) can be used as a base for subsequent conjugation with biomolecules. SAM-based films, while effective, often lack the reproducibility required for reliable, quantitative assays. Therefore, we are exploring alternate surfaces and surface chemistries. We have developed and characterized multilayer, biocompatible polymer films on alumina surfaces and found them to be more reproducible than similar films on gold. The effects on assay performance for various chemistries on top of gold and alumina films will be compared and contrasted as used in the Bead Array Counter (BARC),@footnote 1@ a biosensor system that uses paramagnetic beads. CL Cole and KA Wahowski are employees of Nova Research, Inc., Alexandria, VA. @FootnoteText@ @footnote 1@Edelstein et. al., Biosens. Bioelectron. 2000, 14, 805-813.

10:40am **HS-ThM8 Biocatalytic Nanocomposites as Self-Cleaning Surface Coatings*, J.S. Dordick,*** Rensselaer Polytechnic Institute **INVITED**

The interface of biology and materials science has led to the development of new materials, with unique structural and functional properties, and new process technologies complete with the ability to produce, from "bottoms up", a wide range of biomimetic structures. These materials and their designs have broad application as catalysts, sensors, and devices for use in synthesis, cell and tissue engineering, bioanalysis and screening, and nanoelectronics. We have focused on the generation of nanostructures that are functionalized with and in some cases constructed from biological molecules, complete with tailored selectivities and biocatalytic activities at the molecular and nanoscales.@footnote 1,2@ In one example, we have incorporated enzymes attached to carbon nanotubes and further embedded into polymeric films, coatings, and paints to form biocatalytically active surfaces. These materials are capable of degrading proteins, fats, polysaccharides, and other organic and biological molecules. Furthermore, in some cases, these materials can prevent the microbial fouling often associated with surface coatings, and this may have significant impact in medical devices and in battlefield and homeland defense. This presentation will be focused on the preparation, characterization, and use of different enzyme-nanomaterial-polymer composites and potential broad-based applications arising from this technology. @FootnoteText@ @footnote 1@K. Rege, N.R. Raravikar, D.-Y. Kim, L. S. Schadler, P.M. Ajayan, and J.S. Dordick (2003), "Enzyme-Polymer-Single Walled Carbon Nanotube Composites as Biocatalytic Films", Nano Letters (submitted).@footnote 2@ P. Wang, M. V. Sergeeva, L. Lim, and J. S. Dordick (1997), "Biocatalytic Plastics as Active and Stable Materials for Biotransformations", Nature: Biotechnology 15, 789-793.

11:20am **HS-ThM10 Novel Surface-Segregating Materials for Chem-Bio Applications*, J.A. Orlicki,*** *M.S. Bratcher, R.E. Jensen, C.A. Winston, S.H. McKnight,* Army Research Laboratory, AMSRL-WM-MA

Macromolecular surfactants based upon hyperbranched polymer scaffolds have been employed to deliver functional groups to the surface of a substrate. Careful selection of end group chemistry allows the control of thermodynamic phase segregation, leading to an increased loading of additive at a substrate surface relative to the bulk concentration. The high number of end groups of a hyperbranched polymer permits the covalent attachment of additional moieties for added functionality (e.g. solubility control, reactive groups, ligand binding sites). Employing these molecules as additive to bulk polymer systems will provide a method to impart chemical or biological resistance upon delicate materials (electronics packaging, clothing) at minimal cost. We have developed polymers capable of chelating metal centers (polyoxometalates), and have shown their ability to transport the metals to a substrate surface. Contact angle and XPS analysis indicated the segregation of metals to the surface only when interacting with the macromolecular surfactant. These results will be discussed, along with the accompanying synthetic techniques to spur the development of novel active groups for surface functionalization.

11:40am **HS-ThM11 Opportunities in Materials Chemistry at DARPA**, ***L.J. Buckley***, Defense Sciences Office, DARPA

Materials chemistry at the surface impacts many areas of science and engineering. As one approaches nanometer dimensions, the surface properties will dominate the material behavior. The Defense Advanced Research Projects Agency (DARPA) has many opportunities for the application of materials chemistry for the general modification of surface behavior. A summary of these opportunities will be presented.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI+SC-ThM

New Spintronic Materials

Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI+SC-ThM1 Materials for Spin Injection Into GaN-Based Devices**, ***C.R. Abernathy****, G.T. Thaler, R.M. Frazier, A. Stewart, S.J. Pearton, F. Ren,* University of Florida*; Y.D. Park,* Seoul National University, Korea*; R. Rairigh, J. Kelly,* University of Florida*; J. Lee,* Seoul National University, Korea*; A.F. Hebard,* University of Florida **INVITED**

Future spintronic devices will likely require injection of polarized currents into semiconductor devices. Though significant work has been carried out in GaAs-based materials, the rapid advancement of GaN-based devices for visible light emission and high power electronics makes this an attractive system for investigation. Two types of spin injection layers appear most promising. One approach is to incorporate magnetic ions into the semiconductor. The introduction of Mn into GaN has been shown to produce ferromagnetism at 300K, making it one of the few DMS materials which may be technologically useful. This method may be limited by the relatively low degree of ordering and the possibility of scattering at the DMS/semiconductor interface. An alternative approach is the use of ferromagnetic layers with metallic conduction, such as MnAs. This material has been used to produce polarized injection into GaAs-based structures, though only at low temperature. Though the lattice mismatch to GaN is greater than for GaAs, the MnAs crystal structure possesses the same Group V symmetry as GaN. This may make growth of a good quality MnAs/GaN interface more achievable than for the MnAs/GaAs heterostructure. This talk will discuss the growth and characterization of both of these types of spin injection layers on GaN. Gas-source molecular beam epitaxy using either an RF nitrogen plasma source, for GaMnN, or AsH3, for MnAs, along with elemental sources for Ga and Mn have been used to deposit thin films on MOCVD GaN buffer layers. Conditions for depositing single phase material with optimum magnetic ordering will be described. The processing challenges associated with integrating these materials into standard GaN/AlGaN light emitting diodes (LEDs) will be discussed along with preliminary electroluminescence results from SpinLEDs fabricated using only low temperature processing. This work was supported by the U. S. Army Research Office (ARO-DAAD19-01-1-0701) and NSF (ECS-0224203).

9:00am **MI+SC-ThM3 Characterization of AlGaN and AlN Based Dilute Magnetic Semiconductors**, ***R.M. Frazier***[1]*, G.T. Thaler, J. Stapleton, C.R. Abernathy, S.J. Pearton,* University of Florida*; M.L. Nakarmi, J.Y. Lin, H.X. Jiang,* Kansas State University*; R. Rairigh, J. Kelly, A.F. Hebard,* University of Florida*; J.M. Zavada,* U. S. Army Research Office*; R.G. Wilson,* Consultant

The realization of room temperature ferromagnetism in GaN@footnote 1@ has ignited interest in the development of magnetic devices based on existing wide bandgap technology. However, in order to integrate magnetic semiconductors into the existing technology, it may be necessary to tailor the bandgap through addition of Al. Thus, AlGaN and AlN are two promising candidates for investigation, but optimization of the material in terms of choice of dopant, magnetic characteristics and crystalline quality is necessary before device fabrication can be undertaken. Ion implantation has been shown to be an effective survey method for optimization of dopant type and concentration. In this study, AlGaN and AlN grown on sapphire substrates by Metal Organic Chemical Vapor Deposition have been implanted with Mn, Cr, and Co at high doses (3x10@super 16@ cm@super -2@, 250 keV). After implantation the samples were annealed at 900°C for activation. Photoluminescence of the AlGaN-based alloys showed no band-edge luminescence before or after ion implantation, but the implantation process did introduce deep emission lines. In AlN, the Co and Cr doped films showed hysteresis at 300K while the Mn doped material did not. Epitaxial AlMnN by contrast does show hysteresis at room temperature suggesting that defects may be deleterious to magnetic ordering. The effects of dopant type and host conductivity type on the magnetic and electrical properties after implantation into AlGaMnN will also be presented. The work was supported by the Army Research Office under ARO-DADD19-01-0-0701, ARO-DAAF190110701 and DAAF 19021420 and by NSF under ECS-0224203, DMR 0101856, and DMR 0101438. @FootnoteText@ @footnote 1@ G. T. Thaler, M. E. Overberg, B. Gila, R. Frazier, C.R. Abernathy, S. J. Pearton, J. S. Lee, Y. D. Park, Z. G. Khim, J. Kim, F. Ren, Appl. Phys. Lett. 80, 3964 (2002).

9:20am **MI+SC-ThM4 Growth and Characterization of GaMnN/AlN Multiple Quantum Wells**, ***G.T. Thaler****, R.M. Frazier, J. Stapleton, C.R. Abernathy, S.J. Pearton, R.P. Rairagh, J. Kelly, A.F. Hebard,* University of Florida

Though a number of recent studies have reported room temperature ferromagnetism in GaMnN, some important questions remain including determining the minimum layer thickness needed for ferromagnetic ordering.@footnote 1,2,3@ In this paper, we report on the growth and characterization of a variety of multiple quantum well structures comprised of layers of GaMnN and AlN. XRD analysis of the layers showed sharp satellite peaks indicative of good interfacial quality. By contrast to the GaMnAs system, magnetic ordering was maintained even for structures with 5nm GaMnN layer thicknesses. The magnetic moment of the GaMnN/AlN layers was determined to be ~1.7 Bohr magnetons per Mn, much higher than the 1.1 Bohr magnetons per Mn obtained in 200nm GaMnN films grown under the same conditions. This increase is believed to be due in part to improved crystallinity brought about by the presence of the AlN and also due to strain induced by the smaller lattice constant of the AlN. The use of strained superlattices has been shown to increase the activation of the deep acceptor Mg in p-GaN and p-AlGaN.@footnote 4,5@ It is likely that a similar effect is increasing the concentration of Mn+2 relative to Mn+3, resulting in a higher moment than in the thicker films. Attempts to tailor the strain, and the magnetic properties, by varying the Al content in the buffer and barrier layers will be discussed, as will the potential for using these phenomena to make magnetic strain sensors. This work was supported by the Army Research Office under: ARO-DAAD19-01-1-0701 and by NSF under: ECS-0224203 and DMR 0101856. @FootnoteText@ @footnote 1@ G.T. Thaler, et al. Appl. Phys. Lett. 80, 3964 (2002). @footnote 2@ S. Sonada, et al. J. Cryst. Growth 237-239, 1358 (2002). @footnote 3@M.L. Reed, et al. Appl. Phys. Lett. 79, 3473 (2001). @footnote 4@ Y.-L. Li, et al. Appl. Phys. Lett. 76, 2728 (2000). @footnote 5@P. Kozodoy, et al. Appl. Phys. Lett. 74, 3681 (1999). .

9:40am **MI+SC-ThM5 Theory of Dilute Magnetic Semiconductors**, ***P. Bruno***, Max Planck Institute of Microstructure Physics, Germany **INVITED**

10:20am **MI+SC-ThM7 Materials Characterization and Magnetic Studies of Epitaxial Co@sub x@Ti@sub 1-x@O@sub 2-x@ Deposited on Si(001) by Molecular Beam Epitaxy**, ***T.C. Kaspar***[2]*,* University of Washington*; T. Droubay,* Pacific Northwest National Laboratory*; A.C. Tuan,* University of Washington*; C.M. Wang, S.A. Chambers, J.W. Rogers, Jr.,* Pacific Northwest National Laboratory

For spintronic devices such as spin-FETs, efficient injection of spin-polarized electrons into a semiconductor material is necessary. Progress has been made using ferromagnetic metals to tunnel spin-polarized electrons into AlGaAs/GaAs quantum well structures. However, for devices compatible with current semiconductor technology, efficient spin injection into Si is desired. Diluted magnetic semiconductors (DMSs) that can be grown epitaxially on Si are prime candidates. The epitaxial growth will result in a high-quality interface, reducing depolarization caused by scattering at interfacial defects. Further, the conductivity of the DMS can be tuned by doping to match that of Si, greatly increasing the spin injection efficiency. While most known DMS materials have Curie points well below room temperature, anatase Co@sub x@Ti@sub 1-x@O@sub 2-x@ has been shown to have a Curie temperature of at least 700K when deposited on LaAlO@sub 3@(001). In addition, anatase is well lattice-matched to Si. To prevent interfacial reactions between the film and substrate resulting in SiO@sub 2@ and/or silicide formation, a buffer layer of epitaxial SrTiO@sub 3@ (STO) is first deposited. In this study, a STO buffer layer and Co@sub x@Ti@sub 1-x@O@sub 2-x@ film on Si(001) are deposited by

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[1] **Falicov Student Award Finalist**

[2] **Falicov Student Award Finalist**

molecular beam epitaxy (MBE), which has been shown previously to result in higher quality Co@sub x@Ti@sub 1-x@O@sub 2-x@ films than pulsed laser deposition (PLD). Magnetic films have been successfully deposited with Co in the +2 charge state. The growth mode of Co@sub x@Ti@sub 1-x@O@sub 2-x@ has been investigated to minimize the formation of Co-rich anatase particles on the film surface. Thorough materials characterization of the Si interface, the STO buffer layer, and the Co@sub x@Ti@sub 1-x@O@sub 2-x@ film will be presented, paying particular attention to the possibility of metallic Co atoms in the film. In addition, the electronic and magnetic properties of the structure will be presented.

10:40am **MI+SC-ThM8 Ferromagnetic Co-doped Anatase TiO@sub 2@: Are All Growth Methods Created Equal?**, ***T. Droubay***, *S.M. Heald,* Pacific Northwest National Laboratory*; T.C. Kaspar,* University of Washington*; C.M. Wang, S.A. Chambers,* Pacific Northwest National Laboratory

With both theoretical and experimental underpinnings, a flurry of activity has centered around new candidate diluted magnetic semiconductors (DMS) based on doping semiconducting oxides with magnetic impurities. With a Curie point of ~700K, high remanence, and high saturation, Co-doped TiO@sub 2@ in the Anatase form stands out as the most magnetically robust oxide DMS. Following the initial discovery in 2001, several groups have explored the synthesis and properties of Co-doped anatase using an array of different growth methods. While most of these techniques produced materials exhibiting room temperature ferromagnetic behavior, the resounding message learned has been to accurately determine if minority phases are present. Thin film growth of this novel oxide material has been dominated by pulsed laser deposition (PLD) and oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) on SrTiO@sub 3@(001) and LaAlO@sub 3@(001). We have consistently produced epitaxial materials by OPAMBE in which the saturation moment is consistently found to be ~1.1 - 1.3 µ@sub B@/Co at room temperature. In contrast, Co@sub x@Ti@sub 1-x@O@sub 2@ grown by PLD typically has a saturation magnetization at room temperature of 0.3 µ@sub B@/Co. We will discuss the similarities and differences between materials produced by these two techniques highlighting morphological, electrical and magnetic properties. We will also discuss our recent post-growth annealing study of MBE grown specimens in which the magnetic properties do not change when the films are annealed in vacuum at 825K. This is particularly interesting in light of recent seemingly contradictory results of annealed PLD grown films. Shinde et al. report that Co metal inclusions in an Anatase film can be dissolved within the matrix and substituted for Ti as a result of a 1200K anneal in 1atm. argon. In contrast, Kim et al. found that Co came out of solution and formed Co metal as a result of a 700K anneal in 10@sup -6@ torr O@sub 2@.

11:00am **MI+SC-ThM9 Ferromagnetism in Optically Transparent Semiconducting Co Doped SnO@sub 2-d@ Films**, ***R.J. Choudhary***[1], *S.B. Ogale, S.R. Shinde,* Univ. of Maryland*; J.P. Buban,* Univ. of Illinois at Chicago*; S.E. Lofland,* Rowan Univ.*; S.N. Kale, V.N. Kulkarni, J. Higgins,* Univ. of Maryland*; C. Lanci,* Rowan Univ.*; J.R. Simpson,* Univ. of Maryland*; N.D. Browning,* Univ. of Illinois at Chicago*; S. Das Sarma, D. Drew, R.L. Greene, T. Venkatesan,* Univ. of Maryland

Thin films of Co doped SnO@sub 2-d@ grown by pulsed laser deposition on single crystal sapphire substrates are examined for their magnetic, structural, electrical, magnetotransport and optical properties. The films exhibit room temperature ferromagnetism with a Curie temperature close to 650 K. In addition, the films with 5 % of Co doping exhibit a giant magnetic moment of 7.5 ± 0.5 µ@sub B@/Co. The films are highly transparent even at 27 % of Co doping. The optical bandgap shows a redshift with Co doping. Ion channeling data show a fair degree of channeling for Sn but no channeling for Co, implying Co atoms to be structurally incoherent. However, no clustering of Co can be observed in high-resolution transmission electron microscopy even up to 27 % of Co doping. The electrical resistivity shows a rapid increase with Co doping. Possible scenarios about the microscopic state of this system and the origin of ferromagnetism will be discussed.

11:20am **MI+SC-ThM10 Elaboration and Characterisation of Cobalt Doped ZnO Thin Films for Spintronic Applications**, ***A. Anane***, *K. Rode, J.L. Maurice, J.P. Contour,* UMP CNRS-Thales and Paris XI University, France

ZnO is a large gap II-VI semiconductor potentially interesting for UV opto-electronic applications. We have investigated the structural and the magnetic properties of cobalt substituted ZnO thin films deposited on sapphire (0001) substrates by pulsed laser deposition. The films show clear ferromagnetic behavior up to 400K, the saturation moment does not exceed 1.3 ÂµB / Co atom which far away from is expected for the ionic Co2+ (3d7). We have ruled out parasitic phases as the origin of the measured magnetism by many experimental techniques, including High resolution transmission electron microscopy, X-ray edge spectroscopy and X-ray magnetic-circular-dichroism. Preliminary transport measurements on magnetic tunnel junctions based on Zn0.75Co0.25O will be presented.

11:40am **MI+SC-ThM11 Ferromagnetism in Cobalt Doped La@sub 0.5@Sr@sub 0.5@TiO@sub 3-d@ Films**, ***S.R. Shinde***, *S.B. Ogale, Y.G. Zhao, J. Higgins, R.J. Choudhary,* University of Maryland*; S.E. Lofland, C. Lanci,* Rowan University*; J.P. Buban, N.D. Browning,* University of Illinois at Chicago*; S. Das Sarma,* University of Maryland*; A.J. Millis,* Columbia University*; V.N. Kulkarni, R.L. Greene, T. Venkatesan,* University of Maryland

Epitaxial films of lightly cobalt doped La@sub 0.5@Sr@sub 0.5@TiO@sub 3-d@ are shown to exhibit ferromagnetism at room temperature. A clear hysteresis loop with coercevity ~150 Oe and the Curie temperature around 450 K are observed for these (001) oriented films grown by pulsed laser deposition at oxygen pressure of 10@super -4@ Torr on LaAlO@sub 3@ substrates. For cobalt doping up to ~2%, no inhomogeneity is observed by scanning transmission electron microscopy (S-TEM). The magnetization is found to change non-monotonically (in the range 1-3 µ@sub B@/Co) as a function of conductivity in films deposited at different partial pressures. The films range from being opaque metallic to transparent semiconducting depending on the oxygen pressure during growth and are yet ferromagnetic at and above room temperature.

Nanometer Structures
Room 308 - Session NS-ThM
Advances in Scanning Probes

Moderator: R. Bennewitz, University of Basel, Switzerland

8:20am **NS-ThM1 Autonomous Atom Assembly***, ***R.J. Celotta***, *J.A. Stroscio, A.P. Fein, S.R. Blankenship, A. Lacaze, J. Cugini,* National Institute of Standards and Technology

The ability to use an STM to move and position atoms with lattice site precision provides us with a quantum workbench to study the effects of quantum confinement and the electronic structure of perfect nanostructures. So far, atomic manipulation has been performed manually, or with rudimentary computer assistance. In this talk, we describe an Autonomous Atom Assembler (AAA), which is an instrument capable of assembling a desired nanostructure from an unknown random collection of atoms without human intervention. It is based on an existing low temperature STM system, with hardware and software extensions. In operation, a dilute coverage of adsorbate atoms is deposited on a clean, flat substrate. The AAA then instructs the STM to image the random adsorbate pattern, identifies the position of each adsorbate atom relative to the substrate lattice, and plans a series of moves to place the available atoms at positions specified in a previously entered diagram. The plan minimizes construction time, follows a set of extensible rules, and allows for error correction. The AAA then instructs the STM to execute the plan and, upon completion, provide an image of the final assembled nanostructure. In our initial trials, Co atoms were deposited to a coverage of 0.003 monolayer on a Cu(111) substrate initially held at 7 K in UHV. Subsequent STM measurements were performed at a 4.3 K sample temperature. Simple confinement structures were autonomously assembled involving tens of atoms. We will report our first results, including the accuracy of positioning, speed of operation, reliability, and scalability of our design. * Supported in part by the Office of Naval Research

8:40am **NS-ThM2 Combined Scanning Force Microscope and Mass Spectrometer**, ***A. Wetzel,*** University of Basel, Switzerland*; D.-W. Lee,* IBM Research, Zurich Research Laboratory, Switzerland*; R. Bennewitz,* University of Basel, Switzerland*; M. Despont, P. Vettiger,* IBM Research, Zurich Research Laboratory, Switzerland*; Ch. Gerber,* University of Basel, Switzerland*; E. Meyer,* University of Basel, Switzerland

We have constructed a scanning force microscope in ultrahigh-vacuum where the tip position can be switched between the sample surface and a local electrode that serves as entrance for a time-of-flight mass spectrometer. Material shall be picked up at the surface and chemically identified in the mass spectrometer after field- induced desorption from the tip. Tip, force sensor, switch, and local electrode are integrated in one

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[1] **Falicov Student Award Finalist**

silicon device. We will describe the technical details, proof the concept of the device, and discuss the important requirements to the tip quality. Finally, we will present first experimental results obtained with the new instrument.

9:00am **NS-ThM3 Imaging Semiconducting Samples by Scanning Capacitance Force Microscopy (SCFM) and Scanning Capacitance Microscopy (SCM)*, K. Kobayashi,*** *K. Kimura, H. Yamada, K. Matsushige,* Kyoto University, Japan

We recently developed scanning capacitance force microscopy (SCFM) based on electrical force detection which is capable of mapping local differential capacitance (dC/dV) without an ultrahigh frequency capacitance sensor. While an electric field alternating at a fixed frequency (f) is applied between a tip and a sample, an induced electrostatic force (ESF) oscillating at its third harmonic frequency (3f) as a differential capacitance (dC/dV) signal is detected by a lock-in technique. SCFM works both in contact mode and dynamic mode. Since the sensitivity of SCFM is inherently high owing to the extremely high force sensitivity in scanning force microscopy (SFM), SCFM can be a high-resolution dopant-profiling technique for semiconducting samples. In this paper, we investigate the imaging mechanisms of SCFM using a silicon test sample having several microfabricated patterns of p-type, n-type and heavily-doped n-type regions. Image contrast changes depending on the applied bias voltage to the sample and the laser light irradiation were discussed. Conventional scanning capacitance microscopy (SCM) imaging were also performed and the results obtained by both techniques are compared and their advantages and limitations are discussed.

9:20am **NS-ThM4 AFM Force Measurements: MEMS Devices for Easy and Accurate Cantilever Spring-Constant Calibration*, P.J. Cumpson,*** National Physical Laboratory, UK*; J. Hedley,* University of Newcastle, UK*; P. Zhdan,* University of Surrey, UK

A value for the spring-constant of Atomic Force Microscope (AFM) cantilevers@footnote 1@ is necessary for the measurement of nanonewton and piconewton forces, which are critical to analytical applications of AFM in the analysis of polymer surfaces, biological structures and organic molecules.@footnote 2@ We have developed compact and easy-to-use micromachined reference artefacts for this calibration. The principal device consists of an array of dual spiral-cantilever springs, each supporting a polycrystalline silicon disc of 170 micrometres in diameter. These were fabricated by a two-layer polysilicon surface micromachining method. Doppler velocimetry is used to measure the fundamental resonant frequency of each device accurately. We call such an array a Microfabricated Array of Reference Springs (MARS). These devices have a number of advantages. Firstly, modelling the fundamental resonant frequencies of the devices is much more straightforward than for AFM cantilevers,@footnote 3@ because the mass and spring functions are isolated in different parts of the structure. Secondly, the spring constant of each spring is in linear proportion to the mass of the device, given that the resonant frequency is measured accurately. The thickness and hence the mass can be measured accurately by AFM or interferometry. These factors lead to much lower uncertainty than previous methods in which spring constant is proportional to the cube of a critical dimensional measurement. The array spans the range from 0.1 N/m to 10 N/m important in AFM, allowing AFM cantilevers to be calibrated easily and rapidly. New devices that extend this range down to around 0.03 N/m, and up to around 80 N/m will also be discussed. @FootnoteText@ @footnote 1@ N A Burnham et al, Nanotechnology 14 (2003) 1-6 @footnote 2@ J Colchero in Procedures in Scanning Probe Microscopies, Ed. R J Colton et al (Wiley, Chichester, UK, 1998)@footnote 3@C T Gibson et al, Nanotechnology, 7 (1996) 259-262. .

9:40am **NS-ThM5 Thermal Approach to Cantilever Calibration over a 200 kHz Bandwidth***, G.A. Matei,* Wayne State University*; E.J. Thoreson,* ***N.A. Burnham,*** Worcester Polytechnic Institute

A cantilever's stiffness can be determined from an analysis of its thermal distribution spectrum, making use of the equipartition theorem k = k@sub B@T, where k is the cantilever stiffness and k@sub B@T is the thermal energy. We recently showed that it is possible to obtain good values for k, even when the cantilever's resonance is close to the edge of the data acquisition bandwidth with the formula k = k@sub B@TQ@DELTA@@nu@/(@pi@@nu@@sub k@).@footnote 1@ Here, Q is the quality factor, @DELTA@@nu@ the frequency resolution of the data acquisition, @nu@@sub k@ is the resonant frequency, and is the mean-square amplitude at resonance. The initial work was limited to a 30 kHz bandwidth, that is, to cantilevers of stiffness less than approximately 0.4 N/m. Thermal calibration methods are independent of materials properties, coating thickness, cantilever geometry, and the viscosity of the medium, so there is good motivation to extend the methodology to higher bandwidths and thus stiffer cantilevers. We have now expanded the frequency range to 200 kHz, the bandwidth of the preamplifier of our AFM. By monitoring the raw A-B signal with an oscilloscope, then downloading the signal to a computer in order to manipulate the data, we have determined the stiffness of a 180 kHz cantilever to be 3.9 ± 0.2 N/m. By comparing our results for "force-calibrated" cantilevers with the manufacturer's stiffness calculation, we estimate that the accuracy of our method is 5%. By inverting a coated cantilever and repeating the measurement on the uncoated side, we believe that the precision is a similar value. Moreover, consistent with finite-element analyses, we find that the coating can perturb the stiffness by twenty percent. @FootnoteText@@footnote 1@Comparison of Calibration Methods for Atomic-Force Microscopy Cantilevers," NA Burnham, X Chen, CS Hodges, GA Matei, EJ Thoreson, CJ Roberts, MC Davies, SJB Tendler, Nanotechnology 14 (2003) 1-6.

10:00am **NS-ThM6 Are V-shaped Atomic Force Microscope Cantilevers Obsolete?*, J.E. Sader,*** University of Melbourne, Australia

The performance of the atomic force microscope (AFM) is underpinned by the mechanical properties of its force-sensing microcantilever. Originally, the AFM cantilever was handcrafted from a thin film of gold, in the shape of a rectangular plate. Shortly after, microfabrication techniques were introduced to facilitate the construction and mass production of AFM cantilevers, and a number of different cantilever geometries were proposed. Of these, rectangular and V-shaped cantilevers have emerged as the accepted standards for AFM applications. The V-shaped cantilever was proposed initially as an alternative to the rectangular cantilever, with the explicit aim of minimizing the effects of lateral forces on the deformation of the cantilever. However, the motivating premise that V-shaped cantilevers are more resistant to lateral forces than rectangular cantilevers was never examined. Consequently, in this talk I shall present a detailed comparison of the complementary performance of V-shaped and rectangular cantilevers, with regards to their stability to lateral forces. In so doing, I shall rigorously establish that contrary to accepted thinking and the original intent, use of V-shaped cantilevers will enhance the effect of lateral forces in comparison to rectangular cantilevers. This counterintuitive finding is independent of whether the cantilevers are in contact with a surface or not, and suggests that rectangular cantilevers should be used in preference to V-shaped cantilevers for applications where the effects of lateral forces are to be minimized. This finding strongly contradicts established operating principles of the AFM, which dictate that V-shaped cantilevers should be used to minimize the effects of lateral forces. Consequently, drawing on the findings of this study, a case will be presented for the universal use of rectangular cantilevers in the AFM, which in turn will improve the performance of the instrument while greatly simplifying its operation.

10:20am **NS-ThM7 Electronic Properties of Individual Defects in Carbon Nanotubes by Scanning Probe Microscopy*, V. Meunier,*** *S.V. Kalinin, R.J. Harrison, A.P. Baddorf,* Oak Ridge National Laboratory

Electronic devices based on carbon nanotubes and semiconductor nanowires require development and understanding of quantitative tools for transport measurements at nanoscale dimensions. Scanning Gate Microscopy (SGM) and Scanning Impedance Microscopy (SIM) are both capable of detecting atomic-scale defects in carbon nanotubes. In SGM individual defects are visualized as a decrease in the current through the dc circuit, since defects are depleted for tip voltages that are related to the local electronic structure of the defect. In SIM the local ac potential amplitude and phase are recorded; the defects are manifest as potential drops (back gate regime) or potential minima (tip gate regime). Here, a method for quantitative characterization of the electronic structure of individual defects from SGM and SIM results is presented. The interaction between a carbon nanotube and a point charge is studied using both atomistic first principles calculations and continuum electrostatic methods. The results are compared and extrapolated to real tip geometries in order to simulate the interaction of the scanning tip with an adjacent nanotube. Comparison with experimental data suggests that the gate voltage dependence of the image contrast is a direct measure of the difference in Fermi energies at these defects. The potential of the present approach for the identification of individual defects is discussed.

10:40am **NS-ThM8 Real-Space Imaging of the Vortex Lattice in V@sub 3@Si Using Low Temperature Scanning Tunneling Microscopy***, ***J.A. Stroscio****, C.E. Sosolik, M.D. Stiles,* National Institute of Standards and Technology*; E.W. Hudson,* Massachusetts Institute of Technology*; S.R. Blankenship, A.P. Fein, R.J. Celotta,* National Institute of Standards and Technology

In Type II superconductors, the expulsion of an applied magnetic field from the superconductor, the Meissner effect, is not complete for fields above the lower critical field. In this applied field regime, magnetic flux penetrates the superconductor as quantized vortices that interact through shielding currents. In equilibrium the vortices form a lattice with symmetry, and orientation relative to the crystallographic axes, determined by microscopic electronic properties. In this talk we present low temperature scanning tunneling microscopy measurements of the structural evolution of the vortex lattice in a single-crystal V@sub 3@Si sample. Large-scale conductance maps obtained at 2.3 K provide a real-space image of the vortex lattice formed with a magnetic field applied parallel to the [001] crystal axis. Atomic resolution topography of the V@sub 3@Si (001) surface shows the underlying Si sublattice and allows for a determination of the orientation of the measured vortex lattice relative to the underlying crystal axes. The conductance maps reveal a change in the symmetry of the vortex lattice from hexagonal to nearly square over the field range of 0 T to 4 T. A strong anisotropy in the long-range translational order of the vortex lattice is observed near the transition field of 4 T. These observations give evidence for nonlocal electrodynamics in the vortex-vortex interactions of this Type II superconductor. Calculations that account for the role of these nonlocal effects in determining the structure and symmetry of the vortex lattice are presented and compared to our experimental results. * This work is supported in part by the Office of Naval Research.

11:20am **NS-ThM10 Adatom Hopping Induced by Tunneling Electrons: Br on Si(100)-(2x1)**, ***K.S. Nakayama****, E. Graugnard, J.H. Weaver,* University of Illinois at Urbana-Champaign

Tunneling electrons from the tip of a scanning tunneling microscope can be used to induce adatom hopping on Br-terminated Si(100)-(2x1) at low current and without voltage pulses. Hopping does not occur when electrons tunnel from a sample to a tip. The threshold energy is +0.8 V, and tunneling spectroscopy shows antibonding Si-Br states 0.8 eV above the Fermi level. Electron capture in these states is a necessary condition for hopping, but repulsive adsorbate interactions that lower the activation barrier are also required. Such interactions are strong near saturation for Br but are insufficient when the coverage is low or when Br is replaced by Cl.

11:40am **NS-ThM11 Elucidation of the Electronic Properties of Isolated Alkanethiolate-Passivated Undecagold Clusters by Low Temperature Scanning Tunneling Microscopy and Spectroscopy**, ***S.U. Nanayakkara****, R.K. Smith, T.P. Pearl, B.A. Mantooth, P.S. Weiss,* The Pennsylvania State University*; G. Woehrle, J.E. Hutchison,* University of Oregon

We have studied the electronic properties of isolated, octanethiolate-stabilized undecagold clusters [Au@sub 11@(S(CH@sub 2@)@sub 7@CH@sub 3@)@sub 10@] using low temperature scanning tunneling microscopy (STM) and spectroscopy (STS). The clusters, d@sub CORE@ = 0.8 ± 0.2 nm, were immobilized by inserted dithiol molecules in an alkanethiolate self-assembled monolayer (SAM) on Au(111). The clusters were synthesized in solution by ligand exchange of Au@sub 11@(PPh@sub 3@)@sub 8@Cl@sub 3@ with octanethiol, resulting in a complete octanethiolate ligand shell, and were subsequently deposited upon a SAM. The geometry of the STM tip-vacuum-gold cluster-SAM-Au(111) assembly can be modeled as a double barrier tunnel junction, which may give insight into controlling the movement of single or small numbers of electrons. Discrete quantum energy levels are more evident in this cluster size range where the atomic character of the metal is prominent. We have observed Coulomb blockade of these clusters at 4 K. The current-voltage characteristics show uneven spacing between adjacent current steps, showing quantized energy states. The observed, large zero-conductance gaps result from quantum size effects, where the bound octanethiolate ligand shell further reduces the free volume in which the electrons can move. This study assesses the impact of sub-nanometer sized clusters on single electron transport properties, enlightening the future of nanoscale electronics.

Nanotubes
Room 317 - Session NT-ThM
Nanotube Growth and Processing

Moderator: K. Matsumoto, AIST, Japan

8:20am **NT-ThM1 Analyses of Early Stages of Vertically Aligned Carbon Nanotube Growth**, ***Y. Hayashi****, K. Ueda, Y. Watanabe, S. Nishino,* Kyoto Institute of Technology, Japan

Vertically aligned carbon nanotubes are expected to be used for the electron emitters of a field emission display, which demands large-area and low-voltage operation. We have developed the method of large-area growth of well-aligned carbon nanotubes by hot-filament assisted dc plasma chemical vapor deposition (HF/DC-P CVD).@footnote 1,2@ In order to obtain high electron emission density at low voltage, the crystallinity and alignment of carbon nanotubes should be controlled. However the growing mechanisms of aligned carbon nanotubes, especially early stages, have not well been understood. Therefore we are analyzing substrate surface states in the early states of aligned carbon nanotube growth in HF/DC-P CVD by in-situ ellipsometry along with other ex-situ analytical methods. The ellipsometer is a rotating-analyzer type and the light source is a diode laser of the wavelength of 690 nm. Carbon nanotubes were grown on an iron film about 500 nm thick in the DC plasma of 20 % methane diluted in hydrogen after the pretreatment in a pure hydrogen plasma. The trajectory of ellipsometric parameters in the early stages was compared with that of simulation which was performed using the effective medium approximation for the calculation of the optical indexes of a film equivalent to aligned carbon nanotubes of a certain diameter and density. From the results of the ellipsometry and SEM observation, it was found that an incubation period of about 2 min exists before the growth of carbon nanotubes and the carbonization of iron fine particles, which were formed during the pretreatment process, was occurred in the incubation period. @FootnoteText@@footnote 1@Y.Hayashi , T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19 (2001) 1796. @footnote 2@K.Ueda, T.Negishi, Y.Hayashi and S.Nishino, in preparation for publication.

8:40am **NT-ThM2 Iron-carbide Cluster Thermal Dynamics for Catalysed Carbon Nanotube Growth**, *F. Ding, K. Bolton,* ***A. Rosen****,* Goteborg/Chalmers University, Sweden

The mechanism of the growth of carbon nanotubes by chemical vapor deposition (CVD) method is still not well understood. It seems that the catalyst particles play a key role in controlling the size, defects, number of walls and chirality of the nanotubes. Knowledge about thermal properties of the catalyst particles in the temperature range (500-1200)@super o@C used in the CVD growth would be beneficial to the understanding of the growth mechanism. We have used molecular dynamics (MD) simulations for studies of the thermal behavior of C@sub m@Fe@sub N-m@ clusters with N up to 2400. Comparison of the computed results with experimental data shows that the simulations yield the correct trends for the liquid-solid region of the iron-carbide phase diagram as well as the correct dependence of cluster melting point as a function of cluster size. The calculations also show that the melting points of both pure Fe clusters (m=0) with diameter larger than 3 nm (about N>1000) and clusters composed of 10% C with diameter larger than 4 nm (about N>2400) are higher than 1000@super o@C. This indicates that, when nanotubes are grown on large catalyst particles at these lower temperatures, the catalyst particles are primarily in the solid - and not the liquid - state. The simulations indicate that nanotube growth may depend only on the surface melting of these clusters. This surface melting behavior and the coalescence of C@sub m@Fe@sub N-m@ clusters at temperatures lower than the melting point is also studied. At these low temperatures surface melting results in the coalescence of two clusters, where the final structure is similar to the minimum energy geometry.

9:00am **NT-ThM3 Growth & Control Mechanisms for Directed Assembly of Vertically Aligned Carbon Nanofibers: Fundamental Studies and Nanotech. Applications**, ***D.H. Lowndes****, V.I. Merkulov,* ORNL*; A.V. Melechko,* ORNL, U. Tennessee*; M.A. Guillorn,* ORNL*; M.L. Simpson,* ORNL, U. Tennessee*; H. Cui,* ORNL*; J. Liu,* Duke U.*; J.B.O. Caughman, M.J. Doktycz, T.E. McKnight,* ORNL*; L. Zhang, X. Yang,* ORNL, U. Tennessee*; D.K. Hensley,* ORNL **INVITED**

Although vertically aligned carbon nanofibers (VACNFs) are structurally quite imperfect in comparison to single-wall carbon nanotubes (SWNTs), their synthesis and assembly is highly controllable using a DC plasma-enhanced method and--unlike SWNTs-- they can be precisely positioned in large arrays. VACNFs grow simultaneously by two mechanisms, catalytically controlled vertical growth and defect-mediated lateral growth, and the morphology of isolated VACNFs is readily controlled. Their growth rate can be increased by changing the feedstock transport from diffusive to forced flow, and their growth mode can be altered from 'base-type' to 'tip-type' without changing the type of substrate or catalyst. Their alignment angle relative to the substrate also can be controlled via the direction of local plasma electric-field lines, so that deliberately tilted or kinked CNFs can be grown. Recent extensions to grow VACNFs using radio frequency (RF) PECVD and from nanometer-scale metal catalyst particles also will be described. Phenomenological models that explain important aspects of VACNF growth will be presented and validated with experimental results. Potential nanotechnology applications of VACNFs will be demonstrated, including multi-electrode vacuum nanoelectronic devices using field emitting VACNF cathodes; tubular nanopipes that can be deterministically positioned using VACNFs as templates; the use of VACNFs as an intracellular interface for monitoring and controlled biochemical manipulation of phenomena within viable cells; and their use to form semi-permeable membranes that mimic some features of biological cells, in combination with microfluidic and electronic structures.

9:40am **NT-ThM5 Synthesis of Carbon Nanotube Array by Radio-frequency Plasma Enhanced Chemical Vapor Deposition for Field Emission Application***, **J. Wang**, M. Zhu, R.A. Outlaw, X. Zhao, N.D. Theodore, D. Manos, B.C. Holloway,* The College of William and Mary*; V.P. Mammana,* International Technology Center

In this presentation we report on the synthesis, characterization, and applications of large periodic carbon nanotube arrays. A polystyrene and silica nanosphere lithography technique was used to create nickel catalyst arrays on silicon substrates. Nanotubes, with a diameter of about 50 nm, were synthesized on the nanodot arrays by radio-frequency plasma enhanced chemical vapor deposition (CVD) using an acetylene and hydrogen mixture. Scanning electron microscopy has been used to determine the density, height, and interspacing of the carbon nanotubes as a function of array patterning and deposition conditions. The suitability of such arrays for use in field emission devices is discussed within the framework of field emission electron spectroscopy, Kelvin probe and diode measurements.

10:00am **NT-ThM6 Magnetic Entrapment of Carbon Nanotubes for the Fabrication of Electrically Conductive Bridging Structures***, **D.P. Long**, J.L. Lazorcik, R. Shashidhar,* Naval Research Laboratory

The unique electrical properties of carbon nanotubes have made them ideal candidates for their use in future molecular electronics. The successful application and mass production of CNT-based nanoelectronics will require methods for the efficient and reliable fabrication of large numbers of CNT devices simultaneously across a substrate. Here we present recent experiments on the generation of electrically conductive carbon nanotube bridged structures fabricated in parallel by magnetic entrapment. By utilizing devices composed of individually addressed nickel lines and containing gaps 1 micron wide, we have demonstrated that moderate external magnetic fields can induce domain alignment in the ferromagnetic material and generate locally intense fields within the feature junctions able to attract and bind carbon nanotubes. Magnetic field strength, nanotube solution concentration, and feature gap width and thickness are used to control the trapping process. Junctions ranging from 2-4 microns were selective for large tube bundles while devices containing gaps of 1 micron or less were more selective for individual CNTs or small ropes of tubes. By making use of electrically isolated devices on silicon containing a thermally grown oxide layer we have measured the basic electrical properties of the bridged structures.

10:20am **NT-ThM7 Novel Approaches to Developing Carbon Nanotube Based Polymer Composites***, N. Raravikar, G. Viswanathan, N. Chakrapani, C.Y. Ryu, **P.M. Ajayan**,* Rensselaer Polytechnic Institute **INVITED**

Polymer-carbon nanotube composites combine the unique properties of nanotubes with the ease of processability of polymers. Alignment of nanotubes, the nanotube-matrix interface and the dispersion of nanotubes are issues critical to successful applications. Infiltration of polymer into pre-aligned arrays of nanotubes provides simultaneous control over the degree of alignment as well as the dispersion of nanotubes. The infiltration is achieved by introduction of the monomer and subsequent polymerization into a pre-aligned array of multi-walled carbon nanotubes grown by chemical vapor deposition technique. The resultant composites show better hardness and thermal stability compared to the parent polymer, and can have applications as thermo-mechanically strong, antistatic polymeric coatings. Especially for application as structural reinforcements, a good interface between the nanotubes and the host matrix should exist for efficient load-transfer. We have also developed a novel route for grafting polystyrene chains onto single-walled nanotubes to obtain homogeneous, well-dispersed composites, using an anionic polymerization scheme. The mechanism of functionalization and the enhancement of interfacial properties studied using thermal analysis and spectroscopic techniques will be discussed.

11:00am **NT-ThM9 Filling and Chemical Modification of Carbon Nanotubes***, **N. Naguib**, H. Ye, Y. Gogotsi,* Drexel University

The possibility of filling of carbon nanotubes at elevated temperatures and pressures has been demonstrated. Carbon nanotubes can be filled with different fluids such as water, ethylene glycol and isopropyl alcohol or different gases such as Argon and Nitrogen. Understanding the penetration of fluids in nanochannels is important for the efficient storage of gasses. The effect of changing variables (pressure and temperature) on the filling process has been demonstrated. Wall structure of the nanotubes after treatment has been investigated. Hydrothermal treatment makes nanotubes hydrophilic. During the hydrothermal treatment, nanotubes can be completely or partially filled with liquids. Lattice fringe imaging of the tube walls showed a very strong interaction between the tube walls and the liquid. If a liquid inclusion was present in the area where some graphite planes terminated within the tube (inner diameter change or bending of the tube), swelling of the tube walls was observed and the wetted graphite layers pointed away from the wall toward the tube axis. Polymerization of ethylene glycol and isopropyl alcohol occurred inside and outside of the nanotubes, producing nanotube-reinforced composites. The liquid could also penetrate between the carbon layers causing this behavior. The exact chemical composition of the fluid, as well as the presence of the gases inside the nanotubes after hydrothermal treatment, have been studied by using TEM, EELS, EDS, Raman and Infrared microspectroscopy techniques.

11:20am **NT-ThM10 Polyatomic-Ion Beam Induced Chemical Functionalization of Carbon Nanotube-Polystyrene Composites***, Y. Hu, **S.B. Sinnott**,* University of Florida

Classical molecular dynamics simulations with empirical potentials are used to study polyatomic-ion deposition on nanotube-polystyrene composites. The forces in the simulation are calculated with a many-body, reactive empirical bond-order potential for hydrocarbons and fluorocarbons. The ion beam consists of 50 C@sub 3@F@sub 5@@sup +@ ions and the composite consists of (10,10) single-walled carbon nanotubes embedded in crystalline polystyrene. The ions impact at random points on the composite slabs along the substrate normal. The composites differ in the embedding depth of the nanotube within the polystyrene matrix and the orientation of the nanotubes relative to the polystyrene chains. The simulations predict that chemical modification of the carbon nanotubes can be achieved through polyatomic-ion beam deposition. They also predict the dependence of such modifications on the incident energy of the ions and embedding depth of the carbon nanotubes. The findings could have important implications for the production of carbon nanotube-based nanocomposite materials with improved load-bearing capabilities. The work is supported by the National Science Foundation through grant CHE-0200838.

11:40am **NT-ThM11 AC Electrical Transport Behavior of Epoxy Matrix/Single-Walled Carbon Nanotube Composites***, **L. Valentini**, D. Puglia, I. Armentano, J.M. Kenny,* University of Perugia, Italy*; S. Santucci,* University of L'Aquila, Italy

A study of the ac electrical transport properties of a diglycidyl ether of bisphenol A-based epoxy resin (DGEBA) polymerized with a diethylene triamine (DETA) and reinforced with single wall carbon nanotubes (SWNTs) is presented. The main objective is the investigation of the particular electrical behavior of the conductive filler in the composite and the development of new nanocomposite materials based on epoxy resins with controlled structural and electrical properties. The structural and electrical characterization of the SWNTs-DGEBA/DETA hybrid system, performed by differential scanning calorimetry, Raman and ac impedance spectroscopy show interesting effects, including the particular interaction between the polymer and nanotubes, the tendency of the nanotube structure to increase the rate of reaction and substantial effects of the nanotubes bundle conformation, dependent on matrix intercalation, on the dielectric behavior of the composite.

Plasma Science and Technology
Room 314 - Session PS1-ThM

Plasma-Surface Interactions: Deposition

Moderator: S.M. Han, University of New Mexico

8:20am **PS1-ThM1 Reactive Sputtering of Metallic Tin in a Mixture Ar - O2 : Comparison between an Amplified and a Classical Magnetron Discharge***,* ***R. Snyders****,* Mons-Hainaut University, Belgium

Industrially, magnetron sources are widely used for coating and surfaces treatments. The problem encountered by "classical" magnetron sputtering is the shadowing effect when complex substrates have to be treated. Neutral particles arrive on the substrate surface with a broad angular distribution of trajectories and as a consequence the deposited film is of poor quality. Ionizing the sputtered particles can solve this problem. Velocity control and normal trajectory of the ionized species can be achieved by applying a bias voltage to the substrate. For that purpose, a R.F. (13.56 MHz) power supplied copper coil (diameter of 4 cm) has been set up, between the DC tin magnetron target and the substrate holder. The applied R.F. power used to create the secondary plasma can be raised up to 200 W. The aim of this work is to estimate the RF coil influence on the chemical behaviour of both the discharge and the films during the deposition of SnOx thin films in a mixture Ar - O2. During the deposition, the discharge is characterized by the target voltage, the deposition rate and glow discharge mass spectrometry whereas the prepared films compositions are obtained from in-situ XPS measurements. During the work, we have observed the influence of both the gas mixture composition and the RF power on the discharge and on the films. By increasing the RF power on the coil, we have observed on both the plasma and the films compositions an increase of the oxidation level for the same ratio O2 / Ar. On the other hand, the metal â€“ compound transition at the target, observed on the discharge voltage and on the deposition rate measurements are not influenced by the coil. So, using the RF coil the films oxidation can be reached at lower reactive gas flow and consequently at higher deposition rate.

8:40am **PS1-ThM2 Selective Plasma-induced Deposition of Fluorocarbon Films on Metal Surfaces for Actuation in Microfluidics***, P. Bayiati,* ***A. Tserepi****, E. Gogolides, K. Misiakos,* National Center for Scientific Research (NCSR) "Demokritos", Greece

Plasma-induced deposition of polymer films on surfaces is an important issue in etching plasmas, since on one hand it allows selective etching of materials,@footnote 1@@footnote 2@ while on the other it provides side wall passivation necessary for anisotropic high-aspect ratio etching. The present work focuses on the selective deposition of fluorocarbon (FC) films on metal surfaces, specifically on aluminum, over SiO@sub 2@ surfaces, in order to obtain surfaces of distinct wettability. If, in addition, the wettability of the modified metal surface can be controlled electrostatically and consequently the surface be varied from a hydrophobic to a hydrophilic one, such plasma-modified metal surfaces can be used as electrodes employing electrowetting for actuation of fluid transport in microfluidic devices.@footnote 3@ Since polymer layers on surfaces are easily formed in fluorocarbon discharges with high concentrations of radical CFx species, fluorocarbon gases such as C@sub 4@F@sub 8@ and mixtures of CHF@sub 3@/CH@sub 4@ were used in our experiments. For the selection of conditions appropriate for selective deposition of FC films on Al over SiO@sub 2@, plasma parameters such as plasma power, bias voltage, electrode temperature, and gas composition were varied. The wettability of SiO@sub 2@ and Al surfaces exposed to FC plasmas under different plasma deposition conditions was characterized by contact angle measurements (without and with voltage application). Contact angles as a function of the applied voltage were used to yield the thickness of the FC film deposited on Al, and to indicate the breakdown voltage for the films under consideration. The results demonstrate the feasible use of such plasma-deposited films on Al for electrostatic actuation with application of relatively small voltages (less than 10 V). @FootnoteText@ @footnote 1@G. Oerlein, Surface Science 386, 222 (1997); and G. Oerlein et. al., J.Vac. Sci. Technol. A 12(2), 333 (1994).@footnote 2@L.Rolland, M.C. Peignon, Ch. Cardinaud, G. Turban, Microel. Engin. 53, 375 (2000).@footnote 3@M. Pollack, R. Fair, A. Shenderov, Appl. Phys. Lett. 77(11), 1725 (2000).

9:00am **PS1-ThM3 Deposition of Transparent Tin Oxide Films by PECVD on Polymers***,* ***F. Arefi-Khonsari****, J. Pulpytel,* Laboratoire de Genie des Procedes Plasma et Traitement de Surface ENSCP, France*; H. Cachet,* UPR15-CNRS, France **INVITED**

Transparent conductive tin oxide films have been deposited at low temperature(< 50°C) from a mixture of O@2sub@/Ar/TMT on two substrates for two different applications : 1) biofouling reduction for underwater instrumentation on polymer windows and 2)as sensitive layers of gas microsensors on silicon wafers. In order to obtain carbon free tin oxide films, mass spectrometry was performed by using a calibration mixture composed of inert gases. The latter allowed us to determine the molar fraction of the stable species produced in the discharge, such as CO & CO@2sub@ namely those which witness the carbon etching of the organometallic precursor. For this study the role of the two major parameters i.e. power and oxygen partial pressure in the reactor have been studied. The biofouling reduction was based on seawater electrolysis at the optical surface for producing active chlorine species. In order to limit the ageing effect of tin oxide films deposited on polymers, they were doped with fluorine atoms which gave rise to higher conductivities and limited also the ageing effect. Precursors such as SF@6sub@ and C@4sub@F@6sub@ were introduced in the plasma mixture in order to dope the tin oxide films in a one step process. In the case of SF@6sub@, an increase of the electrical conductivity and charge carriers were obtained for very small flow rates of SF@6sub@ introduced in the discharge. For higher flow rates, a sharp decrease of the conductivity was observed. For such flow rates, competitive etching and functionalization processes, assisted by fluorine atoms present in the discharge, took place giving rise to a sharp decrease of the deposition rate and the incorporation of Sn-F and C-F bonds in the deposited films. This has been explained by the formation of new species such as S O@2sub@, SOF, SOF@2sub@ and HF. Oxygen being consumed to form such species, it is much less involved in forming CO, CO@2sub@ and H@2sub@O species, therefore leading to the incorporation of carbon species in the deposit which explains the sharp decrease of the conductivity of the films.

10:20am **PS1-ThM7 Temperature Dependence of the SiH@sub 3@ Surface Reactivity During Plasma Deposition of a-Si:H Studied by Time-resolved CRDS***,* ***J.P.M. Hoefnagels***[1]*, Y. Barrell, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

The surface reactivity of SiH@sub 3@ - the dominant radical during deposition of hydrogenated amorphous silicon (a-Si:H) from SiH@sub 4@ plasmas - has been investigated to obtain information on the elemental surface reactions during a-Si:H film growth. To do so, we have measured the surface reaction probability @beta@ of SiH@sub 3@ for substrate temperatures in the range of 50-450 °C by means of the novel time-resolved cavity ringdown spectroscopy (@tau@-CRDS) method. In this method, the highly-sensitive CRDS absorption technique is used to map the temporal decay of the SiH@sub 3@ radical density (probed at the Ã@super 2@A@sub 1@'<-@td X@@super 2@A@sub 1@ transition) after a minor periodic modulation of the density during regular plasma operation. From measurements of the SiH@sub 3@ loss time versus the SiH@sub 4@ partial pressure, it has been verified that SiH@sub 3@ is not lost by gas phase reactions, as is, e.g., the case for the Si radical. The surface reaction probability of SiH@sub 3@ has been deduced for different substrate temperatures from the pressure dependence of the SiH@sub 3@ loss time using information on the gas temperature and the diffusion of SiH@sub 3@ towards the surface. The gas temperature - determined from Doppler broadening of Si absorption lines - is ~1500 K and is unaffected by the substrate temperature. This procedure has revealed that the surface reaction probability of SiH@sub 3@ is independent of the substrate temperature with a value of @beta@=0.30±0.03. For comparison, the surface reaction probability of Si has been determined for 200 °C and is very close to unity (0.95<@beta@@<=@1). These observations will be discussed in terms of the contribution of different plasma radicals to film growth and the possible SiH@sub 3@ surface reactions taking place. The results suggest a two-reaction step growth mechanism for a-Si:H with a temperature-independent abstraction reaction of H from the surface as the rate-limiting step.

10:40am **PS1-ThM8 Creation of SiOF Films with SiF@sub 4@/O@sub 2@ Plasmas: from Gas-Surface Interactions to Film Formation***,* ***J. Zhang****, E.R. Fisher,* Colorado State University

Fluorinated SiO@sub 2@ (SiOF) films have been studied because of their relatively low dielectric constant and their potential as a replacement for

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

SiO@sub 2@ in the microelectronics industry. Despite the intense scrutiny, many of the details of the mechanisms for SiOF film deposition remain unclear. Here, we deposited SiOF films using SiF@sub 4@/O@sub 2@ plasmas. The plasma parameters of SiF@sub 4@ percentage in the feed gases (%SiF@sub 4@) and applied rf power (P) were studied as well as the effects of ion bombardment and substrate temperature on film deposition. Fluorine incorporation in the film increases with increasing %SiF@sub 4@ and P. Film deposition rate also increases with P, whereas its dependence on %SiF@sub 4@ is more complex. Ion bombardment decreases the film deposition rate and affects film composition significantly. On the molecular level, we examined the surface reactivity of SiF and SiF@sub 2@ during SiOF film deposition using the imaging of radicals interacting with surfaces (IRIS) technique. SiF shows high surface reactivity, R, which varies from 0.95 ± 0.08 to 0.60 ± 0.07, depending on plasma parameters. In contract, SiF@sub 2@ shows significant surface production. The scattering coefficient, S, varies from 1.12 ± 0.08 to 2.52 ± 0.16. The surface interactions of SiF and SiF@sub 2@, along with plasma gas-phase composition, were correlated with film characteristics to reveal the possible film-deposition processes.

11:00am **PS1-ThM9 Study of Fluorocarbon Deposition Mechanism with a Small Gap Structure in Fluorocarbon Plasmas***, **L. Zheng**, X. Li, X. Hua, L. Ling, G.S. Oehrlein,* University of Maryland, College Park*; E.A. Hudson,* Lam Research Corp.

We designed a small gap structure to study the deposition of fluorocarbon film in a high aspect ratio feature in an inductively coupled rf plasma (ICP) reactor in an effort to provide information on fluorocarbon film formation mechanisms for highly selective dielectric etching processes. The small gap structure exhibits three regions for fluorocarbon film formation: A region exposed to the full plasma, transition region and a completely shadowed region where only long-lived species can arrive after multiple collisions with the walls. Both in situ (real time) and external He-Ne ellipsometers were used to monitor the deposition rate of the fluorocarbon film on the base wafer. X-ray photoelectron spectroscopy (XPS) was used to analyze the detailed surface chemistry of the fluorocarbon film. CFx (x = 1-3) radicals produced in fluorocarbon discharges act as precursors for the formation of fluorocarbon film. Effects of different gases (C4F8, C4F6), Ar addition, gap height, pressure on refract index and deposition rate of the fluorocarbon film in the three regions were studied and a simple model based on Knudsen diffusion mechanism was developed to describe the fluorocarbon film deposition in the completely shadowed region. We also will describe an equivalent set of studies performed in a 40 MHz (source power) - 13.56 MHz RF (bias power) dual frequency capacitively coupled system.

11:20am **PS1-ThM10 Plasma Chemistry and the Growth Kinetics of Silicon Nitride Deposited by the SiH@sub 4@-N@sub 2@ Reactant Mixture***, **F.J.H. Van Assche**, J. Hong, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Plasma ions and radicals in a remote plasma operated on an Ar-H@sub 2@-N@sub 2@-SiH@sub 4@ mixture have been studied by several diagnostics such as Langmuir probe measurements, ion mass spectrometry, cavity ringdown spectroscopy, and threshold ionization mass spectrometry. It is shown that the H radicals that emanate from the plasma source react with the SiH@sub 4@ admixed downstream and create a high SiH@sub 3@ density. Si and SiH radicals have also been measured but they have a much lower density in the downstream plasma. Ground-state N radicals emanating from the plasma source do not react with the SiH@sub 4@ injected downstream leading to a high N density under the silicon nitride deposition conditions. This has lead to the conclusion that N and SiH@sub 3@ radicals dominate the silicon nitride growth process as has also been confirmed by the correlation between the SiH@sub 3@ and N density in the plasma and the incorporation flux of Si and N atoms into the silicon nitride films. Furthermore, from this correlation very reasonable sticking probabilities of the N and SiH@sub 3@ radicals have been obtained. >From these results, the following kinetics for silicon nitride growth from the N@sub 2@-SiH@sub 4@ reactant mixture are proposed: During deposition an amorphous silicon-like surface layer is created by the SiH@sub 3@ radicals and simultaneously this amorphous silicon-like surface layer is nitridated by the N radicals leading to silicon nitride formation. Further support for this mechanism is obtained by experiments in which silicon nitride films have been created by exposing amorphous silicon films to a high flux of N radicals.

11:40am **PS1-ThM11 Molecular Dynamics Simulations of Organic Polymer Etching by H@sub 2@/N@sub 2@ and NH@sub 3@ Plasmas***, **H. Yamada**, S. Hamaguchi,* Kyoto University, Japan

Using classical molecular dynamics (MD) simulations, plasma-surface interactions have been investigated for organic polymer etching processing with H@sub 2@/N@sub 2@ and NH@sub 3@ plasmas. To perform MD simulation in such systems, we have developed an interatomic potential model applicable to systems consisting of H, C, and N atoms [i.e., (H,C,N) systems]. Further we have also worked with the Abel-Tersoff-Brenner (ATB) potential proposed for (H,C) systems. Reducing the dielectric constants of insulating materials for interconnect circuits is of significant importance for the manufacturing of fast computer chips based on the copper wiring. For this purpose, organic polymers with low dielectric constants (i.e. low-k) have been studied recently as an alternative to SiO@sub 2@. In addition to such use, organic polymers have been studied for other applications, for example, substrates of healthcare chips and optical waveguides. Hydrogen and nitrogen based plasmas such as N@sub 2@+H@sub 2@ or NH@sub 3@ plasmas are often used to etch such polymer surfaces with micron and submicron structures. The goal of this work is to study plasma-surface interactions of polymer etching process, using classical MD simulations. To represent surface reactions correctly, it is critical to employ realistic interatomic potential functions for MD simulations. In this work, therefore, we present interatomic potential functions for (H,C,N) systems, extending the Stillinger-Weber potential with some modification such as the inclusion of double and triple bonds. To compare simulation results with our potential model with those with other potential models, we have also run MD simulations with the ATB potential. Because many low-k organic polymers contain Benzene-like rings, we use poly (1,4-phenylene) as our model substrate. Preliminary results of the MD simulations will be presented.

Plasma Science and Technology
Room 315 - Session PS2-ThM

Low k Dielectric Etch

Moderator: R. Turkot, Intel Corporation

8:20am **PS2-ThM1 Smart Nanoprocess for Organic Low-k Film Etching***, **M. Hori**,* Nagoya University, Japan **INVITED**

Conventional plasma etching process depends on the external parameters such as gas pressure and input power, and hereby the optimal process condition must be obtained by investigating etching characteristics for each process. On the other hand, smart nanoprocess, where both etching rate and pattern profile are controlled with the assistance of feedback system based on the information of species monitored in situ, will enable us to realize the high performance in nano-scale fabrication. In this study, we have focused on monitoring the behavior of radical densities in the plasma to understand gas phase and subsurface reactions of radicals. By choosing internal parameters of densities (radicals and electrons) and a substrate temperature, both etching rate and fine pattern profile were controlled precisely. The behavior of species in the gas phase and their effects on the etching characteristics of organic low-k film were investigated in 500 MHz ultrahigh frequency (UHF) plasma and 13.56 MHz inductively coupled plasma using N@sub2@/H@sub2@ and N@sub2@/NH@sub3@ gas chemistry. The absolute H and N radical densities were measured by vacuum ultraviolet absorption spectroscopy employing a very compact light source. The vertical profile with a high etch rate of about 400 nm/min was successfully obtained in both plasmas simply by choosing a radical density ratio of H/H+N=0.8 and a substrate temperature of 20°C. The time evolution of plasma-induced subsurface reaction for the vertical profile was observed by Fourier transform infrared attenuated-total-reflection (FT-IR ATR) and in-situ XPS. Furthermore, the fundamental etching mechanism was clarified using multi-beams of ions and radicals. It is indicated that the smart nanoprocess is promising for the precise etching of organic low-k films.

9:00am **PS2-ThM3 Etching Mechanisms of Methylsilsesquioxane Low-k Material in High Density Fluorocarbon Plasma***, **D. Eon**, V. Raballand, G. Cartry, M.C. Peignon-Fernandez, C. Cardinaud,* CNRS, University of Nantes, France

At present, performances in integrated circuit (IC) are limited by interconnection delay, which increases with the reduction of feature size (below 100 nm). One solution to reduce interconnection delay, is to diminish the parasitic capacitance between levels by replacing SiO@sub 2@ (k=4.5) conventional interlevel dielectric by a low dielectric constant material (low-k). The integration of these into IC fabrication requires i) that a selective etching is achievable with respect to the mask and bottom layer ii) that the etching does not adversely affect the permittivity of the film. This study concerns the etching of the methylsilsesquioxane based materials (SiOC k=2.9, SiOC with 40% of porosity k=2.2) and compared to SiC etch stop layer (k=4.5), with the aim to investigate etch mechanisms. We used a 13.56 MHz Inductively Coupled Plasma source mounted above a diffusion chamber where the substrate is biased separately. Etch rates are measured in real time by in-situ multi-wavelength ellipsometry. Surface composition is analysed by quasi in-situ XPS. Langmuir probe is used in order to determine plasma densities, ion flux, and electronic distribution. Mass spectrometer and optical emission spectroscopy measurements are carried out to obtain chemical composition of the plasma. Etching has been performed in C@sub 2@F@sub 6@ in mixture with H@sub 2@, Ar, N@sub 2@, or O@sub 2@. According to these results, we studied thoroughly the mixture C@sub 2@F@sub 6@/H@sub 2@ (25%/75%), which gives the best compromise between selectivity and etch rate. For all materials and conditions, the etch rate and the atomic F concentration are strongly correlated. On another hand, XPS shows that CF@sub x@ species, when present, play an important role on the etching mechanism of SiC and SiOC. Conclusion is that selective etching requires to control precisely the formation of the passivation layer.

9:20am **PS2-ThM4 Low Damage Low-k Film Etching using Advanced Neutral Beams***, **H. Ohtake**, N. Inoue, T. Ozaki, S. Samukawa,* Tohoku University, Japan

Low damage processes on the porous MSQ by using neutral beam were investigated. The porous MSQ is very vulnerable to the plasma exposure. Especially, the methyl is drawn out from the porous MSQ during the ashing process, which causes the increase of dielectric constant. In this paper, we investigated the application of the neutral beams to the ashing processes without the effect of ions and photons. In oxygen beam, we observed the increase of the dielectric constant of low-k film as much as that in the oxygen plasma. However, when we used the hydrogen beam, the MSQ dielectric constant did not change while it increased in the case of hydrogen plasma. According to the XPS analysis, it was found that the modified layer of carbon hydride is generated on the surface of porous MSQ by hydrogen beam exposure. This modified layer is thought to prevent the methyl from being drawn out from the porous MSQ. On the other hand, in the hydrogen plasma, it is thought that the generation of this modified layer is restricted by the photons or the ions. In addition, when we used the gas mixture beam of hydrogen and nitrogen, the modified layer of carbon nitride is generated on the surface of MSQ. This layer also prevents the methyl extraction from the porous MSQ. Accordingly, the low damage ashing-processes can be achieved by using hydrogen or hydrogen- nitrogen beam because of the generation of the modified layer.

9:40am **PS2-ThM5 Control of Degradation Thickness on SiOCH Surface***, **T. Tatsumi**, T. Saitoh, A. Ando, K. Nagahata, Y. Morita,* Sony Corporation, Japan

We investigated ashing technologies for low-k/Cu integration. SiOCH film oxidizes easily forming a degradation layer that must be minimized to suppress the CD variations during wet treatment. We used an ashing system using ICP and evaluated the ashing rate, residue, and the thickness of the damaged layer (T@sub d@) on the side-wall of the SiOCH via hole. When we used H-based plasma for ashing, T@sub d@ was relatively thin. However, it was difficult to maintain a high etch rate and to remove the residue completely. Hence, we had to use O-based gas chemistry in mass production. Using O@sub 2@ plasma, T@sub d@ depended on (a) the O radical density, (b) the thickness of the C-F polymer formed on the sidewall during via etching, and (c) wafer temperature. The density of O radical depended on the partial pressure of O@sub 2@ and dissociation degree of O@sub 2@, which could be related to the number of collision with electrons: N@sub e@<@sigma@v>, where N@sub e@, @sigma@, and v were electron density, collision cross-section for dissociation, and electron energy, respectively. We estimated N@sub e@<@sigma@v> from the intensity of the optical emission of Ar (750 nm, I@sub Ar@=N@sub Ar@N@sub e@<@sigma@v>) and we found that the ashing rate, as well as the thickness of the damaged layer under various conditions, clearly depended on the "partial pressure of O@sub 2@" x "I@sub Ar@/N@sub Ar@". When we minimized the radical density by using low density (< 6 x 10 cm@super -3@) and low pressure (< 3Pa) conditions, the thickness of the damaged layer could be suppressed below 10 nm while the ashing rate was higher than 500 nm/min with no residue. To fabricate reliable Cu interconnects, we not only need to etch various low-k materials, but also quantitatively control the degradation of these materials.

10:00am **PS2-ThM6 Three-dimensional Feature Profile Evolution during Etching of Porous Dielectric Materials***, **Y.H. Im**, M.O. Bloomfield, T.S. Cale,* Rensselaer Polytechnic Institute

Porous materials are being widely investigated for use as low dielectric constant materials for state-of-the-art integrated circuit (IC) interconnects. The patterning of these materials is one of the current challenges to be overcome for application to next generation ICs. Although conventional etching technologies can be used for this purpose, one of the barriers in adapting them to these materials is the lack of the fundamental understanding of how the complicated etching mechanisms interact with the inherently 3D structure of porous materials. It is desirable to employ 3D computer simulations to answer questions that cannot be addressed by 2D simulators. We present a fully 3D simulation study of feature topography evolution under various etching processes. As a part of this effort, we have used the parallel levelset environment for nanoscale topography evolution (PLENTE) to track the evolution of systems in 3D. PLENTE is used with the ballistic transport and reaction based process simulator EVOLVE, which in turn uses a 3D Monte Carlo view factor code, to predict the fluxes and coverages of chemical species on the evolving substrate. We compare the shape of etched feature profiles to experimental data for porous dielectric materials. Etch rate and feature profile evolution were examined as functions of process conditions and porous material properties such as porosity and average pore size. This simulation technique is designed to help process engineers understand new phenomena observed in etching of porous dielectric materials and smooth the adaptation of conventional etching recipes to porous substrates.

10:20am **PS2-ThM7 Etching of a Porous SiOC with Varied Porosity in Fluorocarbon Based-plasma***, **N. Posseme**,* STMicroelectonics, France*; T. Chevolleau, L. Vallier, O. Joubert,* CNRS/LTM, France*; I. Thomas-Boutherin,* STMicroelectronics, France

In CMOS technology, the traditional SiO@sub2@ is being replaced by Low-k materials in order to reduce the total resistance capacitance delay in the interconnect levels. Before Low-k materials can be implemented successfully, many problems must be solved such as the materials stability during etch and stripping processes. This work focuses on the etching of porous methylsilsesquioxane (MSQ) materials (spin on SiOC, k = 2.2) with different porosity (30%, 40% and 50%) in fluorocarbon based plasmas (CF@sub4/Ar). The surface and bulk modification after partial etching is studied using different surface analysis techniques such as quasi in-situ X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (FTIR), mercury probe capacitance measurement (C-V) and spectroscopic ellipsometry. The etching of these materials is performed on blanket wafers in a Magnetically Enhanced Reactive Ion Etcher. Similarly to non porous SiOC materials, a decrease in etch rate of porous SiOC films is observed with either increasing Ar dilution or polymerizing gas addition (CH@sub2@F@sub2@) leading in this last case to an etch stop phenomenon. The etch rate increases with higher porosity in the SiOC film, since less material per unit thickness need to be removed as the porosity increases. After partial etching, FTIR analysis indicate that the remaining film is altered by the direct impact of ion bombardment that induces a physical degradation of porous SiOC. This film modification increases with the amount of porosity in the film. The XPS results indicate that the interaction layer formed at the film surface has almost the same composition whatever the porosity of the films studied. Complementary study, from angle resolved XPS analyses reveals also that the C and F atoms diffuse inside the pores of the different films and induce bulk modification observed on FTIR spectra. XPS analysis are also conducted on the porous SiOC sidewalls using the chemical topography analysis technique.

10:40am **PS2-ThM8 In-situ Real-time Monitoring of Profile Evolution During Plasma Etching***, **H. Gerung**, C.J. Brinker, S.R.J. Brueck, S.M. Han,* University of New Mexico

We have employed attenuated total reflection Fourier transforms infrared spectroscopy (ATR-FTIRS) to monitor profile evolution during etching of mesoporous low-k SiO@sub 2@ film in-situ and real time. The porous SiO@sub 2@ films, stacked with anti reflective coating (ARC) and patterned photoresist, are etched in an inductively coupled plasma reactor, using CHF@sub 3@ and Ar. During etching, the integrated IR absorbance by Si-O-Si asymmetric stretching modes near 1080 cm@sup -1@ decreases, and the rate of decrease in integrated Si-O-Si absorbance translates to the SiO@sub 2@ removal rate. When corrected for the exponentially decaying evanescent electric field, the removal rate helps monitor the evolution of the etch profile in real time. We have extended this technique to etching Ge. The results from Ge etching will be also discussed.

11:00am **PS2-ThM9 Critical Issues in Dual Damascene Etch***, **M. Hussein**, M. Heckscher, S. Suri,* Intel Corporation

This work examines the critical etch issues facing dual damascene integration scheme for the 90nm technology node and beyond. Emphasis will be placed on selectivity needs during via and etch stop layer etch, in particular. We investigated etching chemistries containing fluorine, and fluorocarbon-generating radicals using 300mm wafer size substrate. We will present and discuss the impact of chemistry and etching system configuration on etch selectivity during via and etch stop layer etch. Attaining a manufacturable level of selectivity between silicon-based low-k ILDs and advanced etch stop layers, in spite of the similarities in composition and characteristics of these materials, is shown to be quite challenging.

11:20am **PS2-ThM10 In-Situ Etch-Stop Etch for Cu/Low-k Damascene Etch Applications***, **P. Jiang**, R. Kraft, E. Burke,* Texas Instruments

An in-situ plasma etch process was developed for the 90nm technology in which damascene structures (vias or trenches) and their etch-stop layers are etched in a single chamber. The in-situ process sequence includes BARC opening, low-k dielectric (OSG) etch with high selectivity to etch-stop layer (SiC), and SiC etch-stop removal. This process has provided significant cost reduction and productivity benefits to the Cu single damascene integration schemes, due to fewer process steps and higher process yield. Preserving feature CDs and etch profiles for low-k dielectric etches with 193nm lithography is particularly challenging due to the poor etch resistance of 193nm resists and small CDs (<150nm). The in-situ process has reduced via etch CD bias by ~15nm as compared to the conventional ex-situ etch-stop etch. It has also eliminated via profile bowing induced typically by ex-situ etch-stop etch and post-etch cleans, and increased the selectivity of SiC to OSG by ~80% in the etch-stop etch step. More importantly, equivalent or better via yield was achieved with smaller CDs using the in-situ process, due to improved profiles. In this paper, we will discuss the development of in-situ etch-stop etch process for single damascene via etch. The detailed results about the process, and its impact on process and electrical performance will be reported.

11:40am **PS2-ThM11 Study of CO addition to C@sub 4@F@sub 8@ or C@sub 4@F@sub 8@/Ar Plasmas for Selective Etching of Organosilicate Glass (OSG) over SiC***, **L. Ling**, G.S. Oehrlein, X. Hua, X. Li,* University of Maryland, College Park*; F.G. Celii, K.H.R. Kirmse, P. Jiang,* Texas Instruments

We have examined the effect of CO addition to C@sub 4@F@sub 8@ or C@sub 4@F@sub 8@/Ar plasmas for selective etching of organosilicate glass over SiC etch stop layers. The variation of important gas phase species, thin film etching rates and surface chemistry with feedgas composition was determined. CO addition exhibits dramatically different consequences on OSG/SiC etching selectivity when added to either C4F8 or C@sub 4@F@sub 8@/Ar plasmas containing a high proportion of Ar (greater 80%). An improvement of the OSG/SiC etching selectivity results from CO addition to C@sub 4@F@sub 8@. Our data indicate little CO dissociation in this case, which is plausible considering the lower dissociation energy threshold of C@sub 4@F@sub 8@ relative to CO. X-ray photoelectron spectroscopy (XPS) analysis of OSG and SiC surfaces shows that the etching selectivity improvement for C@sub 4@F@sub 8@/CO may be explained by some incorporation of CO into deposited fluorocarbon films, an increase of the thickness and a reduction of the F/C ratio of the steady-state fluorocarbon surface layer on the SiC surface during etching. Adding CO to C@sub 4@F@sub 8@/90%Ar discharges leads to a reduction of the OSG/SiC etching selectivity. Significant dissociation of CO in Ar-rich C@sub 4@F@sub 8@/Ar/CO discharges is observed, consistent with the fact that the dissociation energy threshold of CO is lower than the Ar ionization and metastable energies. Oxygen incorporation in deposited fluorocarbon films and a reduction of the steady-state fluorocarbon surface layer thickness on SiC are observed by XPS in this case, explaining the loss of OSG/SiC etching selectivity for C@sub 4@F@sub 8@/Ar/CO discharges.

Semiconductors
Room 326 - Session SC-ThM

Heteroepitaxy and Strain Engineering

Moderator: R.S. Goldman, University of Michigan

8:40am **SC-ThM2 Strain Engineering of SiGe/Si Structures***, **P.M. Mooney**,* IBM T.J. Watson Research Center **INVITED**

Heteroepitaxy allows the growth of semiconductor structures for a wide variety of device applications. When the materials are also lattice mismatched, the strain can be tailored to enhance the electronic properties of the active device layers. At the same time, however, misfit dislocations and other defects that tend to degrade device characteristics may be present. Strained Si MOSFETS are being developed for high-speed logic applications. These devices are built in a Si layer under biaxial tensile strain that is grown pseudomorphically on a so-called virtual substrate, typically a thick, strain-relaxed SiGe buffer layer on a Si(001) substrate. Key to the success of this application is the control of the misfit dislocations required to relieve the strain in the SiGe layer to achieve a low density of threading dislocations in the active device layers. Two types of SiGe/Si structures will be discussed. Strain-relaxed SiGe buffer layers produced by the implantation of He below the interface between a pseudomorphic SiGe layer and the Si(001) substrate and subsequent annealing are significantly more relaxed compared to layers of the same thickness that were not implanted. Platelet defects that are formed near the top of the Si substrate during annealing serve as dislocation nucleation sources. Elastic (defect free) strain relaxation of SiGe/Si structures is also under investigation. We have recently demonstrated that a pseudomorphic SiGe layer grown on free-standing Si relaxes elastically. The strain is shared with the free-standing Si layer resulting in Si under biaxial tensile strain.

9:20am **SC-ThM4 Strain Relaxation of Step-graded InAsP Buffers on InP Grown by Molecular Beam Epitaxy***, **M.K. Hudait**, Y. Lin, S.A. Ringel,* The Ohio State University

Compositionally graded metamorphic buffers grown on InP substrates to increase the substrate lattice constant are of interest to support a range of high-speed electronic and infrared optoelectronic devices based on the InGaAsP material system. Recent work by our group has shown that grading the composition of the anion sublattice using InAsP buffers as opposed to the group-III cation sublattice using In(Al,Ga)As buffers is advantageous for such applications since decoupling the growth rate (Indium flux) from the composition control (As:P flux ratio) results in superior morphological properties of relaxed layers. Here, we discuss the strain relaxation properties of step-graded InAs@sub y@P@sub 1-y@ out to a nominal composition of y = 0.4, representing a total misfit of ~ 1.2% with respect to InP. For this study, InAs@sub y@P@sub 1-y@ buffers were grown on both on-axis and 2° off-cut (001) InP substrates under identical solid source MBE growth conditions with an average grading rate of 20% As/µm. The relaxation of each layer within each buffer was measured along [1-10] and [110] directions using TAXRD to evaluate asymmetric relaxation and tilt relative to the initial substrate orientation. For both substrate types, the strain relaxation was found to be symmetric and greater than 90% for the top InAs@sub 0.4@P@sub 0.6@ layer. This indicates that @alpha@ ([1-10] direction) and @beta@ ([110] direction) slip systems have similar activation energies for dislocation nucleation. Moreover, a small epilayer tilt of ~190 arcsec was observed for both substrate orientations, which indicates that tilt generated by @alpha@ and @beta@ dislocations will be in proportion to the substrate offcut resolved in [110] and [1-10] directions, respectively. The relation between these observations and properties of group-V and group-III core dislocations, and a comparison to cation based graded layers will be made to optimize the growth of these buffers.

9:40am **SC-ThM5 Effects of InAlSb Buffer Layers on the Structural and Electronic Properties of InSb Films***, **X. Weng**, N.G. Rudawski, R.S. Goldman,* University of Michigan*; D.L. Partin, J. Heremans,* Delphi Research and Development Center

InSb is useful for a variety of device applications, including long wavelength light sources and magnetoresistive sensors. InSb films are generally grown on GaAs substrates, with a 14.6% lattice mismatch which results in a high density of threading dislocations. In earlier work, we showed that electron scattering from the strain field associated with threading dislocations is the primary mobility-limiting mechanism in highly mismatched InSb films.@footnote 1@ The electron mobility of InSb films increases with the film thickness due to the decrease of threading dislocation density. Recently, highly mismatched resistive buffers such as InAlSb showed promise for increasing the electron mobility of thin InSb films.@footnote 2@ However, the mechanisms of buffer strain relaxation and the consequent increase in InSb electron mobility are not well understood. Thus, we have studied the effects of In@sub0.94@Al@sub0.06@Sb buffers on the structural and electronic properties of InSb films. We find a significant increase of electron mobility for InSb films grown on In@sub0.94@Al@sub0.06@Sb buffers, in comparison with those grown directly on GaAs. Cross-sectional transmission electron microscopy (TEM) reveals bending of threading dislocations at the InSb/In@sub0.94@Al@sub0.06@Sb interface, suggesting that the InSb/In@sub0.94@Al@sub0.06@Sb heterojunction plays an important role in suppressing the propagation of threading dislocations. Plan-view TEM shows a more than 50% decrease of threading dislocation densities in InSb films grown on In@sub0.94@Al@sub0.06@Sb layers compared with those grown directly on GaAs, suggesting that the electron mobility increase is likely due to the reduction in dislocation density. The effects of the buffer composition on the structure and properties of the InSb films will also be discussed. @FootnoteText@@footnote 1@ X. Weng, R.S. Goldman, D.L. Partin, and J.P. Heremans, J. Appl. Phys. 88, 6276 (2000). @footnote 2@D.L. Partin, J. Heremans, and C.M. Thrush, J. Vac. Sci. Technol. B 17, 1267 (1999).

10:00am **SC-ThM6 Heteroepitaxy of III-Se Materials: Compatibility to Si and Their Growth Studied by In-situ Scanning Probe Microscopy*, T. Ohta,* *A. Klust, J.A. Adams, Q. Yu, M.A. Olmstead, F.S. Ohuchi,* University of Washington

Heteroepitaxy of semiconductors on silicon is essential for expanding Si-based technology beyond standard microelectronics. Materials consisting of Group III (Ga and Al) and selenium (Se) are of particular interest, combining Si compatibility with structural versatility and optical band gaps (Eg(Ga@sub x@Se@sub y@)=1.8-2.6eV and Eg(Al@sub x@Se@sub y@)>3.1eV). We present a study of heteroepitaxy of layered GaSe on Si(111) using scanning tunneling microscopy (STM). GaSe is composed of a stack of iono-covalently bonded quad layers (QL) of Se-Ga-Ga-Se with van der Waals interactions between the layers. Of general interest for the growth of layered materials whether the full QL is required for layer nucleation. During growth, we observed: (1) formation of a pseudomorphic GaSe-bilayer, (2) development of triangular QL nuclei, followed by (3) layer-by-layer growth of GaSe layers. The first GaSe bilayer perfectly passivates the Si(111), making its surface environmentally inert. Triangular islands, one QL thick, nucleate on this passive surface with their edges aligned to of Si(111). Nuclei with two orientations, rotated by 180°, are observed, leading to orientational domains in thicker layers. We characterized their electronic structures and the type of defects incorporated in the domains. In thicker films, GaSe layers often extended over substrate atomic steps, showing a "carpet-on-steps" morphology. This work is supported by NSF Grant DMR 0102427 and the M. J. Murdock Charitable Trust. T. O. further acknowledges support by UIF Nanotechnology fellowship of the University of Washington, and A. K., the Alexander von Humboldt-Foundation, Germany.

10:20am **SC-ThM7 Characterization of High Quality GaAs(100) Films Grown on Ge(100) Substrates*, A. Wan,* *V.M. Menon, D. Wasserman, A. Kahn, S.R. Forrest, S.A. Lyon,* Princeton University

We have grown GaAs (100) films by MBE on off-axis Ge(100) substrates cut 6° towards the (110) plane and 6Âº towards the (111) plane. The motivation for this work is the integration of GaAs and lattice matched InGaAsN on Si and SiGe. Vicinal surfaces with regular arrays of double steps are crucial in eliminating anti-phase domains in III-V/elemental systems.@footnote 1@ We used electron diffraction, STM, AFM, X-ray and ultraviolet photoemission, electron channeling, photoluminesence (PL) and Raman spectroscopy to investigate the quality of the GaAs films. We observed two domains (1 x 2 and 2 x 1) on the surfaces of the Ge substrates both after annealing and after Ge buffer growth, on each of the off-cut orientations. GaAs films grown on Ge substrates cut towards the (110) exhibited poor morphology, with evidence of faceting and polycrystalline domains, whereas films grown on substrates cut towards the (111) exhibited much higher crystalline quality with a (4 x 2) recontruction. Low temperature PL exhibited a sharp narrow peak at 1.51 eV on samples grown on substrates cut towards (111), indicative of high quality material. We also investigated the effects of using different growth conditions including migration enhanced epitaxy, which have been reported to reduce both the APD and doping at the GaAs/Ge.@footnote 2,3@ We conclude that high quality GaAs can be grown at a variety of growth temperatures and conditions on off axis Ge(100) substrates cut 6° towards the (111). @FootnoteText@ @footnote 1@J.M. Zhou et al., Appl. Phys Lett. 68, 628 (1996) @footnote 2@R.M. Sieg et al., J. Vac. Sci. Technol. B 16, 1471 (1998) @footnote 3@J.A. Carlin et al., Appl. Phys Lett. 76, 1884 (2000).

10:40am **SC-ThM8 In Situ Monitoring of Stress Relaxation in Semiconductors*, E. Chason,*** Brown University **INVITED**

Understanding stress relaxation in heteroepitaxial semiconductors is important if we want to be able to control surface morphology and dislocation density. Because the relaxation process is a complex interaction of many kinetic processes, it is useful to be able to monitor the evolution of the stress and surface morphology in real time. We have developed several optical diagnostics that can be used during growth without interrupting the growth process. Stress relaxation is monitored by measuring the curvature induced in the substrate by the strained film. The technique is robust and has been used in a number of processing environments including MBE, MOCVD and sputter deposition. Examples of stress relaxation due to islanding and dislocation motion will be presented. Spectroscopic light scattering is used to measure the power spectral density of the surface height distribution without having to rotate the sample or detector. This has enabled us to measure the density of strain-relieving islands in heteroepitaxial layers and to understand the effect of elastic interactions between islands on their shape and alignment.

11:20am **SC-ThM10 Strain Effects in Si-Ge Growth on Vicinal Si Surfaces Prepared by Laser Texturing*, F. Watanabe,*** *D.G. Cahill, J.R. Serrano, S. Hong, T. Spila, J.E. Greene,* University of Illinois at Urbana-Champaign

Growth of Si-Ge strained layers on Si substrates is of great interest because of its multiplicity of growth modes. These growth modes are a complicated function of temperature, alloy content, growth rate, and substrate vicinality. Laser texturing of Si provides contamination- and defect-free curved surfaces for our studies of how the morphology depends on vicinality. The surface features produced by fluid flow in the laser melt are approximately 5 µm in diameter and 200 nm in depth, and contain vicinal surfaces with orientations 0-10 degrees off (001). SiGe layers are grown by gas-source MBE. At high strain (~80% Ge), film growth is similar to that of 100% Ge, but the formation of dislocated islands at high coverage is less pronounced. At a growth temperature of 600 °C, nucleation of dome-shaped three dimensional islands takes place preferentially on vicinal surfaces with orientations within one degree of (001). Island nucleation is suppressed on surfaces oriented more than a degree off (001). At these higher vicinalities, ripple shaped morphologies form along directions. The preferred regions for these instabilities are 5-10 degrees miscuts in the directions inside and outside the laser dimples.

Surface Science
Room 310 - Session SS1-ThM

Patterned Growth and Etching of Semiconductors

Moderator: A.C. Kummel, University of California, San Diego

8:20am **SS1-ThM1 Self-Assembly of Atomic Chains on Stepped Silicon*, F.J. Himpsel,*** University of Wisconsin, Madison **INVITED**

It is now possible to systematically engineer one-dimensional chain structures of metal atoms on silicon using self-assembly. Stepped Si(111) templates offer the opportunity to vary the chain spacing with atomic precision and to control the electron count, including fractional band filling. Two applications of chain structures are explored: 1. An atomic scale memory is constructed using self-assembled, 5-atom wide tracks that form on Si(111)5x2-Au.@footnote 1@ Extra Si atoms in lattice sites on top of the tracks are used to store data, one bit per atom with an empty buffer space of 5x4 atoms. The density is comparable to that in DNA (32 atoms/bit). This memory serves as test structure for finding the fundamental limits of data storage density and readout speed. They are given by the correlation between adjacent atoms@footnote 2@ and the shot noise in STM.@footnote 1@ 2. One-dimensional electrons in metallic chains are characterized by mapping their band structure and Fermi surface.@footnote 3@ While metallic surface electrons are completely de-coupled from the Si substrate, the metal atoms are locked into Si lattice sites which makes a Peierls transition to an insulator unfavorable. The dimensionality is varied between 1D and 2D via the chain spacing. @FootnoteText@ @footnote 1@ R. Bennewitz, et al., Atomic scale memory at a silicon surface, Nanotechnology 13, 499 (2002)@footnote 2@ A. Kirakosian, et al., Correlations in a one-dimensional lattice fluid on Si(111)5x2-Au; Phys. Rev. B, in press.@footnote 3@ R. Losio, et al., Band splitting for Si(557)-Au: Is it spin-charge separation?, Phys. Rev. Lett. 86, 4632 (2001); K. N. Altmann, et al., Electronic structure of atomic chains on vicinal Si(111)-Au, Phys. Rev. B 64, 035406 (2001); J. N. Crain, et al., Fermi Surfaces of Surface States on Si(111) + Ag, Au, Phys. Rev. B 66, 205302 (2002); J. N. Crain, et al., Fractional band filling in an atomic chain structure, Phys. Rev. Lett., in press.

9:00am **SS1-ThM3 Length Scale Dependence of Evolution of Corrugations During Sublimation from Patterned Vicinal Si(111) Surfaces***, *T. Kwon, H.C. Kan, **R.J. Phaneuf,*** University of Maryland

We describe the results of a combinatorial approach toward controlling the evolution of topography during sublimation from silicon. Arrays of lithographically-patterned cylindrical pits on vicinal Si(111) surfaces interfere with the motion of "straight" steps at temperatures near 1200C. On each substrate, pit diameters are varied from 0.7 microns to 8 microns, with the pit-spacing equal to twice the diameter. Within this range, a critical length scale is found, above which straight steps wrap around pits, leaving a pronounced corrugation within the surface plane, but beneath which the evolution is quickly to straight step bunches, with a pronounced corrugation perpendicular to the surface plane. In the simplest model, this critical length scale is set by the competition between the sublimation induced spreading pressure on the steps and their intrinsic stiffness. Preliminary observations on vicinal Si(111) surfaces also indicate the importance of step-step interactions in the evolution of the topography, with a pronounced inward relaxation of the pit wall on the "uphill" side, and an inward bowing of otherwise straight steps on the "downhill" side. *Work supported by the Laboratory for Physical Sciences and an NSF-MRSEC.

9:20am **SS1-ThM4 Current-Induced Pattern Formation on Vicinal Surfaces**, ***T. Zhao**, J.D. Weeks,* University of Maryland

Vicinal surfaces can exhibit a number of different morphological instabilities that may be important in crystal growth and nano-scale device fabrication. Particularly interesting step bunching and step wandering patterns arise from electromigration on Si(111) surfaces; these patterns are observed depend on both the current direction and the temperature. We develop a new two-region diffusion model where adatoms in a small region near a step are assumed have different diffusion rates from those on terraces due to different surface reconstruction or bonding configurations near the step. A linear stability analysis of this theoretical model yields both the bunching behavior and the most unstable wavelength for in-phase wandering. We find good agreement with existing experiments.@footnote 1@ Moreover, to account for the long time behavior of such surfaces, we use a geometric representation of the interface to derive a nonlinear evolution equation for a step in the presence of anisotropic diffusion arising from the electric field. The evolution of the step resulting from fields oriented with different angles off the z-axis bears strong resemblance to the experiments.@footnote 2@ @FootnoteText@ @footnote 1@ See M. Degawa, K. Thürmer, I. Morishima, H. Minoda, K. Yagi, and E.D. Williams, "Initial stage of in-phase step wandering on Si(111) vicinal surfaces," Surf. Sci. 487, 171 (2001)@footnote 2@ See M. Degawa, H. Minoda, Y. Tanishiro, and K. Yagi, "In-phase step wandering on Si(111) vicinal surfaces: Effect of direct current heating tilted from the step-down direction," Phys. Rev. B 63, 045309/1 (2001).

9:40am **SS1-ThM5 Effects of Diffusion and Chemical Reactivity on Step Bunching: The Formation of Macrosteps During Etching**, ***S.P. Garcia**, H. Bao, M.A. Hines,* Cornell University

The chemical production of macroscopic features on etched silicon surfaces was investigated using scanning tunneling microscopy and atomistic, kinetic Monte Carlo simulations. Macroscopic features arise when atomic steps bunch together into enormous macrosteps with heights on the order of microns. In aqueous silicon etching, step bunching is driven by spatial inhomogeneities in the etchant, as demonstrated by experiments in which diffusive transport is controlled. Under conditions of step-flow etching, inhomogeneities can be enhanced when random fluctuations bring some steps close together. The inhomogeneities can influence the etch rate locally. For example, etchant depletion can lead to local deceleration of step etching, whereas heat released by the etching reaction can lead to local acceleration. This coupling of chemical reactivity to diffusion-controlled processes may cause closely spaced steps to speed up or slow down. To understand how atomic-scale chemical processes and mesocale diffusion produce step bunching, we have developed a simulation that combines an atomically realistic, two-dimensional model of etching with a continuum model of diffusion. Simulations generated by this technique show that step bunching can give rise to a variety of etch morphologies, all of which are strongly affected by the site specificity of etching and by the effect of diffusion on local reactivity.

10:00am **SS1-ThM6 Equilibrium Morphologies for Cl-roughened Si(100) at 700 - 750 K: Experiments and Monte Carlo Modeling**, ***G.J. Xu**, K.S. Nakayama, B.R. Trenhaile, C.M. Aldao, J.H. Weaver,* University of Illinois at Urbana-Champaign

Adsorbed halogen atoms on Si(100)-(2x1) can induce roughening at temperatures where material removal (etching) is minimal. Variable temperature scanning tunneling microscopy was used to follow roughening at 700 - 750 K for surfaces with 0.1 - 0.99 ML of Cl. Dimer vacancies and Si adatoms were observed at short times, and at longer times the progression toward a state of dynamic equilibrium was traced. Once dynamic equilibrium was reached, the appearance of individual pits and regrowth islands changed but their densities and mean sizes did not. The results show that the roughness depends non-linearly on Cl coverage with surfaces having 0.3 ML being nearly ten times rougher than those with 0.1 ML. The importance of Cl-free dimers is stressed, and the role of Cl as an impediment for vacancy and adatom diffusion is demonstrated. Roughening is attributed mainly to adsorbate-adsorbate repulsive interactions. Further insight can be gained from Monte Carlo simulations, where the consequences of adsorbate-adsorbate interactions are explored and the resulting morphologies are compared with those experimentally observed. While adsorbate-adsorbate interactions may be the main driving force responsible for roughening, contributions from other interactions cannot be ruled out.

10:20am **SS1-ThM7 Adsorbate Interactions and Roughening of Sub-monolayer Halogenated Si(100) Surfaces**, ***D. Chen,*** University of North Carolina at Chapel Hill*; J.J. Boland,* Trinity College Dublin, Ireland

Spontaneous roughening of halogen terminated Si(100) surfaces was previously shown to arise from steric repulsions between adsorbates.@footnote 1@ However, more recent studies have shown that significant roughening occurs even for coverages that are substantially below a monolayer and calls into question the role of steric repulsions. Here, we present a comprehensive study of the roughening process on a sub-monolayer chlorinated Si(100) surface, and in particular its correlation with both the surface coverage and spatial distribution of adsorbates. We find the roughening is due to steric repulsions and this interpretation is supported by DFT calculations. A new model is developed to describe the dependence of roughening on halogen coverage. @FootnoteText@ @footnote 1@C.F.Herrmann, D.Chen, J.J.Boland, Phys. Rev. Lett. 89, 096102 (2002)

10:40am **SS1-ThM8 Atomistic Modeling of Morphological Evolution During Active and Passive Oxidation of Si(100)**, ***M.A. Albao**, D.-J. Liu,* Iowa State University*; C.H. Choi,* Kyungpook National University, South Korea*; M.S. Gordon, J.W. Evans,* Iowa State University

Prolonged exposure of Si(100) surfaces to oxygen produces: etching at high temperatures (T) characterized by the formation of monolayer-deep elliptical etch pits in successive layers (active oxidation); simultaneous etching and formation of oxide-capped Si-nanoprotrusions at moderate T (transition regime); and coverage of the substrate by an oxide layer at low T (passive oxidation). We develop a simple atomistic model with the goal of describing evolution of the complex far-from-equilibrium surface morphology for a broad range of temperatures across the transition regime. Model development is guided by experimental observations, by general concepts from nucleation theory for the formation of etch pits and oxide islands, and by input from ab-initio quantum chemistry (e.g., indicating different SiO desorption barriers for perfect and defective surfaces).

11:00am **SS1-ThM9 Oxygen Etching of Low- and High-Index Si Surfaces**, *J.L. Skrobiszewski, **A.A. Baski,*** Virginia Commonwealth University

When Si surfaces are exposed to O@sub 2@ at elevated temperatures, both oxide nucleation and etching can occur, with etching dominating at higher temperatures. We have used scanning tunneling microscopy (STM) to study the transition regime where both processes occur on the low-index (001) and (111) surfaces, as well as on the high-index (5 5 12) and (113) surfaces. All of these surfaces were exposed to O@sub 2@ at sample temperatures of 675 to 750°C, pressures on the low 10@super -7@ Torr scale, and exposures of 5 to 400 Langmuirs. On the low-index surfaces, the surface morphology can be significantly disrupted in this transition regime by etch pits, as well as monoatomic height islands caused by etching around oxide-induced pinning sites. The original terrace-plus-step morphology is only maintained for temperatures above 750°C, where only step-flow etching occurs. For the transition regime on the high-index Si(5 5 12) surface, no etch pits are found on the terraces, but three-dimensional pyramidal or linear islands are observed on terraces and along step edges. These islands presumably form at oxide nucleation sites and grow in size as the surrounding surface is etched away. Interestingly, both the pyramidal and linear islands incorporate (113) facet planes, indicating an enhanced stability of this orientation against etching. When the Si(113) surface is exposed to O@sub 2@ under similar conditions, the resulting morphology also shows no etch pits and incorporates 3D islands, but without any well-defined facet planes. The etching behavior of the high-index surfaces in the transition regime is therefore qualitatively different from that observed for the low-index planes.

11:20am **SS1-ThM10 Growth of Gd on the High-Index Si(113) and Si(5 5 12) Surfaces***, E. Morris, **J.W. Dickinson**, A.A. Baski,* Virginia Commonwealth University

The growth of rare earth metals on the low-index Si(001) surface has been of recent interest due to the appearance of silicide "nanowires."@footnote 1@ This nanowire formation is presumably due to a close lattice match between the rare earth silicide and Si lattice along the [1bar10] row direction, and poor match perpendicular to it. In this study, we have used scanning tunneling microscopy (STM) to examine the growth of the rare earth metal Gd on two high-index Si surfaces: Si(113) and Si(5 5 12). These two surfaces are oriented 25.2° and 30.5° down from (001) towards (111), respectively. When very low coverages of Gd are deposited onto these surfaces and annealed at 600°C, (113) terraces with a well-ordered 2x2 reconstruction are formed. In the case of Si(5 5 12), the reconstructed (113) terraces are opposed by other facet orientations. When the coverage is increased to approximately 0.5 ML, isolated nanowires nucleate at step edges and extend along the [1bar10] direction. These nanowires are 5 to 15 nm wide, 1 to 2 nm tall, and grow up to 0.5 micron in length. Because the lattice periodicity along the nanowire direction is identical for the (001), (113), and (5 5 12) surfaces, the appearance of such nanowires on the high-index surfaces provides further evidence for a lattice mismatch mechanism. Interestingly, the anisotropic structure of these high-index surfaces results in nanowire growth that causes fewer disruptions to the initial step morphology than observed for (001). @FootnoteText@ @footnote 1@ C. Ohbuchi, J. Nogami, Phys. Rev. B 66, 165323 (2002) and references therein.

11:40am **SS1-ThM11 Attempts on Synthesizing Linear Atomic Metal Chains on GaN(0001)***, C. Lung, **C. Chang**,* National Taiwan University, R.O.C.

The continuing advances in miniaturization of semiconductor devices have seriously challenged the fields of materials processing and circuit designs. This work explores the chemical reaction involved in the possible formation of nanowires using a pyridylamino chelate that contains a linear atomic chain of chromium for CVD. The adsorption, surface reaction, and thermal pyrolysis of this metal string chelate on GaN(0001) were characterized using synchrotron radiation-induced core-level photoelectron spectroscopy, secondary ion mass spectrometry, and temperature-programmed desorption. Secondary ion mass spectrometric studies showed that pyridylamino trinuclear chromium complex may react with the GaN(0001) surface to produce pyridine and pyridylamino fragments even at a very low substrate temperature of less than 150 K. Upon increasing exposure of the trinuclear chromium metal-chain complex on GaN(0001), the Cr3p photoelectron profile altered substantially, revealing an evolution in bonding configuration of the chromium metal-chain chelate on the surface. At low exposures, the Cr3p profile contained three features, peaked at different binding energies, of equal areas. The number of distinguishable features in the Cr3p spectrum increased to five as the chelate coverage on GaN(0001) was increased to more than one monolayer. Increasing the substrate temperature not only caused a change of the bonding geometry of the chromium string on the surface but also induced decomposition of the chromium chelate in two different stages. Desorption of the dipyridylamino ligand took place at a substrate temperature of 340 K, while disruption of the chromium string occurred at about 540 K. Results of this work point to the possibility of forming chromium nanospecies on the semiconductor surface through vacuum chemical deposition using organometallic metal strings. The fundamental aspects and the formation of nanowires involved in the nano-contact technology will be discussed.

Surface Science
Room 327 - Session SS2-ThM

Catalysis III: High vs. Low Pressures

Moderator: J.N. Russell, Naval Research Laboratory

8:20am **SS2-ThM1 Oxide Nucleation Kinetics on Al(111): The Role of Short-range and Long-range Interactions between Chemisorbed O Atoms***, D.E. Oner, B. Kasemo, **I. Zori@aa c@**,* Chalmers University of Technology and Göteborgs University, Sweden

Experimental work indicates that oxide nucleation on Al(111) takes place in a heterogeneous surface phase, at an average coverage of chemisorbed O atoms of about 0.15ML, specifically at the edges of chemisorbed O islands containing 10-15 O atoms. The former observation was based on spectroscopic evidence while the latter was directly observed in STM experiments. In this contribution we suggest that the rate for oxide nucleation is strongly influenced by a combination of a long-range repulsive (elastic) interaction in competition with a short-range (nearest neighbor) attractive interaction between O adatoms. The model used to describe oxide formation is an extension of an earlier kinetic model that in addition to the oxide nucleation step also includes adsorption/chemisorption step. In the pure chemisorption phase O@sub 2@ dissociative adsorption takes place that leads to an O island size distribution in agreement with the STM observations. Chemisorbed O atoms interact via superimposed short-range nn attractive and long-range repulsive interactions. The oxide nucleation is simulated via a place exchange step. The latter step is the rate-limiting step for oxide nucleation. The short-range nn interaction stabilizes the chemisorbed phase, while the repulsive long-range interaction promotes oxide formation, i.e. it enhances the place exchange jump rate. Our Monte Carlo simulations, based on the transition theory approach, can account for: a) the observed threshold in O island size needed for oxide nucleation to occur, b) the total oxygen uptake kinetics and c) the oxide formation kinetics, reported in recent STM-surface spectroscopic experiments. The two important parameters in the model are the strengths of the long-range and short-range interactions, respectively. Agreement between simulation predictions and experimental data is achieved for a unique and reasonable choice of model parameters.

8:40am **SS2-ThM2 Chemical Inhibition of Aluminum Surface Oxidation***, **V.J. Bellitto**,* Naval Surface Warfare Center*; J.N. Russell, Jr.,* Naval Research Laboratory

Aluminum powders are used to tailor the energetic content of propulsion and explosive systems. As the size of aluminum particles approach the nano-scale, the performance of the energetic materials may be enhanced by providing greater surface to volume ratios, but not if the nano-particle is largely comprised of aluminum oxide. Therefore, we are examining chemical methods for passivating aluminum surfaces and inhibiting oxidation. We report the surface chemistry of a series of perfluoro- and perhydro- carboxylic acid compounds on an Al(111) surface and their ability to inhibit aluminum surface oxidation. Using x-ray photoelectron spectroscopy and infrared reflection absorption spectroscopy we established the compounds chemisorb on the atomically clean Al(111) surface through scission of the O-H bond and formation of carboxylate species. We monitored the temperature dependent chemistry of the adsorbates, demonstrating the greater thermal stability of the fluorinated surface species. The oxidation rates of the clean, partially functionalized (0.5 ML) and fully functionalized (1ML) Al(111) surfaces were compared. The fully functionalized surface did not exhibit spectroscopic features characteristic of O@sub 2@ chemisorption or Al@sub 2@O@sub 3@ formation even after being exposed to > 1 x 105 L of O@sub 2@ at room temperature. The thermal dependence of the oxidation inhibition is under investigation.

9:00am **SS2-ThM3 Methane Dissociative Chemisorption on Ni(100): Closing the Non-equilibrium Gap between Surface Science and Catalysis***, **H.1 Abbott**,* Unaffiliated*; A. Bukoski, D. Kavulak, I. Harrison,* University of Virginia

A simple, 3-parameter microcanonical unimolecular rate theory of gas-surface reactivity is shown to predict experimental dissociative sticking probabilities for methane dissociative chemisorption on the Ni(100) surface over roughly 10 orders of magnitude variation in both pressure and sticking - even at quantum state resolved levels of detail. Facile energy randomization within the transiently formed gas-surface collision complexes is postulated to make the pooled energy from 15 local degrees of freedom statistically available to surmount the barrier to dissociation. The apparent threshold energy for C-H bond cleavage of CH@sub 4@

incident on Ni(100) is 65 kJ/mol, down from 432 kJ/mol in the gas phase. Interestingly, this threshold energy is in quantitative accord with ab initio quantum chemistry calculations, but 15-45% smaller than calculations based on generalized gradient approximation density functional theory. More generally, some of the difficulties faced when interpreting non-equilibrium surface science experiments and comparing them with equilibrium catalysis experiments will be discussed.

9:20am **SS2-ThM4 High Pressure STM Studies of Metal and Alloy Surfaces: Adsorption Induced Phase Separation***, **E.K. Vestergaard**, R.T. Vang, F. Besenbacher,* University of Aarhus, Denmark

A major issue in the catalytic community concerns the validity of applying surface science data obtained under Ultra-High Vacuum (UHV) conditions to "real" catalytic processes occurring at atmospheric pressure and above. Using high-pressure scanning tunneling microscopy (HP-STM) we have studied the adsorption structures on Pt(111) and Ni(111) at 1 bar of CO, and for these simple systems we demonstrate that the CO adsorption structures at high pressures are similar to structures formed under low pressure and low temperature conditions. Furthermore, we present results concerning the influence of high CO pressures on the stability of a Au/Ni surface alloy. Exposing the Au/Ni(111) surface alloy to 1 bar of CO results in a Ni(111) surface covered with small Au clusters, showing that high CO pressures induce a phase separation of the alloy. When scrutinizing this process at slightly lower pressures (10-20 torr), we have been able to follow the phase separation in real time. STM movies show that the Au cluster formation starts at the step edges of the Ni surface. Ni atoms are removed from the steps, and as the steps thus move over the surface Au clusters are nucleated and left behind in the wake of the moving steps. We propose that the removal of Ni-atoms is caused by Ni-carbonyl formation; CO is known to react with Ni surfaces at elevated pressures to form Ni-carbonyls, which are volatile at room temperature and therefore leave the surface. This latter study provides an example of a pressure gap, where model systems studied under UHV conditions certainly lack important aspects of the processes found at more realistic conditions.

9:40am **SS2-ThM5 STM Observation of Model Catalysts in Action: from Vacuum to High Pressures***, **J.W.M. Frenken**, B.L.M. Hendriksen, M. Ackermann, S. Bobaru,* Leiden University, The Netherlands **INVITED**

Surface-science research in the field of catalysis is plagued by the presence of a large disparity between the gas pressures acceptable in most surface-sensitive instruments and the pressures used in practical catalysis. This so-called 'pressure gap' can easily be as large as ten orders of magnitude. One may expect that there are several phenomena that behave non-linearly over this enormous pressure range, which makes it difficult, and in some cases even impossible to simply extrapolate the results of low-pressure experiments to the high-pressure reality of catalysis. In order to bridge the pressure gap, we have recently constructed a special-purpose STM, which is integrated with a tiny flow reactor cell. Only the tip of the STM is inside the reactor. With this new instrument, we have obtained a first atomic-scale look at 'live' (model) catalysts, while they were active under semi-realistic conditions, namely high pressures and elevated temperatures. Simultaneously with the STM-observation, the instrument can analyze the composition of the gas leaving the reactor. Results will be shown for CO-oxidation on Pt(110), Pt(111), and Pd(001). These results reveal a new reaction mechanism, the so-called 'Mars-van-Krevelen'-mechanism, which is only active at high pressures. On each of these surfaces, the surface structure and the chemical reactivity are observed to switch simultaneously at a specific pressure ratio between O@sub2@ and CO. In each case, the most active structure is identified as a thin surface oxide, which takes part in the reaction with CO. @FootnoteText@ @footnote 1@ B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev. Lett. 89 (2002) 046101.@footnote 2@ STM movies of cataysts in action can be viewed on our website: http://www.physics.leidenuniv.nl/sections/cm/ip.

10:20am **SS2-ThM7 Universality in Heterogeneous Catalysis***, **J.K. Nørskov**,* Technical University of Denmark, Denmark **INVITED**

Electronic structure methods based on density functional theory have reached a level of sophistication where they can be used to describe complete catalytic reactions on transition metal surfaces. This gives an unprecedented insight into these processes, and it allows us to pinpoint the origin of the catalytic activity of a metal in terms of its electronic structure. The ammonia synthesis is used to exemplify the approach. It will be shown that by combining density functional calculations with kinetic modelling we can now predict relative catalytic activities of different metals. The generality of the approach is illustrated by including a number of other catalytic reactions into a universal property-activity scheme, which identifies the surface properties that determine the catalytic activity for a whole class of reactions.

11:00am **SS2-ThM9 Lateral Interactions in the Kinetics of Surface Reactions***, **D.L.S. Nieskens**, D. Curulla Ferre, A.P. van Bavel, J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands

The rate of a chemical reaction on a surface depends strongly on the presence of neighboring adsorbate species. As lateral interactions between adsorbates are predominantly repulsive, their effect becomes notable at highly covered surfaces. Lateral interactions can change the kinetic parameters (the activation energy and the pre-exponential factor) of a reaction. A change in these kinetic parameters can cause a reaction to occur at a different temperature or pressure. Lateral interactions can even enable a certain reaction pathway which otherwise would be inaccessible. Our goal is first to quantitate these lateral interactions, and second to make good use of them in enabling new reaction pathways. For this we do experiments on single crystal surfaces. We use a combination of techniques: Temperature Programmed Desorption (TPD), Static Secondary Ion Mass Spectrometry (SSIMS), Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectroscopy (HREELS). Using this combination of techniques we obtain a complete picture of the concentration of species, both in the gas phase as well as on the surface. Furthermore we can detect any ordering that occurs on the surface. In addition to the experimental work we also performed Density Functional Theory (DFT) calculations on the same kind of systems. Our strategy for determining lateral interactions is to find ordered structures of an adsorbate A on the surface, then co-adsorb a species B and determine the effect of A on the desorption of this species B. By using an ordered structure of adsorbate A, we are able to "count" the number of "A-neighbors" of the desorbing species B and thus assign the total interaction energy to a known number of neighbors. This enables us to quantify the lateral interaction energy between adsorbate A and B. The energies acquired by the experiments are quite consistent with the ones determined by the computational approach.

11:20am **SS2-ThM10 Strategies for the Study of Methanol and CO Electrocatalysis on Nanometer-Scale Catalysts***, **C. Korzeniewski**,* Texas Tech University

The electrochemical oxidation of methanol and related small molecules has been of special interest in relation to fuel cell research. The development of fuel cells that operate below 100 Â°C on methanol, or H2 has stimulated interest in the reaction steps involved in methanol and carbon monoxide oxidation at metal electrodes. In addition to being a by-product of methanol oxidation, carbon monoxide can also be present as an impurity in H2. Adsorption of carbon monoxide on the anode catalyst generally degrades its performance. We have approached the study of methanol and carbon monoxide oxidation with the use of electrochemical techniques in combination with in situ infrared spectroscopy and wet-analytical methods. This presentation will focus on the surface electrochemistry of methanol and carbon monoxide at nanometer scale Pt and bimetallic Pt materials. Catalysts are adsorbed onto smooth gold and highly ordered pyrolytic graphite (HOPG) electrodes. Gold enables infrared sampling in a standard reflectance geometry, while HOPG allows particle characterization with respect to size distribution and spatial arrangement by atomic force microscopy. Properties of nanometer-scale metal particles in relation to CO oxidation and methanol oxidation pathways will be discussed.

11:40am **SS2-ThM11 The Water Formation Reaction on a Palladium and Platinum Catalysts, Studied with Laser-induced Fluorescence and Kinetic Modelling***, **A. Johansson**, M. Forsth, A. Rosen,* Goteborg University and Chalmers University of Technology, Sweden

The noble metals palladium and platinum are widely used as catalysts where the most important application is said to be the cleaning of exhaust gases. In addition, high-temperature data, especially for palladium are very scarce. In this study we have studied water formation on the palladium metal at high temperatures (1300 K) and moderate pressures (13-26 Pa). The OH desorption was studied with laser-induced fluorescence and the water production with microcalorimetry as a function of the hydrogen mixing ratio, @alpha@@sub H2@. With basis on the experimental data a theoretical model was also obtained using Chemkin. The result was compared with similar experiments for platinum. The following differences were observed. The maximum in OH desorption occurs at the same @alpha@@sub H2@ for both platinum and palladium, however the maximum in water production is measured to be at different @alpha@@sub H2,H2Omax@; at 20% for platinum and 40% for palladium. From the model the initial sticking coefficients for hydrogen and oxygen are found to be about a factor of ten larger on Pd than for Pt. The OH desorption was also seen to have a first order coverage dependence on palladium, no such behaviour was found for platinum. The main route for water formation on a platinum surface is the hydrogen addition reaction however, the main water forming reaction on palladium is not straightforward to determine because of the coverage dependent OH desorption. The reverse of the hydrogen addition reaction was found to be more important for the OH formation on Pd than on Pt. The apparent desorption energy as a function of @alpha@@sub H2@ was also measured for palladium. It was seen that it is increasing with @alpha@@sub H2@ to a maximum and then stays constant. It is interesting to note that the maximum in apparent desorption energy occurs at the same @alpha@@sub H2@ as the maximum in water production. The same phenomenon is also observed on platinum, but at a different @alpha@@sub H2@.

Surface Science
Room 328 - Session SS3-ThM
Oxide Structure, Growth, and Defects

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

8:20am **SS3-ThM1 Effect of Atomic Polarization on Adsorption on Ferroelectric Surfaces: BaTiO@sub 3@ (100)***, **J. Garra**, D.A. Bonnell,* University of Pennsylvania

Ferroelectric surfaces have become the focus of recent interest as templates for directed assembly and as thin film devices, yet the surface properties are largely unknown. It has been shown, however, that the local chemical reactivity on ferroelectric surfaces depends on the orientation with which the polarization vector intersects the surface. For example photo reduction (electron donation) occurs over domains with positive surface termination, while photo oxidation (hole donation) occurs over domains with negative surface termination. In order to determine how atomic polarization affects reaction mechanisms, we compare LEED and TPD measurements of desorption from BaTiO@sub 3@ (100) single crystals. Samples are poled in UHV above the Curie temperature and cooled in the electric field in order to achieve homogeneous and predefined polarization orientation before adsorption. Domain structure is confirmed with Piezo Force Microscopy. Water, methanol, and ammonium are used as probe molecules. Adsorbate bond energies above and below the ferroelectric-to-paraelectric phase transition will be discussed in the context of the magnitude of local electric fields.

8:40am **SS3-ThM2 Sodium Segregation and Morphology on Co@sub 3@O@sub 4@ Single Crystal Surfaces***, **S.C. Petitto**, M.A. Langell,* University of Nebraska-Lincoln

The Co@sub 3@O@sub 4@(110) single crystal surface was characterized in its clean and sodium covered states using Low Energy Electron Diffraction, (LEED), X-Ray Photoelectron Spectroscopy, (XPS), and Auger Electron Spectroscopy, (AES). Annealing Co@sub 3@O@sub 4@(110) at T = 650K results in sodium segregation from the bulk material, quantified here by the AES I@sub Na@/I@sub Co@ intensity ratio. LEED analysis of the clean Co@sub 3@O@sub 4@(110) surface shows a well-ordered pattern with sharp diffraction features, whereas the Co@sub 3@O@sub 4@(110)-Na surface presents a more poorly ordered structure with a hexagonal superimposed pattern due to the sodium oxide overlayer. Concurrent with sodium segregation, the Co@sub 3@O@sub 4@(110) surface is reduced and the surface cannot be fully reoxidized as long as sodium remains present even upon extended oxygen annealing. XPS of the clean Co@sub 3@O@sub 4@(110) is characteristic of the spinel structure with Co@super 3+@ occupying the octahedral sites within the lattice and Co@super 2+@ in tetrahedral sites. Co@sub 3@O@sub 4@(110)-Na cobalt XPS, however, shows the cobalt chemical environment is closer to that in CoO with Co@super 2+@ in octahedral sites. Upon flashing to T@>=@ 800K, sodium desorbs from the surface, primarily as NaOH. Pre-dosing with H@sub 2@O does not appear to catalyze NaOH desorption but rather suppresses it, and the hydrogen is assumed to come from the ambient background in the UHV chamber.

9:00am **SS3-ThM3 Resonant Photoemission of Cobaltite Perovskites and Double Perovskites***, **W.R. Flavell**, A.G. Thomas, D.T. Tsoutsou, A.K. Mallick, M. North,* UMIST, UK*; E.A. Seddon, C. Cacho, A.E.R. Malins,* CLRC Daresbury Lab, UK*; R. Stockbauer, R.L. Kurtz, P.T. Sprunger,* Louisiana State U.*; S.N. Barilo, S.V. Shiryaev, G.L. Bychkov,* Belarus Academy of Sciences **INVITED**

Double perovskites based on Co(III), e.g. GdBaCo@sub2@O@sub5.5@, show GMR behaviour and a range of poorly understood spin-state transitions. Whereas the Co(III) ion occupies only octahedral sites in perovskites such as LaCoO@sub 3@, in double perovksites, Co is present in two environments, octahedral and pyramidal. In order to investigate the electronic structure of these oxides, resonant photoemission of single crystals of the double perovskites GdBaCo@sub 2@O@sub 5.5@ and DyBaCo@sub 2@O@sub 5.5@ and of the perovksite HoCoO@sub 3@ has been carried out at the UK Synchrotron Radiation Source. Co 3p->3d resonance photoemission has been shown to be a powerful diagnostic of the LS (low spin) state of d@super 6@ Co(III) in cobaltites. The resonance onset position of features associated with the LS state lies typically around 2.5 eV higher than those associated with Co (III) in HS (high spin) or IS (intermediate spin) states. This is thought to be because the t@sub 2g@ states are full in the LS state so the Co 3p -> 3d transitions are delayed until the e@sub g@ states, which lie ~2-3 eV higher, can be occupied. This diagnostic test is used to explore the Co spin fluctuations in double perovskites with temperature. In contrast with previous data for LaCoO@sub 3@, we see no delayed resonance for GdBaCo@sub 2@O@sub 5.5@ or DyBaCo@sub 2@O@sub 5.5@ at temperatures as low as 50 K, consistent with the idea that the Co spin in the pyramidal sites does not fluctuate with temperature. However, a delayed resonance is observed at temperatures up to 400 K in HoCoO@sub 3@. This resonance delay disappears as the temperature is raised, as does a low binding energy feature of the valence band associated with LS Co(III). These observations are consistent with a LS to IS transition in octahedral Co(III) in HoCoO@sub 3@. The giant RE 4d->4f resonances are also probed, and used to identify the 4f DOS. We show that the DOS closest to the Fermi energy for all materials is of TM 3d/O2p character, with no RE 4f contribution. Comparison is made with recent LDA+U calculations.

9:40am **SS3-ThM5 Growth Modes in a System Requiring Bulk Mass Transport: Step Motion and Island Nucleation on TiO@sub 2@ (110) Exposed to Oxygen***, **K.F. McCarty**, J.A. Nobel, N.C. Bartelt,* Sandia National Laboratories

We use low-energy electron microscopy (LEEM) to systematically investigate how the (110) surfaces of oxygen-deficient rutile crystals grow when exposed to oxygen. This growth is interesting because it requires a combination of bulk and surface diffusion -- as established by Onishi and Iwasawa (1996) using scanning tunneling microscopy, growth occurs as titanium interstitials from the bulk react with ambient and adsorbed oxygen. If the reaction only occurred at step edges, then one might expect to observe only step-flow growth. Instead, we find that distinct growth processes occur, depending primarily on temperature and oxygen pressure. The temperature/pressure dependence of these growth regimes has been systematically determined for a slightly reduced crystal. At high temperature, TiO@sub 2@ growth occurs by pure step flow without the nucleation of new islands. At low temperatures, however, crystal growth proceeds by two-dimensional islands nucleating and spreading laterally. In this layer-by-layer growth regime, the surface periodically oscillates between structures with 1x1 and 1x2 periodicity. The threshold temperature above which island nucleation does not occur depends upon the local terrace width and pressure. For a range of temperatures around the threshold, nucleation occurs on wide terraces but not on narrow terraces. In the regime of pure step flow, we analyze the rate at which isolated islands and interacting island arrays grow. Comparison of the experimental data to numerical simulations of island growth allows us to discuss the relative importance of Ti transport through the bulk and oxygen-containing species on the surface.

10:00am **SS3-ThM6 The Effect of Nitrogen Doping on Rutile Single Crystals - A Photochemical Surface Science Study***, **O.E. Diwald**, T.L. Thompson, J.T. Yates Jr.,* University of Pittsburgh

A major goal in the development of new materials for photocatalysis and photo electrochemistry is to shift the solid's photoresponse into the visible light region, in order to utilize solar light more efficiently. Recently, doping of polycrystalline TiO@sub 2@ with non metal ions such as nitrogen@footnote 1@ has attracted much attention, as these materials have shown activity under visible light irradiation (@lambda@ @<=@ 550 nm). In order to investigate the effect of nitrogen doping on the photoactivity of TiO@sub 2@(110) single crystals, nitrogen incorporation into the rutile lattice was achieved either by sputtering with mixtures of N@sub 2@@super +@ and Ar@super +@ ions or by thermal treatment in ammonia (NH@sub 3@). Secondary Ion Mass spectroscopy and X-ray photoelectron spectrocopy were employed to measure depth distribution and chemical state of the implanted nitrogen. For rutile single crystals, these two doping methods result in different chemical states of the incorporated nitrogen. Ion implantation by sputtering produces substitutionally bound nitride species N@super -@, whereas NH@sub 3@ treatment leads to the formation of a N-H bonded dopant in the rutile lattice. For investigation of the photoactivity, the photodesorption of O@sub 2@ was measured as a function of excitation energy and photon flux.@footnote 2@ Compared to the undoped TiO@sub 2@ (110) rutile crystal, the action curve of the crystal that was doped with substitutionally bound nitride exhibits an unexpected blueshift. These findings will be related to changes in the electronic structure of rutile TiO@sub 2@ due to the different dopant species. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD-19-01-0-0619. @FootnoteText@@footnote 1@ R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science, 293, 269 (2001),@footnote 2@ G. Lu, A. Linsebigler, J. T. Yates Jr., J. Chem. Phys., 102, 4657, (1995).

10:20am **SS3-ThM7 STM Study of Defect Production on the TiO@sub 2@(110)-(1x1) and TiO@sub 2@(110)-(1x2) Surfaces Induced by UV-light***, **P. Maksymovych**, S. Mezhenny, D.C. Sorescu, J.T. Yates, Jr.,* University of Pittsburgh

The photoinduced hydrophilicity of the TiO@sub 2@ surface has been the subject of extensive research due to its technological importance in the development of antifogging and self-cleaning coatings. The phenomenon has been postulated to be due to structural changes of TiO@sub 2@; however, the exact mechanism of the process is unknown. The effect of broadband UV radiation on the stochiometric TiO@sub 2@(110)-(1x1) and the reduced TiO@sub 2@(110)-(1x2) surfaces was observed using the scanning tunneling microscope (STM) in ultra-high vacuum. It was found that the TiO@sub 2@(110)-(1x1) surface is not affected by UV radiation within the statistical error of the experiment. The majority of defect sites on the surface are the bridging oxygen vacancies, and their surface density remains unchanged after UV irradiation. In contrast, production of line defects in the direction was observed on the TiO@sub 2@(110)-(1x2) surface. The overall defective area of the surface was found to increase linearly with UV-exposure, the estimated cross section of the defect formation being 10^-23.5±0.2 cm@super 2@/photon (hv @>=@ 3.0 eV).The origin of the defects is attributed to collective removal of oxygen from the surface. In order to determine whether the UV-induced defects can cause hydrophilicity of TiO@sub 2@, adsorption of H@sub 2@O on the TiO@sub 2@(110)-(1x2) surface was studied by STM. At 300K adsorption of H@sub 2@O occurred preferrentially on the crosslinks of the TiO@sub 2@(110)-(1x2) surface. However, cooling the surface to 110K during H@sub 2@O exposure led to more efficient adsorption, which took place on the added rows of the TiO@sub 2@(110)-(1x2) surface in addition to the crosslinking sites. No changes in the topology of the UV-induced defects were observed after H@sub 2@O exposures.

10:40am **SS3-ThM8 The Oxygen Chemistry of Rutile TiO@sub 2@(110) - A Comprehensive STM Study***, **R. Schaub**, E. Wahlström, A. Ronnau, E.K. Vestergaard, F. Besenbacher,* Interdisciplinary Nanoscience Center, Denmark

The detailed understanding of the oxygen chemistry on titanium oxide is an important issue for chemical and photo-chemical processes on this material. We present a thorough high resolution variable temperature STM investigation of the interaction of oxygen molecules with the (110) surface of TiO@sub 2@. Single oxygen molecules interact with oxygen vacancies, mediating their diffusion through a simple oxygen atom exchange mechanism. Surprisingly, this mechanism does not account for healing of the vacancies as speculated in the literature until now. The adsorption of molecular oxygen leads also to the creation of different oxygen-related species, which are readily distinguishable by their contrast in STM images and their dynamics in time-resolved STM experiments. The subtle interaction of these different species present on the surface accounts for the healing of the vacancies through an unanticipated and complex mechanism discussed in detail.

11:00am **SS3-ThM9 Measuring Defect Sites on TiO@sub 2@(110): The CO@sub 2@ Probe***, **T.L. Thompson**, O.E. Diwald, J.T. Yates, Jr.,* University of Pittsburgh

Defect sites govern the chemical and photochemical behavior of TiO@sub 2@ rutile surfaces. We have found that CO@sub 2@ binds more strongly (54.0 kJ/mol) to oxygen-vacancy Ti@super +3@ defect sites made by thermally reducing TiO@sub 2@(110) than to the fully-oxidized 5-fold coordinated Ti@super +4@ surface sites (48.5 kJ/mol). Enhanced surface reduction at temperatures up to 1000K causes an increase in the relative amount of the strongly-bound CO@sub 2@.

11:20am **SS3-ThM10 Surface Structure and Properties of Vanadia Supported on Anatase TiO@sub 2@(001)***, **W. Gao**, E.I. Altman,* Yale University

We have successfully grown epitaxial anatase TiO@sub 2@(001) thin films on LaAlO@sub 3@(001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). A two-domain (1x4)/(4x1) reconstruction was observed by reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED). With OPA-MBE, monolayer to multi-layer vanadia was deposited on the reconstructed anatase (001) surface. Photoelectron spectroscopy (UPS and XPS) was used to characterize the chemical state of the vanadia. XPS results showed that the vanadia was predominantly in the 5+ oxidation state after deposition of a monolayer at 525 K, while UPS showed a small peak in the TiO@sub 2@ bandgap consistent with a small amount of V@super 4+@. After 1 ML vanadia was deposited on anatase (001), the anatase (1x4)/(4x1) LEED and RHEED patterns were replaced by (1x1) patterns indicating that the vanadia lifts the reconstruction and suggesting that the monolayer is pseudomorphic. The reducibility of the monolayer was studied by monitoring XPS peak shifts as a function of annealing temperature. At temperatures between 625 K to 875 K, the vanadia was reduced to the 3+ oxidation state; these results were very similar to vanadia on SiO@sub 2@. XPS results also showed a decrease in the intensity of the V peaks with increasing temperature. At ~875 K, nearly no vanadium was detected by XPS and the (1x4)/(4x1) pattern of the bare surface was restored suggesting that V migrated into the bulk. Vanadia growth beyond the first monolayer caused the RHEED pattern to fade and produced no discernible LEED patterns suggesting that pseudomorphic growth cannot be continued beyond 1 ML. The structural evolution of the surface as vanadia was deposited was also characterized by scanning tunneling microscopy (STM).

11:40am **SS3-ThM11 Initial Stages of Cu@sub 2@O Nano-Clusters Formation on SrTiO@sub 3@(100)@footnote 1@***, **I. Lyubinetsky**, S. Thevuthasan, A.S. Lea, D.E. McCready, D.R. Baer,* Pacific Northwest National Laboratory

Self-assembled crystalline cuprous oxide (Cu@sub 2@O) nano-clusters have been grown on the SrTiO@sub 3@(100) substrate using oxygen plasma assisted molecular beam epitaxy. The growth mechanism, composition and structure were examined by x-ray photoelectron spectroscopy, x-ray induced Auger electron spectroscopy, scanning probe microscopy, scanning Auger microscopy, and x-ray diffraction. Growth parameters for the formation of pure Cu@sub 2@O nano-clusters have been optimized accordingly to the surface phase diagram of the Cu-O system, which has been determined for temperature versus oxygen pressure. Unlike typical semiconductor systems, e.g. Si-Ge, initial stages of the growth for studied here metal oxide system proceed without formation of the wetting layer, with formation of the 3D truncated square Cu@sub 2@O dots starting already at sub-monolayer coverages. At following stages of the growth, nano-dots underwent shape/structure transformation similar to the semiconductor systems. Under different surface conditions of the SrTiO@sub 3@(100) substrate (high temperature annealed, perfect TiO@sub 2@-terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nano-clusters distribution have been observed. Complications due to the re-growth of the Sr-rich nanostructures in addition to the Cu@sub 2@O nano-dots formation at the certain substrate conditions will be also discussed. @FootnoteText@ @footnote 1@ This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the U. S. Department of Energy.

Thin Films
Room 329 - Session TF-ThM
Modeling & Fundamentals in Thin Film Deposition

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

8:20am **TF-ThM1 Mechanisms and Energetics of H Insertion into Si-Si Bonds in Hydrogenated Amorphous Silicon Films***, S. Sriraman, **M.S. Valipa**[1], E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts

Understanding the mechanism of chemically-induced disorder-to-order structural transitions is relevant to the synthesis of various technologically important materials, including nanocrystalline silicon thin films used in the fabrication of solar cells and flat panel displays. Thin hydrogenated amorphous silicon (a-Si:H) films crystallize at low temperatures when exposed to H atoms from an H@sub 2@ plasma, or when the SiH@sub 4@ feed gas is heavily diluted with H@sub 2@. Recently, we showed that H-induced crystallization is mediated by insertion of H atoms into strained Si-Si bonds as the H atoms diffuse through the a-Si:H film.@footnote 1@ This presentation focuses on analyses of the mechanisms and energetics of various pathways for H insertion into Si-Si bonds in a-Si:H. These pathways are generated through molecular-dynamics simulations of repeated H atom impingement on a-Si:H films, grown computationally on crystalline Si (c-Si) substrates. Prior to insertion, the diffusing H atom bonds to one of the Si atoms that form the original Si-Si bond; upon insertion, an intermediate bridging configuration forms where the H atom is bonded to both Si atoms. After the H atom leaves the bridging configuration, the Si-Si bond may be further strained or broken, or it may relax to restore the Si-Si bond closer to the equilibrium c-Si bond length. A diffusing H atom can also occupy the bond-centered (BC) location between two Si atoms that are not bonded together. However, after the H atom diffuses away from this BC location, the two Si atoms form a Si-Si bond. The activation energy barriers are calculated for the H insertion reactions; the resulting distribution of activation energies is correlated with the Si-Si bond strain. The role of these H-insertion reactions in the structural relaxation of the a-Si:H network that results in disorder-to-order transitions is discussed. @FootnoteText@@footnote 1@ S. Sriraman, S. Agarwal, E. S. Aydil, and D. Maroudas, Nature 418, 62-65 (2002).

8:40am **TF-ThM2 Effect of Crosshatch Formation on the Kinetics of Si@sub 1-x@Ge@sub x@ Growth on Si(001) from Hydride Precursors***, **T. Spila**,* University of Illinois*; P. Desjardins,* École Polytechnique de Montréal, Canada*; J. D'Arcy-Gall, R.D. Twesten, J.E. Greene,* University of Illinois

Compressively-strained Si@sub 0.7@Ge@sub 0.3@ layers were grown on Si(001) by gas-source molecular beam epitaxy from Ge@sub 2@H@sub 6@/Si@sub 2@H@sub 6@ mixtures at 450 °C. The combination of the relatively low growth temperature and high steady-state hydrogen surface coverage, @theta@@sub H@ = 0.52 ML, suppresses strain-induced roughening and provides extremely flat surfaces with root mean square widths w < 1.5 Å for fully-coherent layers. These samples were used to probe mechanisms controlling misfit-dislocation-induced surface roughening (i.e., crosshatch) along 90°-rotated directions. For film thicknesses t just larger than the critical value for misfit dislocation formation, t@sub c@ = 1000 Å, the surface roughness (w = 3.1 Å at t = 1350 Å) is dominated by single- and multiple-atomic-height steps generated by the motion of threading dislocations associated with the interfacial misfits. The surface steps are preferential H desorption sites and the increased total step length results in a decrease in @theta@@sub H@ on terraces as well as at step edges. The latter effect allows higher adatom crossing probabilities at ascending steps leading to the formation of periodic ridges (w = 27 Å at t = 4400 Å) in response to local strain fields associated with the misfit dislocation clusters. Simultaneously, the decrease in @theta@@sub H@ on terraces strongly affects film growth kinetics as deposition rates increase from 10 Å min@super -1@ with t < t@sub c@ to 60 Å min@super -1@ with t = 1400-4400 Å. Overall, for films with strain relaxation R < 5%, crosshatch is due to surface steps that result from multiple misfit dislocations on single glide planes, but for R = 22-78%, crosshatch becomes dominated by local strain-induced roughening and leads to periodic ridge formation.

9:00am **TF-ThM3 Initial Growth of High Rate Deposited Silicon Thin Films Studied by In-situ Spectroscopic Ellipsometry and Attenuated Total Reflection Infrared Spectroscopy***, **P.J. Van den Oever**, I.J. Houston, J. Hong, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

The trend towards high rate deposition in thin film research - driven by industrial demands - raises several issues in order to maintain good film properties. One particular issue in this respect is the control of the nucleation and initial growth in terms of film density and surface roughness. Therefore, we have investigated the growth of silicon-based films at growth rates up to 10 nm/s as deposited by the expanding thermal plasma technique. The time evolution of the dielectric functions, bulk thickness and surface roughness has been obtained from real time spectroscopic ellipsometry measurements and the surface roughness evolution has been compared to atomic force microscopy data. Attenuated total reflection infrared spectroscopy has been employed to obtain the hydrogen depth profile of the films. For hydrogenated amorphous silicon, the film growth is found to be homogeneous after nucleation. Hydrogenated microcrystalline silicon on the other hand shows a nucleation region of crystallites, which is followed by columnar film growth after the crystallites have reached coalescence. This is supported by the hydrogen depth profile where the nucleation and presence of the crystallites is accompanied by the emergence of surface-like bonded hydrogen that can be attributed to hydrogen passivating the grain boundaries of the crystallites. For silicon nitride films a clear difference has been observed in the surface roughness evolution between silicon-rich and nitrogen-rich films as deposited under different plasma conditions. This difference can be attributed to different growth modes that are determined by the surface free energy and the specific surface reactions taking place during film growth.

9:20am **TF-ThM4 Sn-mediated Ge/Ge(001) Growth by Low-temperature Molecular Beam Epitaxy: Effects on Surface Roughening and Epitaxial Thickness***, **K.A. Bratland**, Y.L. Foo, T. Spila,* University of Illinois*; P. Desjardins,* École Polytechnique de Montréal, Canada*; J.E. Greene,* University of Illinois

Fully-strained single-crystal metastable Ge@sub 1-x@Sn@sub x@ layers were grown on Ge(001) in order to probe the role of dopant and dilute alloy concentrations (C@sub Sn@ = 1x10@super 18@ cm@super -3@ to 6 at%) on surface roughening pathways leading to epitaxial breakdown during low-temperature molecular beam epitaxy (LT-MBE) of compressively strained films. The growth temperature was chosen to be 155 °C due to limited epitaxial thicknesses at lower temperatures and significant Sn surface segregation at higher temperatures. The addition of Sn during Ge(001) LT-MBE was found to give rise to two competing effects. At very low concentrations (x < 0.02), the dominant effect is a Sn-induced enhancement in both the Ge adatom mobility and the rate of interlayer mass transport, thereby suppressing kinetic roughening and resulting in significant enhancements in the critical thickness h@sub 1@ for the onset of epitaxial breakdown. With x = 0.010, for example, the surface width w normalized to h@sub 1@, which is 2.6x10@super -3@ for pure Ge(001) layers, decreases to 1.5x10@super -3@ while h@sub 1@ increases from 7700 Å to 1.40 µm. Furthermore, layers which are fully epitaxial to thicknesses h > 1.9 µm are obtained with the incorporation of Sn in concentrations ranging from 1x10@super 18@ cm@super -3@ to 1.0 at%. However, for x @>=@ 0.02, strain-induced roughening overcomes the Sn-induced surface smoothening effects and gives rise to a rapid decrease in h@sub 1@, which ranges from 5700 Å with x = 0.029 to 2350 Å with x = 0.061.

9:40am **TF-ThM5 Understanding Radical-Surface Interactions in the Plasma-Assisted Deposition of Amorphous Hydrogenated Silicon***, **S. Agarwal**, S. Sriraman,* Univ. of California, Santa Barbara*; A. Takano,* Fuji Electric Corp. R&D, Ltd., Japan*; M.C.M. van de Sanden,* Eindhoven Univ. of Tech., The Netherlands*; D. Maroudas,* Univ. of Massachusetts - Amherst*; E.S. Aydil,* Univ. of California, Santa Barbara **INVITED**

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are widely used in photovoltaic, imaging, and display devices. During plasma-assisted deposition, reactive radicals present in the discharge such as SiH@sub x@ (x = 1,2,3) and H impinge onto the substrate surface leading to film growth and H incorporation. The properties of the deposited films depend on the various reactions of radicals present in the discharge with the growth surface and, therefore, a fundamental understanding of such interactions is required for improving a-Si:H deposition techniques. We have studied radical-surface interactions in the deposition of a-Si:H thin-films through

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[1] **TFD Student Award Winner**

synergic use of experimental diagnostics such as in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and molecular-dynamics (MD) simulations based on the Tersoff's potential for Si. We have identified the various reactions of H and SiH@sub 3@ with a-Si:H films and determined their mechanisms and energetics. Surface H is removed by abstraction through the Eley-Rideal mechanism. Silicon is incorporated into the growing film through radical attachment to surface dangling bonds, as well as radical insertion into Si-Si surface bonds including dissociative adsorption reactions. In addition, reactions that involve radical migration on the surface are identified and analyzed. Finally, the H-induced crystallization of a-Si:H films during their post-deposition treatment by an H@sub 2@ plasma is addressed. The MD simulations show that H atoms diffuse into the a-Si:H film and insert into strained Si-Si bonds to form intermediate bridging and bond-centered H (Si-H-Si) configurations mediating the structural relaxation of the amorphous Si matrix leading to the disorder-to-order transition. The existence of bond-centered H(D) in a-Si:H films exposed to H(D) atoms was verified experimentally through IR spectroscopy.

11:00am **TF-ThM9 From Ab-initio Modeling to Experimental Thin Film Synthesis of a Novel Boron-oxygen-yttrium Phase*, D. Music,*** *V. Chirita,* Linköping University, Sweden*; J.M. Schneider,* RWTH Aachen, Germany*; U. Helmersson,* Linköping University, Sweden

The B-O based material system is a promising candidate for a wide range of tribological applications. For example, crystalline boron suboxide has been reported to have the elastic modulus of 470 GPa. However, typical requirements to form crystalline boron suboxide include high pressure (5-7 GPa) and temperature (>2000 °C), and are very difficult to achieve with standard thin film synthesis techniques such as reactive sputtering. In this work, we use ab-initio calculations to theoretically design and then experimentally grow polycrystalline boron suboxide based films. A new crystalline boron-oxygen-yttrium (BOY) phase is obtained by alloying with Y. The essential element in the modeling is Y substituting for O in the boron suboxide structure with Y/B and O/B ratios of 0.07. The overall effect of electron doping, induced by the Y substitution, is to shorten the chemical bonds in boron suboxide. This renders the formation of the BOY phase characterized by a 45% volume reduction and consequently a 23% increase in bulk modulus (from 235 to 289 GPa). The calculations predict that the BOY phase is 0.36 eV/atom more stable than crystalline boron suboxide and experiments confirm the formation of crystalline thin films. The BOY phase was synthesized with reactive RF magnetron sputtering and identified with x-ray and selected area electron diffraction. Films with Y/B ratios ranging from 0.10 to 0.32, as determined via elastic recoil detection analysis, were grown over a wide range of temperatures (300-600 °C) and found to withstand 1000 °C. Details of the electronic structure of this new phase will also be presented.

11:20am **TF-ThM10 Low Temperature Nitride and Oxide Thin Film Growth using an Energetic Atom Source*, A.H. Mueller,*** *E.A. Akhadov, M.A. Hoffbauer,* Los Alamos National Laboratory

Depositing one or more metals on a substrate exposed to an energetic neutral atom beam allows for the growth of high quality oxide and nitride films at low temperatures. The unique surface chemistry afforded by the exposure of the substrate to oxygen or nitrogen atoms possessing kinetic energies between 1 and 5 eV allows the deposition of dielectric and semiconducting films on materials that would undergo thermal decomposition under the conditions necessary for conventional thin film growth (e.g. CVD, sputtering, laser ablation, etc.). This low temperature epitaxy technique, called Energetic Neutral Atom Beam Lithography/ Epitaxy (ENABLE), permits the growth of semiconducting nitride and dielectric oxide films on substrate surfaces patterned by an organic polymer, as well as substrates consisting entirely of low meting point materials. The crystallinity, optical and electrical properties of ENABLE grown films have been examined using numerous techniques including XRD, TEM, photoluminescence spectroscopy, and four point probe resistance measurements. Results of film deposition on various substrate materials, including patterned film deposition, will be discussed.

11:40am **TF-ThM11 Physical Self-assembly and the Nucleation of 3D Nanostructures by Oblique Angle Deposition@footnote 1@*, T. Karabacak,*** *G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

Thin film growth front morphology formed by physical vapor deposition is controlled by many factors including surface diffusion and shadowing effects. Instabilities can occur if shadowing is more dominant compared to other surface effects and can lead to many diverse physically self-assembled 3D nano-size structures@footnote 2,3@ that are otherwise difficult to produce by lithographical techniques. The unique geometrical shapes from a large variety of materials suggest that shadowing effects can be used as an efficient tool to understand and control the growth morphologies by many traditional deposition techniques. In this paper, we explore the fundamental nucleation and growth mechanisms of these structures. Monte Carlo simulations were carried out to predict the island density, island size distribution, and island-island correlation during the initial stages of growth. The results are compared to that obtained by the oblique angle sputter deposited W films imaged by atomic force microscopy and scanning electron microscopy. Isolated islands with quasi-periodic distribution are formed as a natural consequence of the shadowing effect. Isolated columnar structures are shown to grow on these islands and the width w of the columns is predicted to grow as a function of time t in the form of a power law, w ~ t@super p@, where the exponent p is between 0.3 and 0.5. The predicted p is consistent with the experimentally determined exponent values for growth of column widths from a variety of materials such as W, Co, Cu, and Si. @FootnoteText@ @footnote 1@ Work supported by NSF@footnote 2@ Y.-P. Zhao, D.-X. Ye, G.-C. Wang, and T.-M. Lu, "Novel nano-column and nano-flower arrays by glancing angle deposition", Nano Letters 2, 351-354 (2002). @footnote 3@ K. Robbie, M. J. Brett, and A. Lakhtakia, "Chiral sculptured thin films," Nature 384, 616-616 (1996).

Vacuum Technology
Room 323 - Session VT+MS-ThM

Reproducibility, Precision, and Accuracy of Vacuum and Process Measurements

Moderator: R. Dobrozemsky, Vienna University of Technology, Austria

8:20am **VT+MS-ThM1 Component Requirements for ALD Technology*, T.E. Seidel,*** Genus, Inc*; J. Mason, A. Londergan, S. Ramanathan,* Genus, Inc. **INVITED**

In the last several years Atomic Layer deposition (ALD) has emerged as a commercial technology. This technology is a variant of CVD, and therefore requires reactor and reactor related components for operation under well-controlled vacuum conditions. The requirements include fast gas switching, precisely controlled gas delivery systems with high performance Mass Flow Controller and / or Pressure Controllers, precise control of gas delivery line temperatures, heated walls and substrate susceptors, and quality down stream pumps to provide suitable flow and pressure capacity. Precursor usage and costs must be managed as well. Ancillary requirements include sensitive RGA's and fast response baratrons. There are gaps in he performance of components and the users requirements. As and example, today's fast gas switching valves have a lifetimes of the order of one to a few million cycles, but lifetimes of the order of 10 million cycle are needed. Substrate and gas line temperature control is critical. Additionally, because the precursors used in this technology are particularly reactive, the downstream pump components must be robust. This review provides a generic status and progress of the ALD field followed by generic requirements and requirement gaps for components used in ALD.

9:00am **VT+MS-ThM3 Towards Improved Control of PVD Processes for Nano-Structured Me-aC:H Coatings@footnote 1@*, M.A. Taher,*** *B. Feng, A.G. Shull,* Caterpillar Inc.*; B. Johs, G. Pribil,* J.A. Woollam Company Inc.*; C.C. Klepper, E.P. Carlson, R.C. Hazelton, E.J. Yadlowsky,* HY-Tech Research Corporation

The reliability and durability of machine components such as bearings and gears can be enhanced through the application of metal-containing amorphous carbon (Me-aC:H) coatings, deposited by physical vapor (PVD) techniques such as sputtering. Commercial sputtering systems used for tribological coatings often employ computerized recipe managers to attain a certain level of reproducibility in the coating process. In most cases, these recipe managers control the deposition process through an open loop, time stepping approach where deposition parameters are varied within a particular time frame, and the process is repeated consistently from batch to batch. This type of control generally provides a level of reproducibility that is acceptable in applications where the component benefits from the coating but does not depend on it for full functionality. However, in applications where the coating is integrated into the machine component design, creating a prime-reliance on the coating, higher levels of coating consistency are required. Such levels may involve the adoption of in-situ sensors integrated with a closed-loop deposition control system. To build such a successful control system, knowledge of the relationships between the input process factors, the sensed variables, and the critical coating characteristics is necessary. In this study, a set of in-situ sensors that included a residual gas analyzer, an optical emission spectrometer, an optical absorption spectrometer, a Langmuir probe and a spectroscopic ellipsometer were explored. Three Design-of-Experiment (DoE) test runs were conducted which explored the effects of the coating process input factors on the output sensor signals and the critical coating characteristics. Results of these experiments are presented and a closed-loop control strategy is discussed. @FootnoteText@ @footnote 1@This work was partially supported by the Department of Commerce through its NIST ATP program award number 70NANBH0H3048.

9:20am **VT+MS-ThM4 A Portable Reference Gas for InSitu Calibration of Residual Gas Analyzers***, **R.E. Ellefson,** W.P. Schubert, L.C. Frees,* INFICON, Inc.

A new design for a portable source of reference gas with a fixed flow rate has been developed for producing a repeatable pressure in the ion source of a residual gas analyzer (RGA). The fixed flow rate of gas flowing through the fixed conductance of the isolation valve located between the process vacuum system and the RGA produces a repeatable pressure at the ion source of the RGA. The flow rate of 1x10@super -4@ Torr-l/s of Ar (and selected impurities) through the typical conductance of 10 l/s produces a reference pressure of 1x10@super -5@ Torr in the ion source. The ability to produce a repeatable pressure at the ion source on demand enables calibration of the mass scale, electron multiplier (EM) gain and measurement of absolute sensitivity. Data on sensitivity versus time is shown as an example of a quality assurance method for determining the stability of operation of an RGA and to determine when sensitivity or EM gain adjustment is necessary. The same reference gas source can be used for the calibration of closed ion source RGAs that have their own pumping system. The mechanical design minimizes the pressure burst at turn on and accomplishes viscous flow of the gas mixture. Data is presented on consumption rate, expected lifetime, shipping exemptions, temperature dependence of flow rate and species fractionation over lifetime. Methods for species abundance calibration in the RGA are also presented.

10:00am **VT+MS-ThM6 Specific Reference Calibration - A More Practical Approach to Vacuum Reproducibilty***, **G.D. Lempert,*** Soreq N.R.C., Israel

Increasing demands for quality control, both in production as well as in R&D, have resulted the proliferation of instrument measurement calibration. However, despite the fact that vacuum measurement is often made with significantly larger uncertainties and errors than other physical or thermodynamic quantities, the calibration of vacuum measurement instrumentation, in particular in the high vacuum range, is generally ignored or neglected. Objective practical difficulties have been identified and defined which make vacuum measurement calibration problematic and very often not practically feasible. The requirements for vacuum measurement uncertainties for most practical vacuum systems have been assessed. In an effort to make reproducible vacuum measurement more accessible, a more practical approach to vacuum measurement calibration has been defined and developed. The approach incorporates a vacuum calibration system, whose specifications and design satisfy the accuracy requirements for all but the most demanding users of vacuum technology. Calibration results are presented which provide justification for the approach. In addition the new approach defines a concept of Specific Reference Calibration, SRC. SRC does not necessarily provide calibration of the users vacuum measurement instruments. However SRC does enable practically defining and attaining reproducible vacuum process conditions in the users vacuum system, with significant advantages over conventional calibration. The new approach is aimed to overcome the difficulties, which have inhibited the proliferation of vacuum measurement calibration up to this time, and to facilitate the attainment of reproducible vacuum conditions and processes.

10:20am **VT+MS-ThM7 Characterisation of a Fully Automated, Static Expansion Vacuum Standard at the National Physical Laboratory, UK***, **J.C. Greenwood**, P. Carroll,* National Physical Laboratory, UK

A new, fully automatic, Static Expansion vacuum standard has recently been constructed to replace the existing manually operated system. The new instrument incorporates a number of design improvements which will be described. It is of all metal construction and operates from atmospheric pressure down into the UHV region. This paper discusses some of the procedures and measurements that have been performed to characterise the new standard. These include; mapping temperature distributions across and between the parts of the system; measuring the effects of inter-vessel valves on the pressure distribution; developing an improved measurement equation for the pressure generated in the standard, and comparison against existing vacuum standards that have been involved in recent international comparisons. We will show that calibration results taken from the new standard and the existing standards are equivalent.

10:40am **VT+MS-ThM8 A New Look at the Modulated Bayard-Alpert Gauge***, **B.R.F. Kendall**,* Elvac Laboratories*; E. Drubetsky,* Televac Division of The Fredericks Company

There is an increasing need for accurate vacuum measurements below 10@super-9@ Torr. Ordinary Bayard-Alpert gauges may have large and unpredictable errors at these pressures because of x-ray and other unwanted effects. Several special gauges have been developed to overcome these problems. One of the most cost-effective is the Modulated Bayard-Alpert Gauge (MBAG), first described by P.A. Redhead in 1960 and subsequently investigated in detail in many other laboratories. These gauges were widely used in Europe for several decades. We have evaluated several different MBAGs, ranging from first-generation glass-envelope types to a new miniature metal-envelope version. Performance data are given for operation in various modulation modes. An advantage of these gauge tubes is that, if necessary, they can be used as conventional BA gauge tubes with existing controllers. Some versions can be electronically adjusted for uniform sensitivity. The design of demodulation circuitry is discussed. X-ray errors causing gauges to over-read by several hundred percent at 10@super-10@ Torr can be essentially eliminated by using the modulation principle.

11:00am **VT+MS-ThM9 Dose Reproducibility in Axcelis GSD Implanters Using Stabil-Ion Gauge***, **R.C. Johnson,*** INNOViON Foundry Ion Implantation Engineering

Long-term dose reproducibility and tool to tool dose matching in the Axcelis GSD end-station is critically dependent on process chamber pressure measurement and Pressure Compensation factor selection. Pressure Compensation factor (PCOMP) determination is well-established. Pressure measurement in the GSD end-station depends on accurate, repeatable gauge capability: incorrect pressure measurements directly lead to dose errors. For example, the dose equation using PCOMP tells us that for a modest PCOMP value of 30%, a chamber pressure measurement error of 2E-5 torr can result in a dose error up to 6% at normal process pressures. The original HCIG used for pressure measurement was not capable of meeting the requirements for good dose control since gauge to gauge differences were not controlled and gauge accuracy was only on the order of 30%. Axcelis introduced the Granville-Phillips 360 Stabil-Ion gauge to improve dose reproducibility through much improved gauge to gauge matching (+/-6%) and more accurate gauge output. This paper discusses the details of the care and feeding of the Stabil-Ion gauge system and it's impact on process dose and process trends.

11:20am **VT+MS-ThM10 How Stable are Spinning Rotor Gauges***, **R.F. Chang**,* National Institute of Standards and Technology

The spinning rotor gauge is an excellent transfer standard in the pressure range of 0.0001 to 10 Pa (10@super -6@ to 0.1 torr) because of the remarkable stability exhibited by its accommodation coefficient. The stability comes from the fact that the accommodation coefficient depends mainly on the rotor surface properties of roughness and cleanliness, and does not change as long as these surface properties remain the same. Therefore, as common sense might dictate, one must avoid altering the rotor surface properties mechanically or chemically by not scratching the rotor surface or exposing it to corrosive agents. It is important that the accommodation coefficient remain constant when a spinning rotor gauge is moved from one laboratory to another such as in an inter-laboratory comparison or proficiency test. The level of confidence of the agreement between two laboratories is limited by how much the accommodation coefficient may have shifted in transit. For example, to transfer a spinning rotor gauge from one vacuum chamber to another, one must remove and reinstall the suspension head. During this procedure, the rotor comes into contact with the inner wall of the vacuum housing (thimble) and may be scratched. Sometimes the rotor is removed from the thimble for shipping, which requires additional handling of the rotor. By measuring the accommodation coefficient before and after various handling and cleaning procedures, we have quantified their effects on the accommodation coefficient. The results and impacts on gauge calibrations, including some surprises, will be presented and discussed.

11:40am **VT+MS-ThM11 Practical Procedures for the Frequency Corrections of the Spinning Rotor Gauge Residual Drag*, J. Setina,*** Institute of Metals and Technology, Slovenia

Spinning rotor gauge (SRG) uses a magnetically levitated steel ball as sensing element to measure low gas pressure, which is determined from the decay of the rotational speed of the rotor caused by the momentum transfer to the surrounding gas molecules. In addition we also have a small, gas pressure independent component to the measured SRG signal. This is called a residual drag (RD), and the main sources are eddy currents induced in the ball by asymmetries in the magnetic suspension field and eddy currents induced in surrounding metallic components by the rotating component of the ball's magnetic moment. In general, the RD depends on the ball rotational speed. The SRG operates the ball in a pre-selected frequency window, usually from 405 to 415 Hz, and the RD changes during the gas pressure measurement as the ball speed changes. The frequency dependence can be observed as saw-tooth variation of readings during continuous operation at constant pressure. For accurate measurements the frequency dependence of the RD has to be considered also. The commercial SRG controllers do not have the ability to take into account the frequency dependence of the RD and to make automatic on line corrections. The corrections have to be done separately by the user. We will describe our methods to determine the frequency dependence of the residual drag and procedures to perform the corrections to the pressure readings. The RD and its frequency dependence are unpredictable in magnitude for a given suspension of the rotor. Both can change considerably when the rotor is re-suspended. It is our experience that the frequency dependence remains reproducible during uninterrupted suspension, if vertical alignment or position of the suspension head stays well fixed. It is our experience also, that the behavior of the RD of the same ball is different in various suspension heads of different SRG controllers.

Applied Surface Science
Room 324/325 - Session AS-ThA

Electron and Photon Spectroscopies

Moderator: R. Haasch, University of Illinois, Urbana-Champaign

2:00pm **AS-ThA1 Spin Polarization Modulation through Circular Polarized Light Modulation***, **S. Balaz**, L.G. Rosa, H.K. Jeong, P.A. Dowben,* University of Nebraska, Lincoln

Spin-polarized electron sources have important applications in electron spectroscopies. Such electron spectroscopies can provide considerable insight into the spin- polarized electronic structure of magnetic materials. A variation to the spin polarized electron gun, based on photoemission from a GaAs cathode,@footnote 1@ has been designed for spin polarized inverse photoemission and spin polarized electron scattering.@foonote 2,3@ The goal is to improve the emitted electron spin polarization by improving the control of the incident circularly polarized light, and then modulating the light polarization on the photocathode to modulate the spin polarized photocurrent. A solid state laser, of 780 nm wave length, in combination with a retarder was used to generate the circularly polarized light. Scheme for electron spin polarization modulations, through modulating the applied voltage to a liquid crystal retarder, we show that polarization can be modulated as well. Inclusion of such a spin polarized electron gun as part of spin-polarized inverse photoemission and spin-polarized electron energy loss spectroscopies is discussed. @FootnoteText@ @footnote 1@D.T. Pierce, and F. Meier, Phys. Rev. B 13, 5484 (1976) @footnote 2@F. Ciccacci, E. Vescovo, G. Chiaia, S. De Rossi, and M. Tosca, Rev. Sci. Instrum. 63, 3333 (1992) @footnote 3@Takashi Komesu, C. Waldfried, Hae-Kyung Jeong, D.P. Pappas, T. Rammer, M.E. Johnston, T.J. Gay and P.A. Dowben, in: Laser Diodes and LEDs in Industrial, Measurement, Imaging and Sensor Applications II: Testing, Packaging, and Reliability of Semiconductor Lasers V, Edited by Geoffry T. Burnham, Xiaoguang He, Kurt J. Linden and S.C. Wang, Proceedings of the SPIE 3945, 6 (2000) .

2:20pm **AS-ThA2 A PRBS-modulated TOF-HREELS Spectrometer with High Throughput and Multiplex Advantage***, **B.G. Frederick**, Z. Yang, P. Kleban,* University of Maine

We present an analysis of the factors that control the resolution, dynamic range, throughput-, and multiplex advantage of a novel time-of-flight (ToF) pseudo-random binary sequence (PRBS) modulated high resolution electron energy loss spectrometer (HREELS). We describe probability based spectral estimation methods for signal recovery that achieve a throughput advantage of 100-1000, a factor of 8-16 resolution enhancement, and account for the Poisson noise distribution in the measured data. The multiplex advantage achieved depends upon a number of factors, but significantly improves upon the multiplex disadvantage expected with the conventional cross-correlation or Hadamard transform methods when the detector signal is shot-noise limited. We describe how the optical properties of the chopper affect the PRBS modulated data within a theoretical framework and utilize trajectory calculations over an analytical potential to compare with data measured on azimuthally oriented polytetrafluoroethylene (PTFE, or Teflon) films.

2:40pm **AS-ThA3 Ab initio Modeling of the Vibrational Spectrum of Adsorbed Cyclopentadienyl Anion***, **C.M. Woodbridge**, D. Kemp,* Hillsdale College*; D.L. Pugmire,* Los Alamos National Laboratory*; M.A. Langell,* University of Nebraska, Lincoln

Ab initio methods have been used to model the vibrational spectrum of cyclopentadienyl (Cp), a fragment obtained from the decomposition of metallocenes, adsorbed on various substrates. In the present work, the adsorbate-substrate system was modeled using a single atom as the substrate. Vibrational frequencies, bond lengths, and bonding energies for complexes of the form [Mn@super+@Cp@super-@]@supern-1@ where M=Ag, Ni, and Si have been computed. The complexes were constructed to model two different orientations of the adsorbed Cp ring: one where the plane of the Cp ring is parallel to the surface normal and the other where the plane is perpendicular to the surface normal. The computed vibrational frequencies have been compared to vibrational losses observed in HREEL spectra of Cp, produced from the decomposition of nickelocene, adsorbed the Ag(100), Ni(100), and Si(111)-7x7 substrates. Despite the relative simplicity of the model, the calculated vibrational frequencies are in good agreement with the HREEL spectra.

3:00pm **AS-ThA4 Photon Angle Dependence of Plasmon Loss Measured by the Double Angular Photoelectron Integrated Analyzer System***, **A. Tanaka**,* ULVAC-PHI, Inc., Japan*; H. Yoshikawa,* NIMS, Japan*; M. Kimura,* SPring-8 Service, Japan*; S. Fukushima,* NIMS, Japan

Plasmon loss peaks associated with photoelectron peaks from the silicon specimen is measured. The analyzer and the specimen are tilted simultaneously with maintaining the emission angle constant. This tilting effectively changes the incident angle of photons to the specimen. The angle of photon incidence was ranged from 35 to 90 degree. It caused a change of relative intensity of 1st plasmon loss peaks to the original photoelectron peaks. Photon energy was chosen to match the Si 1s photoelectron energy at the Si 2s energy excited by Mg K@alpha@ x-ray. Ellipsoidal andulation is applied for the synchrotron radiation to simulate the x-ray used for X-ray photoelectron spectroscopy. 3 loss peaks generated by Si 1s, Si 2s and Si 2p are compared. The plasmon loss ratios to mother peaks approximately 10% reduced according to the angle of incidence for all of these spectra, and reduced more at the total reflection conditions. Only for total reflection conditions, this result shows the limitation of excitation range close to the surface, as the energy loss zone becomes smaller comparable with electron inelastic mean free paths. However, this phonomenon is different from surface effect as the emission angle was kept constant at 0±2° and acceptance angle of the analyzer smaller than 10°. When we require precise quantification, we have to consider energy loss process generated in deeper range, too.

3:20pm **AS-ThA5 Photon, Electron, and Ion Spectroscopies Applied to Thin Strained Si Films***, **S. Zollner**, R. Liu, M. Canonico, M. Kottke, Q. Xie, S. Lu, M. Sadaka, T. White, A. Barr, B.-Y. Nguyen, S. Thomas,* Motorola*; C.S. Cook,* Arizona State University*; A. Volinsky,* Motorola **INVITED**

Applied thin-film spectroscopies can be classified by the primary (incident) and secondary (scattered, specularly reflected, diffracted) particle (photon, electron, ion) and by the energy loss (elastic, inelastic) of the interaction. The term spectroscopy implies that the energy of the primary and/or secondary particle is well-known, measured, or varied. We describe applications of various thin-film spectroscopies to thin (15-20 nm) Si layers under tensile biaxial stress, grown pseudomorphically on thick relaxed Si@sub 1-x@Ge@sub x@ buffer layers. Such Si layers have higher electron and hole mobilities than regular bulk Si and are therefore considered for next-generation CMOS technologies. Particular emphasis is placed on the physical mechanism of each spectroscopy technique, the results obtained (thickness, composition, stress), and the potential shortcomings. Specifically, we use UV Raman spectroscopy (325 nm laser excitation) to determine the strain in the Si layer from the frequency shift of the Si-Si lattice vibration. The contributions of the tensile hydrostatic strain and the compressive shear strain to the E1 peak shift (near 3.4 eV) cancel almost exactly, therefore ellipsometry cannot be used to determine strain. However, the piezo-optical effects are significant enough to make ellipsometry unreliable for the determination of the Si thickness or the Ge content of the alloy buffer. Piezo-optical effects are not an issue for x-ray reflectivity, since the dielectric constant of most materials is very close to unity for Cu K@sub alpha@ radiation, but surface roughness can be a problem. We also discuss results from secondary ion mass spectrometry and Auger electron spectrometry to determine composition of the layers.

4:00pm **AS-ThA7 Insights into the Physical and Electronic Structure of Surfaces from Reflection Anisotropy Spectroscopy***, **P. Weightman**,* University of Liverpool, UK **INVITED**

Reflection Anisotropy Spectroscopy (RAS) is a non destructive surface sensitive optical probe capable of operation within a wide range of environments. RAS achieves surface sensitivity by measuring the change in polarisation on reflection of normal incidence light from the surface of a cubic crystal. The technique has been shown to be a sensitive probe of molecular orientation on surfaces@footnote 1,2@ which is capable of monitoring growth at metal/liquid interfaces.@footnote 3,4@ Recent improvements in instrumentation@footnote 4@ have greatly increased the speed of response of RAS equipment so that it can be used to monitor growth at realistic growth rates and to provide information on the orientation and interaction between biological molecules at metal/liquid interfaces on a fast time scale. This talk will present recent results of studies of the physical and electronic structure of metal and semiconductor surfaces and of the RAS of DNA bases and DNA sequences adsorbed at the Au(110)/electrolyte interface. A brief description will be given of how the sensitivity, spectral range and in particular the timescale of RAS will be radically improved by the proposed UK Fourth Generation Light Source (4GLS). @FootnoteText@@footnote 1@J.R. Power, P. Weightman, S. Bose, A.I. Shkrebtii and R. Del Sole, Phys. Rev. Lett. 80 3133-6 (1998).@footnote 2@B.G. Frederick, J.R. Power, R.J. Cole, C.C. Perry, Q. Chen, S.Haq, Th. Bertrams, N.V. Richardson and P. Weightman. Phys. Rev. Lett. 80 4490-3 (1998).@footnote 3@B. Sheriden, D.S. Martin, J.R. Power, S.D. Barrett, C.I. Smith, C.A. Lucas, R.J. Nichols and P. Weightman, Phys. Rev. Lett. 85 4618-21 (2000).@footnote 4@P. Harrison, T. Farrell, A. Maunder, C.I. Smith and P. Weightman, Meas. Sci. Technol. 12 2185-91 (2001).

4:40pm **AS-ThA9 Spectroscopic Ellispometry Analysis of Chemical Vapor Deposited Zirconia Thin Films***, **B.R. Rogers**, Z. Song, R.D. Geil, D.W. Crunkleton,* Vanderbilt University

The integration of high-k dielectric materials into MOSFET fabrication processes will require a non-destructive, fast, and accurate method for film characterization and process control. Spectroscopic ellipsometry (SE) is an outstanding candidate for these applications. This study reports the results of a multi-sample, variable-angle SE (VASE) analysis to characterize zirconia thin films deposited on Si(100) by high vacuum chemical vapor deposition (HVCVD). We evaluated several optical models of the samples to determine which best described the experimental data. A two-layer model consisting of a Tauc-Lorentz layer on the top of a Lorentz interfacial layer resulted in the best fit. This model was used to extract the optical constants of both the zirconia and the interfacial layers. The extracted optical constants were then used as constants in additional models to optimize the analyses. Most of the models fit the data below 6.0 eV extremely well. However, significant differences in goodness of fit were seen between the models'predictions above 6.0 eV photon energies. We feel these differences are due to an increased sensitivity to the interfacial layers for photons above 6.0 eV. The influence of the quality of interfacial layers on the accuracy of extracted optical constants will be discussed. Supporting data from XPS, TEM, and time-of-flight medium energy backscattering analyses will also be presented.

5:00pm **AS-ThA10 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation: On the Selection Rules of Binary Modes***, **P.E: Uvdal**, M. Andersson,* Lund University, Sweden

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The selection rules, that is the absesence/presence of them will be descussed based on recent first principle calculations.@footnote 1@ @FootnoteText@ @footnote 1@M.P. Andersson and P. Uvdal, Phys. Rev. Lett. 90 (2003) 076103.

Technology for Sustainability
Room 320 - Session AT-ThA

Science and Technology Related to Global Effects: Emissions, Climate, and Transport

Moderator: S. Raoux, Applied Materials

2:20pm **AT-ThA2 SeaWiFS Land and Ocean Vegetation Measurements - A Six-year Set of Climate Change Records***, **R.A. Barnes**,* Science Applications International Corporation and SeaWiFS Project

SeaWiFS (the Sea-Viewing Wide Field-of-View Sensor) was launched in August 1997. It commenced on-orbit operations in September 1997 and continues to make images of the Earth surface at a 1 km areal resolution to this day. The SeaWiFS data set currently contains two transitions of the El Nino-Southern Oscillation (ENSO). With an electronic design that includes bi-linear gains, SeaWiFS makes measurements of both the dark ocean and the much brighter surface of the land. As a result, SeaWiFS provides the first truly global measurement set of vegetation changes from a single instrument. SeaWiFS also provides a baseline for one of the multi-decadal climate change data sets proposed by NASA. This data set includes Earth surface measurements from the MODIS (Moderate Resolution Imaging Spectroradiometer) sensors currently flying onboard the Terra and Aqua spacecraft and from the VIIRS (Visible and Infrared Imaging Radiometer Suite) instrument to be flown onboard the NPP (NPOESS Preparatory Program) spacecraft, which is currently scheduled for launch in 2007. Subsequent VIIRS instruments are planned to be flown for several decades into the future, as part of NPOESS (the National Polar-orbiting Operational Environmental Satellite System). For ocean vegetation measurements in particular, the requirements for the Climate Data Records (CDRs) include extensive calibration/validation and atmospheric correction programs, since approximately 90% of the top-of-the-atmosphere radiance measured by the satellite instruments comes from the atmosphere.

2:40pm **AT-ThA3 Environmental Transformation of Uranium-Organic Complexes: Implications for Transport and Remediation***, **C.W. Eng**, G.P. Halada,* State University of New York at Stony Brook*; A.J. Francis, C.J. Dodge,* Brookhaven National Laboratory

Transportation and fate of uranium are fundamentally affected by the nature of their association with pervasive organic environmental molecular constituents resulting from natural or man-made sources. Understanding the role of organic ligands and the transformation of these complexes is essential to the development and optimization of remediation technologies. For example, u-organic complexation adversely affect the ability of certain bacteria to reduce soluble uranium (U(VI)) to a more insoluble form (U(IV)).@footnote 1@ Organic ligands can coordinate with uranium in aqueous solution and perhaps decrease the effectiveness of the ZVI. In literature, the fate of the uranium and organic ligands are not fully elucidated in these systems. Our research provides fundamental information about the structure and transformation of uranium-organic complexes through electrochemical and spectroscopic analyses. The organic ligands chosen in this study will be relatively simple molecules (e.g. salicylic acid, catechol), which are used as analogs for more complex molecules found in the environment. The objectives of this work include a) characterization of the uranium and organic ligands; b) the electrochemical behavior of u-organic complexes; c) the relative stability and mobility of the uranium-organic complexes; and d) the ultimate fate of the uranium and ligands. X-ray Photoelectron Spectroscopy , laboratory and synchrotron-based Fourier Transform Infrared analysis, and in-situ electrochemical experiments will be combined with synchrotron-based X-ray Absorption and Raman spectroscopies. The resulting structural and molecular spectroscopic data is then used to generate computational molecular models, so that molecular orbital structures of complexes can be related to both stability and reactivity of uranium-organic ligands. @FootnoteText@@footnote 1@ Biotransformation of uranium and other actinides in radioactive wastes, A.J. Francis, Journal of Alloys and Compounds (1998), 271-273, 78-84.

3:00pm **AT-ThA4 Managing Greenhouse Gas Emissions using ISO 14064 as a Quantification, Reporting and Verification Guide***, **J.C. Shideler**, J.H. Schaarsmith,* Futurepast: Inc. **INVITED**

Organizations increasingly are identifying greenhouse gas emissions as significant environmental aspects of their operations and activities. Emissions may be direct, such as with the use of SF6 in manufacturing operations, or indirect, such as with the use of energy resources derived from fossil fuel sources. The increasing focus on control and reduction of greenhouse gas emissions from anthropogenic sources has stimulated the development of a management system standard -- ISO 14064 -- that provides a common template for quantification, reporting, and verification of greenhouse gas emissions data. The authors survey the US and international legal and regulatory environment pertaining to greenhouse gas emissions, and describe how ISO 14064 can help organizations develop and report data for internal management purposes or for US or international emissions reporting or trading.

3:40pm **AT-ThA6 Climate, Technology and the Energy Dimension of Sustainable Development***, **J. Edmonds**, G. Stokes, J. Clark,* Pacific Northwest National Laboratory **INVITED**

The global energy system will need to evolve to provide both abundant resources at reasonable prices while simultaneously addressing environmental quality issues ranging from acid rain to mercury emissions to regional air pollution and climate change. Focusing on the goal of the UN Framework Convention on Climate Change, stabilization of greenhouse gas concentrations, we have looked into the inevitable transformation of the global energy system over the next century and beyond. These results suggest that a range of technologies, some likely permanent parts of the future energy and some transitional technologies, will be required to meet the challenge. What emerges are a variety of possible global energy technology strategies where the ability of a particular technology system to meet the cost and environmental goals of society determine the ability of the technology to compete and succeed in meeting the demand for primary energy which may well triple over the course of this century.

Biomaterial Interfaces
Room 318/319 - Session BI+SS-ThA
Biodiagnostics

Moderator: G. Leggett, University of Sheffield, UK

2:00pm **BI+SS-ThA1 Engineered DNA and RNA Molecules as Biochemical Tools*, R. Breaker,*** Yale University **INVITED**

RNA and DNA molecules can be engineered to perform as precision allosteric enzymes, or "molecular switches", that are modulated by specific effectors. These designer sensor elements have numerous applications ranging from the construction of biosensors to the development of novel genetic switches. We have embarked on a program to establish effective molecular engineering strategies for switch construction, and to establish the fundamental principles that dictate the performance characteristics of these molecules. In pursuing our objectives, we have created a variety of RNA molecular switches that are modulated by specific target molecules that range from nucleotides and oligonucleotides to drug compounds, metabolites and toxins. In addition, we have begun to explore the use of immobilized RNA switches for the construction of advanced biosensor arrays. Our findings suggest that RNA and DNA have a significant untapped potential for functioning as precision molecular switches in both industrial and natural settings.

2:40pm **BI+SS-ThA3 Base-dependent Competitive Adsorption of DNA on Gold*, D.Y. Petrovykh,*** University of Maryland and Naval Research Laboratory*; H. Kimura-Suda, M. Tarlov,* National Institute of Standards and Technology*; L.J. Whitman,* Naval Research Laboratory

We characterize the room-temperature adsorption of single-stranded DNA (ssDNA) homo-oligonucleotides from solution onto polycrystalline Au films, including competitive adsorption between all possible pairs of unmodified oligomers. Although recent studies have shown that different DNA bases and homo-oligonucleotides interact differently with Au surfaces, competitive interactions among the bases - which will occur in most practical applications - have not been systematically addressed. We use Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopy to characterize the resulting films, and observe that oligonucleotides adsorb with a strongly base-dependent affinity, adenine (A) > cytosine (C) >= guanine (G) > thymine (T). In competitive adsorption experiments on Au, oligo(dA) strongly dominates over the other oligonucleotides. The relative adsorption affinity of oligo(dA) is so great that it competes effectively against adsorption of thiolated oligomers, and even causes hybridized oligo(dA)*oligo(dT) duplexes to denature in the presence of Au. The asymmetric adsorption affinities of the oligonucleotides must be carefully considered in systems using gold substrates, electrodes, or nanoparticle labels, and are likely to also occur on other substrates of practical importance.

3:00pm **BI+SS-ThA4 MALDI MS of Proteins Separated on a Chemical Gradient Modified Open Channel Microchip***, G.R. Kinsel,* ***X. Li,*** *R.B. Timmons,* University of Texas at Arlington

Efficient methods for protein separation and characterization are critical to the success of a wide array of biological and biomedical research activities. Current methods involve electrophoretic separation of proteins, followed by staining, excision, digestion and analysis of isolated proteins by Matrix-Assisted Laser Desorption / Ionization Mass Spectrometry (MALDI-MS). This approach is both time consuming and subject to significant protein loss resulting from the various manipulations of the sample. Research in our laboratory is directed at circumventing these limitations through the incorporation of the sample separation process directly on the surface of the MALDI-MS sample stage. In our approach substrates suitable for use as the MALDI sample stage are modified to incorporate open electrophoretic separation channels. Substrates that have been employed include PMMA chips, which are patterned using heat-imprinting methods, and silicon wafers, which are patterned using conventional plasma etching methods. A chemical gradient is developed along the separation channel by masking adjacent areas and sequentially depositing thin films on the channel via pulsed RF plasma polymerization of allyl alcohol at various duty cycles. Control mixtures of peptides having varying hydrophilicity are electrokinetically injected into the gradient chemically modified open channel, eletrophoretically separated and then analyzed by rastering the MALDI desorption laser across the channel while acquiring MALDI mass spectra. Successful results obtained to date, demonstrate the potential value of this approach for improving sensitivity and specificity in MALDI MS analysis.

3:20pm **BI+SS-ThA5 Pb@super 2+@ Sensitive Catalytic DNA Assay Integrated into Microfluidic Channels*, R.A. Zangmeister,*** *M. Tarlov,* National Institute of Standards and Technology

Advances in microchip technology coupled with innovative bioassays are advancing the field of biosensors. We previously reported a method for immobilizing single-stranded DNA (ss-DNA) probe molecules in polyacrylamide hydrogels within plastic microfluidic channels. Spatially defined plugs are formed by photopolymerization of a solution containing 19:1 polyacrylamide/bisacrylamide and ss-DNA modified at the 5' end with an acrylic acid group. Low concentrations of fluorescent-tagged ss-DNA targets can be captured and detected in the hydrogels. We aim to couple this technology with a novel bioassay based on the response of catalytic DNA to Pb@super 2+@ ions in solution. It is reported to show > 80-fold selectivity for Pb@super 2+@ over other divalent metal ions, and with fluorescent tag modifiers can be used to detect Pb@super 2+@ ions over a large concentration range (10 nmol to 4 mmol).@footnote 1@ Our goal is to immobilize the enzyme strand sequence of the catalytic DNA duplex into the hydrogel plugs immobilized in microfluidic channels. Our strategy is to electrophorese fluorescently tagged substrate strands into the hydrogel plug where they hybridize with the immobilized enzyme strand to form the catalytic DNA system. Then Pb@super 2+@ is electrophoresed into the hydrogel plug resulting in the catalytic cleavage of the substrate strand and the release of the fluorescent-tagged sequence fragment that is detected using a fluorescence microscope. The combination of these two technologies results in a Pb@super 2+@ detection system with enhanced sensitivity due to the high loading of DNA probes in the hydrogel plug, the spatially confined, directed mass transfer characteristics of the microfluidic channels, and the inherently low fluorescent background of the hydrogels. The immobilization, retention of catalytic DNA activity, and current limits of detection will be discussed. @FootnoteText@@footnote 1@ Li, J.; Lu, Y., J. Am. Chem. Soc. 2000, 122, 10466-10467.

3:40pm **BI+SS-ThA6 Monitoring Neurotransmitters with Voltammetry*, R.M. Wightman,*** University of North Carolina **INVITED**

Carbon-fiber microelectrodes can serve as chemical sensors for the detection of easily oxidized chemical messengers such as dopamine, serotonin, and histamine in biological systems. The electrodes have micron dimensions and can be used on millisecond time scales. Thus, they can be used to measure neurotransmitter release at the level of single cells or in the brain of intact, behaving animals. Such measurements are giving new insights into the complex chemical interactions that regulate behavioral states.

4:20pm **BI+SS-ThA8 Adsorption Behavior of Proteins in Microcapillaries*, A. Bhattacharyya,*** *K. Lenghaus, D. Halagowder, J.J. Hickman,* Clemson University*; J.W. Jenkins, S. Sundaram,* CFD Research Corporation

The dynamics of protein adsorption, desorption and denaturization are important factors in determining the efficacy of a microfluidic device for biotechnology applications. When a protein solution is passed through a microcapillary, the protein molecules can adsorb onto the surface of the capillaries and can often subsequently denature. Hence an understanding of the adsorption behavior of a protein is very important in order to determine the basic parameters for fabrication of a microfluidic based MEMS device. Most of the research on protein adsorption characteristics is based on static systems. However, the adsorption behavior of proteins in static and flow systems is not necessarily the same. Our research focuses on investigating the difference in the adsorption behavior of proteins under flow and static conditions, using enzymatic proteins as probes. We have used enzymes such as alkaline phosphatase, glucose oxidase and horseradish peroxidase in our studies. The microcapillaries used were PEEK (Poly-Ether-Ether-Ketone) and PTFE (Polytetrafluoroethylene). A total protein assay (MicroBCA) was used to quantitate the amount of protein adsorbed to the surface and enzymatic assays were used to estimate the activity of the proteins. A statistical model based on the Langmuir equation was used for extracting the kinetic binding constants and the protein coverage on the surface. Our results indicate that there is a significant difference in the surface affinities and binding site densities observed in static and flow conditions. These results will enable us to improve existing protein adsorption and fluid dynamics software and eventually create design rules for biocompatible MEMS devices.

4:40pm **BI+SS-ThA9 Micro- to Nanofluidic Systems for Bioanalysis*, G.P. Lopez,*** University of New Mexico*; S.S. Sibbett,* Intel Corp.*; D. Petsev,* University of New Mexico*; C.F. Ivory,* Washington State University*; M. Piyasena, A. Garcia, L.K. Ista, M.J. O'Brien, P. Bisong, S.R.J. Brueck,* University of New Mexico

This talk will present an overview of efforts at the University of New Mexico to develop chip based micro- and nanofluidic systems for biosensing and bioseparations. Microfluidic systems to be described include microchip countercurrent electroseparation (in collaboration with Intel Corp.) and affinity microcolumns with fluorescence detection. New methods for fabrication of nanofluidic systems based on interferometic lithography will also be described. These methods are especially well suited for manufacture of bioanalytical systems that incorporate large scale integrated nanofluidic components. Characterization and modeling of fluidic properties of the bioanalytical systems will be emphasized.

5:00pm **BI+SS-ThA10 Chitosan - A Biomaterial Interface that can be Selectively Deposited onto Micropatterned Surfaces and Conjugated to Sensing Biomolecules*, L.-Q. Wu,*** *H. Yi,* University of Maryland Biotechnology Institute*; M.J. Kastantin, S. Li, D.A. Small, J.J. Park,* University of Maryland*; T. Chen,* University of Maryland Biotechnology Institute*; G.W. Rubloff, R. Ghodssi,* University of Maryland*; W.E. Bentley, G.F. Payne,* University of Maryland Biotechnology Institute

We are examining the amino-polysaccharide chitosan as a biomaterial interface. Chitosan's pH-dependent electrostatic properties allow it to be selectively deposited (i.e. "templated") onto micropatterned electrodes in response to an applied voltage. Deposition of chitosan, or chitosan-containing conjugates, is rapid (about 2 minutes) and can be performed under mild conditions. After neutralization, the films are retained without the need for an applied voltage. These films can also be removed from the electrode using mildly acidic conditions (pH<6). Chitosan's amine groups are also nucleophilic and can readily react with a variety of reagents. In particular, standard coupling chemistries can conjugate proteins and oligonucleotides with chitosan. We are exploiting glutaraldehyde coupling chemistries to anchor nucleic acids and proteins onto chitosan surfaces. In one study, we tethered oligonucleotide probes onto an electrochemically deposited chitosan surface and examined the bio-detection of mRNA by a hybridization-based assay. In a second study, we selectively deposited chitosan on an electode surface embedded in the base of a microfluidic channel. The green fluorescent protein (GFP) was subsequently anchored to this chitosan surface. In summary, chitosan is unique interface biomaterial - it can be templated onto a microfabricated surface and conjugated to bio-molecules. We are currently exploiting these capabilities in biosensor and bio-MEMS applications.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI-ThA

Magnetization Dynamics

Moderator: W.H. Rippard, National Institute of Standards and Technology

2:00pm **MI-ThA1 Ultrafast MOKE Study of Magnetization Dynamics in Exchange-Biased FeMn/Co and IrMn/Co Thin Films*, K. Seu,*** *H. Huang, A.C. Reilly,* College of William and Mary*; W.F. Egelhoff, L Gan,* National Institute of Standards and Technology

We have observed coherent magnetization rotation in exchange-biased Co systems by ultrafast laser pump-probe magnetooptical Kerr effect (MOKE). This technique, first introduced by Ju et al. in the study of NiO/NiFe, uses ultrafast photoexcitation to spontaneously decouple the antiferromagnetic/ferromagnetic system.@footnote 1@ The magnetization undergoes coherent precession as described by the Landau-Lifshitz-Gilbert equations of motion.@footnote 1@ Such ultrafast measurements provide opportunity to study the ultimate time scale for these processes as well as determination of fundamental parameters such as anisotropy and damping.@footnote 2@ This is in analogy with FMR, but with the benefit of direct access to the time domain, sub-micron spatial resolution and straightforward in-situ application. Co exchange-biased systems such as FeMn/Co and IrMn/Co, besides being technologically important, offer an interesting comparison to the NiFe systems. It has been observed that magnetization reversal takes place via more complicated processes in Co, involving nucleation of many small domains.@footnote 3@ Also, recent FMR experiments suggest that the damping in IrMn/Co films is not strongly dependent on exchange bias field strength, unlike the NiO/NiFe system.@footnote 4@ We will present measurements of anisotropy and damping parameters in FeMn/Co and IrMn/Co as a function of Co thickness and exchange bias field strength. These will be used to further explore the nature of exchange biasing in these systems as well as investigate the wider applicability of ultrafast optical techniques. @FootnoteText@ @footnote 1@Ganping Ju et al., Phys Rev Lett 82, 3705 (1999), Phys Rev. B., 62, 1171 (2000)@footnote 2@ M. van Kampen et al., Phys. Rev. Lett. 88, 227201 (2002)@footnote 3@ Chan-Gyu Lee et al., J. Appl. Phys. 91, 8566 (2002)@footnote 4@ R.D. McMichael et al., J. Appl. Phys. 83, 7037 (1998).

2:40pm **MI-ThA3 Spatial and Temporal Control of Magnetization Dynamics in Lithographic Elements and Nanocrystalline Composites*, M.R. Freeman,*** *M. Belov, K. Buchanan, A. Krichevsky, A. Meldrum,* University of Alberta, Canada **INVITED**

Time-resolved optical microscopy is a versatile tool for investigations of dynamic phenomena in magnetic thin films, including resonance, reversal, and relaxation.@footnote 1@ Broadband pulsed ferromagnetic resonance studies of square NiFe elements were performed to investigate the control of modal oscillations in inhomogeneously magnetized structures. The spatiotemporal evolution of the magnetization, as excited by a small out-of-plane transient magnetic field, was imaged in the presence of a weak in-plane static bias. In a uniform platelet the spatial response is governed by the nonuniform static magnetization distribution associated with closure domains across the bias field direction. A circular pinhole was patterned in the center of a square platelet to show that the spatial pattern of FMR response also sensitively depends on weak variations of the static magnetization. Comparison to numerical modeling confirms that the experimental observation of spatially-nonuniform damping is a result of the evolution of energy into shorter wavelength modes. The magnetic switching behavior of mesoscopic structures continues to arouse interest for technological applications. Magnetization reversal of mesoscopic structures driven in a crossed-excitation wire (prototype MRAM) geometry will be described. The magnetic and magneto-optical properties of nanocomposite materials created using ion implantation and subsequent thermal processing are also being investigated. Implanting iron ions into a SiO2 host results in a collection of randomly oriented crystalline Fe nanoparticles, the magnetic and microstructual properties of which depend on both the implantation and annealing conditions. Iron implanted SiO2 samples subject to a particular treatment exhibit large Faraday rotation and an extremely fast and tunable response to out-of-plane excitation. @FootnoteText@ @footnote 1@ B.C. Choi, A. Krichevsky, and M.R. Freeman, to be published in Proceedings of the IEEE, June 2003.

3:20pm **MI-ThA5 Real-Time Imaging of Spin Dynamics in Magnetic Vortex Structures*, J.P. Park,*** *P. Eames, D.M. Engebretson, P.A. Crowell,* University of Minnesota **INVITED**

Patterned nanometer-scale magnetic structures have been proposed as media for high-density data storage. A prerequisite for implementing such a technology will be an understanding of the fundamental characteristics of magnetic nanostructures, including switching times, damping constants, and the spatial distribution of collective modes. We use time-resolved Kerr microscopy to study the spin dynamics of individual ferromagnetic disks with thicknesses of 50 nm and aspect ratios @beta@= L/R ~ 0.1 - 0.5, where L is the thickness and R the radius.@footnote 1@ The equilibrium state of each disk in zero field is a vortex with a singularity at the center. As the field is reduced from saturation, the vortex nucleates at one edge of the disk, and it moves across the diameter until it is annihilated at the opposite edge in negative fields. We observe three distinct excitations of this vortex state, in contrast to the simple uniform precession observed in the saturated state. The lowest mode corresponds to the gyrotropic motion of the entire vortex around its equilibrium position.@footnote 2@ The exact nature of the higher modes is being explored through a combination of spatially-resolved spectroscopy and micromagnetic simulations. The frequencies of all three vortex modes are nearly independent of the value of the applied field and hence the position of the vortex inside the disk. This work was supported by NSF DMR 99-83777, the Research Corporation, the Alfred P. Sloan Foundation, the University of Minnesota MRSEC (DMR 02-12032), and the Minnesota Supercomputing Institute. @FootnoteText@ @footnote 1@J. P. Park, P. Eames, D. M. Engebretson, J. Berezovsky, and P. A. Crowell, Phys. Rev. B 67, 020403R (2003). @footnote 2@K. Yu. Guslienko et. al., J. Appl. Phys. 91, 8037 (2002). .

4:00pm **MI-ThA7 High-Frequency Noise and Thermal Fluctuations in GMR Devices*, S.E. Russek,*** National Institute of Standards and Technology

High-frequency (1 GHz to 8 GHz) magnetic noise has been measured in giant magnetoresistive (GMR) devices with dimensions down to 100 nm.

Both commercial recording heads and GMR devices fabricated within microwave circuit structures were measured. The uniform ferromagnetic resonance mode has been measured as a function of applied field, bias current, and temperature. In addition to the uniform mode, other modes have been observed that are due to micromagnetic structure in the devices. The presence of these modes can be correlated with Barkhausen noise in the magnetoresistance data. The data have been fit with simple models based on the fluctuation-dissipation theorem and with numerical models that incorporate more complex dissipation processes.

4:20pm **MI-ThA8 Weak Spin Pumping and Inhomogeneity in Cr/NiFe/Cr Trilayers***, **R.D. McMichael**, A.J. Shapiro, A.P. Chen, W.F. Egelhoff,* National Institute of Standards and Technology

Ferromagnetic resonance linewidth measurements on 10 nm Cr/5 nm Ni@sub 80@Fe@sub 20@/10 nm Cr trilayers show that Cr does not contribute significantly to the damping properties of NiFe. In contrast, measurements in Pt/NiFe/Pt and Pd/NiFe/Pd trilayers have demonstrated strong "spin pumping" enhancements due to the normal metal layers.@footnote 1@ The experiments described here were designed to determine whether similar spin-pump damping effects were likely in CoCr recording media due to the presence of Cr in grain boundaries. We found that the linewidth in Cr/NiFe/Cr trilayers was large relative to Cu/NiFe/Cu trilayers. To discern the origins of the enhanced line width, Cu spacer layers were included between the NiFe layer and either the bottom or top Cr layer and an analysis of the angular dependence of the line width was performed. The results show that the linewidth increase is associated with inhomogeneity at the bottom Cr/NiFe interface. The inhomogenitey at this interface may be a reflection of the growth beginning as bcc-NiFe on bcc-Cr and converting to fcc-NiFe. Growth of Cr on NiFe had an insignificant effect on the linewidth of the NiFe. These conclusions were confirmed by MOIF imaging of the magnetization reversal, which showed nucleation and growth of reversed domains in NiFe on Cr, but which showed low coercivity motion of a single domain wall sweeping out the entire area when the NiFe was deposited on Cu, whether the cap layer was Cu or Cr. @FootnoteText@ @footnote 1@ S. Mizukami, Y. Ando and T. Miyazaki, Jpn. J. Appl. Phys., v. 40, pp. 580-585 (2001).

4:40pm **MI-ThA9 Tunnel Barrier Materials Development for Magnetometer based Josephson Qubits***, **D.P. Pappas**, R. McDermott, D.A. Hte, R.W. Simmonds, K.M. Lang, J.M. Martinis,* National Institute of Standards and Technology

Although Josephson-junction qubits show great promise for quantum computing, the origin of dominant decoherence mechanisms remains unknown. We report Rabi oscillations for a phase qubit, and show that their "coherence amplitude" is significantly degraded by spurious microwave resonances. These resonances appear to arise from changes in the junction critical current, produced by fluctuations in the position of electrons or atoms within the tunnel barrier. We argue this mechanism is a dominant source of decoherence in all present Josephson qubits, and improvements will require materials research directed at the tunnel barriers to remove these spurious resonances. In order to test the influence of the junctions on the cohereance amplitude we have developed tunnel junctions fabricated from both Al/AlO/AL and Al/AlN/Al trilayer structures.

Processing at the Nanoscale
Room 317 - Session PN-ThA

Molecular Monolayers

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

2:00pm **PN-ThA1 AFM-Based Lithography and Conductive Probe Measurements with Substituted Oligo(phenylene ethynylene) Molecular Wires on Au(111)***, **J.C. Garno**, J.D. Batteas,* National Institute of Standards and Technology

AFM-based lithography is combined with conductive probe AFM (CP-AFM) measurements to characterize the surface structure and conductive properties of designed test platforms comprised of substituted oligo(phenylene ethynylene) molecules within a matrix of alkanethiol self-assembled monolayers (SAMs). Oligo(phenylene ethynylene)s on Au(111) are excellent candidates for molecular electronics, due to their rigid, planar structure and pi-conjugated backbone. When substituents are attached to oligo(phenylene ethynylene)s, electronic properties such as negative differential resistance and molecular scale switching behavior have been reported. Nanopatterned test platforms may provide a means to obtain a highly reproducible contact area in which the alkanethiol matrix of the test platforms serves as a boundary and provides an insulating frame of reference in the areas surrounding test elements. In CP-AFM, the probe is placed directly on the surface of the fabricated nanostructure, at a certain applied force. The alkanethiol matrix may be used as an internal calibration for CP-AFM measurements, with direct side-by-side comparisons of the alkanethiol matrix versus test molecule. Nanopatterns generated using AFM-based nanofabrication furnish local measurements of the thickness of molecular wire SAMs, using matrix alkanethiols as a height reference. By systematically varying certain parameters, such as the size, composition, geometry, and arrangement of test elements, we anticipate that changes can be correlated with measured conductivity, to shed light on predicting how electrical properties vary with molecular structure. Useful design parameters for molecular electronics which could be gained from this approach include the critical geometry and size thresholds for functional device elements, differences in electrical conductivity of materials, and the structural motifs best suited for devices.

2:20pm **PN-ThA2 Chemical Nanostructures as Templates for the Fabrication of Laterally Patternend Polymer Brushes***, **A. Paul**, A. Küller,* Universität Heidelberg, Germany*; U. Schmelmer, R. Jordan,* TU München, Germany*; A. Ulman,* Polytechnic University*; M. Grunze, W. Eck,* Universität Heidelberg, Germany*; A. Gölzhäuser,* Universität Marburg, Germany

Chemical Nanolithography@footnote 1@ utilizes electron beams for the controlled modification of self-assembled monolayers (SAMs). E-beam irradiation of SAMs of nitrobiphenylthiol causes a lateral cross-linking reaction of the biphenyl mesogen along with a simultaneous conversion of the terminal nitro groups to the amine.@footnote 2@ Consecutive reactions such as chemical coupling of chromophores or surface-initiated polymerization can be performed in predefined (irradiated) areas.@footnote 3@ We show the fabrication of polymer brushes with lateral dimensions down to 50 nm by utilizing chemical nanolithography templates for surface-initiated polymerization. Limits of resolution and potential applications will be discussed. @FootnoteText@ @footnote 1@ A. Gölzhäuser et al., Adv. Mater. 13, 806, (2001)@footnote 2@ W. Eck et al., Adv. Mater. 12, 805, (2000)@footnote 3@ U. Schmelmer et al., Angew. Chem. Int. Ed. 42, 559 (2003)

2:40pm **PN-ThA3 Reactions of Silicon and Gold Nanostructures on Surface-Templated Molecule Corrals***, **Y. Liu**, Z Zhang, M. Wells, A.V. Teplyakov, T.P. Beebe, Jr.,* University of Delaware

Semiconductor and metal nanostructures display novel size-dependent properties as a result of quantum confinement. New concepts and new challenges evolve with regard to the potential applications of these nanostructures in molecular electronics, sensors, biological interfaces and biomedical applications, advanced material design, charge storage, light-emitting diodes, energetic materials, and other applications that remain unknown at present. Semiconductor and metal nanostructures on surface-templated molecule corrals are unique because large numbers of these nanostructures with controlled size, height, shape, surface density, and position or pattern can be produced quickly and efficiently with a narrow size dispersion in a parallel process that takes only minutes. In this work, the formation and modification of silicon and gold nanostructures templated on the highly oriented pyrolytic graphite (HOPG) basal plane will be discussed. Molecule corrals are typically formed with a high degree of control by a simple bench-top process in an oven operating at approximately 650 Â°C in the ambient air from the preexisting natural defects or manmade (ion-beam bombardment) defects on the surface. Silicon and gold nanostructures are vacuum evaporated onto these size- and shape-controlled molecule corrals. These nanostructures are then functionalized with a number of reagents, including organosilanes and organothiols. Scanning tunneling microscopy, atomic force microscopy, time-of-flight secondary ion mass spectrometry, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy are used to characterize the degree of chemical modification of surface-templated nanostructures before and after modification.

3:00pm **PN-ThA4 Molecular Monolayers for Interfacing Organic and Biological Molecules to Group IV Semiconductors***, **R.J. Hamers**,* University of Wisconsin-Madison **INVITED**

The burgeoning fields of organic electronics, molecular electronics, and bio-electronics are all placing increased emphasis on electrically interfacing inorganic materials such as silicon and diamond with organic and biological materials. Over the last several years we have been exploring new methods for fabricating and patterning hybrid interfaces on silicon and diamond surfaces, and understanding how the specific chemical chemical bonds and nanometer-scale structures control the resulting electrical properties of the interfaces. In ultrahigh vacuum the reactions of C=C bonds, S-H bonds, and O-H bonds can be used as the basis for preparing covalently-bonded layers that exhibit specific reactive and/or non-reactive functional groups, which can in turn be used for linking more complex films (pentacene) and structures (DNA) to the surfaces . Essentially identical reactions are used to link organic molecules with H-terminated silicon and diamond under ambient (atmospheric pressure) conditions, using ultraviolet light to initiate the reactions. We have been assessing the molecular conductivity on an atomic level via STM measurements of the apparent height, and on more macroscopic scales by measuring interfacial impedance after the molecular monolayers are covered with conductive materials such as the pentacene or after they are linked to biological molecules such as DNA. In this talk I will summarize what we have learned about how to use organic monolayers as electrical interfaces to pentacene films, DNA molecules, and other nanometer-scale structures of interest.

3:40pm **PN-ThA6 Covalent Linkage of Hydrocarbon Moieties and Addition of Organic Functional Groups on Si(111)**, ***T. Yamada***, *H.S. Kato, K. Shirasaka, M. Noto, M. Kawai,* RIKEN, Japan

Deposition of unsaturated hydrocarbon moieties (CH@sub 2@=CH- etc.) on H-terminated H:Si(111)(1x1) surface was performed by Grignard reaction, and addition of boranes and halogens to the C=C double bond was attempted by the methods of wet chemical organic synthesis. The adsorbates formed on Si(111) were investigated by HREELS, AES, etc. in ultrahigh vacuum. Treating H:Si(111) in a tetrahydrofuran (THF) solution of CH@sub 2@=CHMgCl) resulted formation of adsorbates with a major amount of -CH@sub 2@- and a minor amount of CH@sub 2@=, detected by HREELS. The formation of saturated -CH@sub 2@- seems to be due to inter-adsorbate bonding of vicinal CH@sub 2@=CH-groups right after deposition. This parasitic reaction was avoided by using a 1:3 - 5 mixture of CH@sub 2@=CHMgCl and CH@sub 3@MgBr in THF to insert inactive CH@sub 3@- groups among CH@sub 2@=CH- adsorbates. HREELS revealed the ratio of CH@sub 3@:CH@sub 2@=CH in the adlayer was approximately equal to that in the Grignard solution. This sort of CH@sub 2@=CH- moieties diluted in CH@sub 3@- can be useful in reactions with bulky reagents. To realize the terminal hydration of CH@sub 2@=CH:Si(111) into OH-CH@sub 2@-CH@sub 2@:Si(111), hydroboration reaction with a borane reagent 9-BBN was attempted in THF. Deposition of boron was detected by AES, indicating that 9-BBN was bonded by breaking CH@sub 2@=CH bonds. Further attempt to complete the hydration by H@sub 2@O@sub 2@ solution was made, and we are trying to distingish the OH group on the -CH@sub 2@-CH@sub 2@- moiety from OH attached on surface SiO@sub 2@ impurities by HREELS. Addition of HBr on CH@sub 2@=CH:Si(111) was performed by a moderate reaction with HBr in organic solvents. Our goal is to gain a freedom of terminating Si surface with desired functional groups. This is a key technology in grafting polymers and biomolecules such as DNA and peptides to construct intelligent chemically functional system on silicon.

4:00pm **PN-ThA7 Templated Growth of One-dimensional Molecular Wires on Si(100) Using Multi-step Feedback Controlled Lithography**, ***R. Basu***, *N.P. Guisinger, M.C. Hersam,* Northwestern University

This study demonstrates the fabrication of one-dimensional molecular wires on the Si(100) surface with atomically precise control over the position and length of each wire. Specifically, styrene molecules, which are known to experience self-directed growth on Si(100) surface along dimer rows, have been induced to grow from individual dangling bonds that have been created on the hydrogen-passivated Si(100)-2x1 surface through feedback controlled lithography (FCL) using a room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM). The site-specific creation of individual dangling bonds allows control over the position of the styrene wires whose growth is confined along a dimer row. FCL has also been used to create an additional pair of dangling bonds at two different positions within the same dimer row to allow for controlled chemisorption of the organic free radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The presence of the bounded TEMPO molecules physically restricts the growth of the styrene chain beyond the specified length along the dimer row and thus allows unprecedented control over the length of the molecular wires. Current-voltage spectroscopy has been performed on the styrene and TEMPO molecules. Based on the spectroscopic data, bias dependent STM conductance images of the molecular wires have been obtained.

4:20pm **PN-ThA8 UHV Characterization of Adsorbates Deposited in Ambient from Solution onto Si(001):H-(2x1)**, ***L.A. Baker***, *A. Laracuente, L.J. Whitman,* Naval Research Laboratory

The marriage of nanoscale organic components with semiconductor devices for molecular electronics and sensing applications requires new approaches to fabrication. For example, whereas most device fabrication occurs in an ultra-high vacuum (UHV) system, organic materials chemistry often begins in a solution-filled beaker. We are using H-terminated Si(001) prepared in UHV as a robust substrate for ambient surface chemistry that can subsequently be characterized in UHV by STM. As demonstrated by Hersam, et al.,@footnote 1@ Si(001) terminated with H in UHV can be removed to an ambient environment for hours and still appear as a relatively clean, well-ordered Si(001):H-(2x1) surface upon return to UHV. We now find that this surface can be exposed in ambient to chlorinated solvents (e.g., CHCl@sub 3@) with minimal surface modification observed following reintroduction to UHV. In addition, we will present results showing that organic molecules, such as porphyrins, can be deposited in this way and subsequently characterized in UHV with STM. @FootnoteText@@footnote 1@M. C. Hersam, et al., Appl. Phys. Lett. 78, 7 (2001).

4:40pm **PN-ThA9 Nanoscale Fabrication and Characterization of Chemically Modified Silicon Surfaces Using Conductive Atomic Force Microscopy in Liquids**, ***C.R. Kinser***, *D.E. Kramer, M.W. Such, P. Bertin, H. Jin, S.T. Nguyen, M.J. Bedyzk, M.C. Hersam,* Northwestern University

Self-assembled monolayers of terminal alkenes on hydrogen passivated silicon provide an attractive route for covalent organic functionalization of silicon surfaces. This talk addresses two important experimental issues that improve the applicability of these surfaces for potential device applications: (1) Means of verifying the conformation of terminal reactive groups; (2) Strategies for patterning these monolayers down to the nanometer length scale. The first issue is addressed using X-ray reflectivity and X-ray standing wave techniques at the monolayer level. X-ray characterization of a bromine tagged analog of ethyl-undecylenate on Si(111) show that the monolayer coverage is 0.59 and the bromine lies 14.6 Å above the silicon surface. This data illustrates that the molecule is reacted to the surface via the terminal alkene, thus presenting the bromine functionality for post-chemistry. In this manner, the effectiveness of subsequent chemical reactions on functionalized silicon surfaces can be efficiently forecasted. The remainder of the talk describes a novel strategy for nanopatterning monolayers on hydrogen passivated silicon directly from the liquid phase. In Liquid Phase Nanolithography, hydrogen desorption is induced by applying a bias across a conductive atomic force microscope tip-sample junction submerged in an organic solvent. Appropriately chosen molecules suspended in the solvent directly chemisorb on the depassivated lines. We will present results for patterning neat undecylenic acid methyl ester on H:Si(111) with 50 nm spatial resolution using this technique and suggest approaches for utilizing this scheme to fabricate biomedical nanosensors.

5:00pm **PN-ThA10 Imaging of Monomolecular Lithographic Patterns by X-ray Photoelectron Spectromicroscopy and X-ray Absorption Spectromicroscopy**, ***M. Zharnikov***, Universität Heidelberg, Germany; *R. Klauser,* National Synchrotron Radiation Research Center, Taiwan; *A. Paul, A. Gölzhäuser,* Universität Heidelberg, Germany; *A. Scholl,* Lawrence Berkeley National Laboratory

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific issue. One of perspective methods applies electron-beam patterning of chemisorbed monomolecular films (so-called self-assembled monolayers - SAMs), with the major advantage to tailor the resist properties through the exact architecture and packing of the molecular constituents. We have utilized scanning soft X-ray photoelectron and X-ray absorption spectromicroscopy to image and characterize different electron-beam patterned SAMs on gold substrates. Both techniques rely on characteristic spectroscopic features, which makes them chemically sensitive. The XPM measurements have been performed with a scanned zone-plate-focused X-ray beam and a 16 channels photoelectron spectrometer while the XAM images were collected with a X-ray PEEM working in a total electron yield (TEY) acquisition mode. The lateral structures in all SAM-based patterns could be clearly distinguished by both XPM and XAM. Chemical and physical changes in some of the resists could be directly monitored. The strength and limits of XPM and XAM to image monomolecular lithographic patterns are discussed. The major constrains of XPM are a strong inelastic background at the position of characteristic emissions and a rather limited (at present) lateral resolution. The major constrain of XAM is a rather poor surface sensitivity due to a large probing depth in the TEY acquisition mode. Ways to overcome the experimental constrains are considered, along with the issue of X-ray damage, which might be relevant at an X-ray exposure required for the acquisition of high-quality XPM and XAM images.

Plasma Science and Technology
Room 315 - Session PS-ThA

Plasma Diagnostics: Mechanisms

Moderator: N.C.M. Fuller, IBM TJ Watson Research Center

2:00pm **PS-ThA1 In-Situ Monitoring of Unstable Neutral Molecules using Ion Attachment Mass Spectrometer*, Y. Shiokawa,*** *M. Nakamura, Y. Hirano, Y. Taneda, T. Fujii,* Anelva Corporation, Japan

Ion Attachment Mass Spectrometer (IAMS)@footnote 1@ has a unique advantage of fragment-free; mass analysis of true original molecule without dissociation, which is impossible by common methods such as electron impact. Therefore, IAMS has been expected to measure unstable neutral molecules in gas processes, and was already applied to analysis of thermal reaction by metallic-organic material for Cu-CVD and of exhaust gas from dry etching system.@footnote 2@ Although conventional IAMS used in these experiments is large and needed higher pressure than 100Pa for sampling, newly developed IAMS@footnote 3@ is compact and needs only 1Pa, so that IAMS in-situ monitor seems to be realized. Therefore we are investigating capabilities of new IAMS for in-situ monitoring of unstable neutral molecules in many processes, including tool for plasma diagnostics. In this experiment, plasma was produced by small inductively coupled source with 2Pa of c-C@sub 4@F@sub 8@ (100%), and new IAMS was put on it at a distance of 10cm apart. Neutral molecules of CF@sub 2@, C@sub 2@F@sub 4@, COF@sub 2@ by IAMS and ions of CF@sub 2@@super +@, C@sub 2@F@sub 4@@super +@, COF@sub 2@@super +@, ionized in plasma, were measured simultaneously. First, when plasma power increased from 25W to 200W, CF@sub 2@@super +@, C@sub 2@F@sub 4@@super +@ did not change largely, but CF@sub 2@ reduced to one-tenth and C@sub 2@F@sub 4@ one-hundredth at only 50W. On the other hand, both COF@sub 2@@super +@ and COF@sub 2@ did not change largely. Next, when pressure decreased from 2Pa to 0 .5Pa, CF@sub 2@@super +@ kept constant but CF@sub 2@ reduced to one-tenth. These results show that behavior of true original molecules is completely different from that of ions ionized in plasma. It is well known too that neutrals such as CF@sub 2@, C@sub 2@F@sub 4@ cannot be detected correctly by electron impact. Therefore it was confirmed that new IAMS is very useful as in-situ monitor in plasma. We would like to present some examples of c-C@sub 4@F@sub 8@ plasma in manufacturing conditions and of SiH@sub 4@ plasma throughout our talk. Precious discussions with Prof. Nakata and Prof. Takayanagi of Tokyo University of Agriculture and Technology are gratefully acknowledged. @FootnoteText@ @footnote 1@ T.Fujii, Mass Spectrometry Review 19(2000) 111, @footnote 2@ M.Nakamura et al, JVST-A 19(2001) 1105,@footnote 3@ Y.Hirano et al, AVS Int.Sympo. PS-TuP3 (2002)

2:20pm **PS-ThA2 Discharge Frequency Dependence of Plasma Parameters in Parallel-plate-electrode VHF Plasmas*, Y. Ichikawa,*** Fuji Electric Co. Ltd., Japan*; T. Sasaki,* Fuji Electric CRD, Japan*; S. Matsumura,* Musashi Institute of Technology, Japan

Recently, plasmas generated by power supplies of VHF band attract considerable interest in plasma CVD technique to increase deposition rate and to improve film properties of silicon related thin films. In this work, we have studied the effect of discharge frequency on the characteristics of plasma with a view to understanding the mechanism why VHF plasmas are more desirable than the conventional 13.56MHz plasma. We used a capacitively coupled plasma CVD apparatus with a pair of parallel plate electrodes of 160mm in diameter; the discharge frequency can be varied from 10MHz to 100MHz continuously. To measure the plasma parameters of VHF plasma precisely, we developed the following two probe diagnostic techniques: (1) A modified capacitance probe to measure the amplitude of plasma potential variation (V@sub sp-p@) at discharge frequency (2) Compensation single probe by which variation of the plasma potential is compensated and precise current voltage characteristics are measured Employing these probe techniques, we measured electron temperature, electron density, time averaged space potential, and V@sub sp-p@ in H@sub 2@ VHF plasmas. The results measured at frequencies of 13, 24.5 and 92.3MHz show that (1) the electron temperature, Te, decreases with increasing discharge frequency; (2) the electron density for 92.3Hz is about 30 times as high as that for 13MHz under the same discharge power condition. The spatial distributions of these plasma parameters and the space potential were also measured. The details of these experimental results will be presented and discussed.

2:40pm **PS-ThA3 Model-based RF Plasma Monitoring under Industrial Conditions*, M. Klick,*** ASI Advanced Semiconductor Instruments, Germany **INVITED**

The increased demand for characterization of plasmas under industrial conditions was mainly driven by the complexity of industrial plasma processes. The interaction of the plasma with the surface determines the quality and performance of the electronic devices on the substrate. Hence a good understanding of the key mechanisms of plasma excitation is required. To address the heating mechanisms of the electrons, knowledge of the electron energy distribution function (EEDF) is imperative - or at least parameters derived from its moments, as the collision rate of electrons for momentum transfer or, taking into account stochastic heating, too, the effective collision rate. Especially the last property, the thermalisation of the electric field's energy, can only be accessed by measuring the self-excited resonance of the electrons in RF plasmas(SEERS, last 's' for spectroscopy). SEERS utilizes nonlinear and resonance effects in the plasma in the sheath and the plasma body leading to a non-sinusoidal RF current. Thus SEERS uses nonlinear and RF effects which usually disturb or even avoid the application of classical methods as Langmuir probes in RF plasmas. The measurement principle is based on a passive RF current sensor and a discharge model involves the effects mentioned above and can be used in reactive plasmas without any restriction. SEERS data based of ten thousands of wafers for different processes show the high efficiency of this approach, in particular under industrial conditions as polymers on chamber wall and sensor itself and undesired effects as arcing at the chamber wall. On the other hand, basic experiments show that plasma physical mechanisms as skin effect in the plasma, ohmic and stochastic heating of electrons can be qualitatively observed in productions tools which are necessary for the understanding and development of process and new chamber types.

3:20pm **PS-ThA5 Study of Pulsed Plasma Doping System by Time-resolved Ion Mass-energy Spectrometry*, L. Godet,*** *B.-W. Koo,* VSEA, France*; G. Cartry, C. Cardinaud,* Institut des Materiaux de Nantes, France*; Z. Fang,* VSEA, France*; A. Grouillet, D. Lenoble,* STMicroelectronics, France

Pulsed PLAsma Doping (P@super 2@LAD) continues to emerge as a viable alternative technique to ion implantation for advanced semiconductor devices,@footnote 1@ since it is capable of delivering high rate dose at ultra low energy (100V to 10kV applied voltage) giving rise to ultra shallow junctions.@footnote 2@ In P@super 2@LAD, plasma is ignited and extinguished with each negative voltage pulse applied to the wafer. During the pulse, positive ions are accelerated across the sheath and implanted within the wafer. This process was studied using a Hiden EQP mass spectrometer implemented within the pulsed electrode, focussing principally on BF@sub 3@ plasma for different implant process conditions. Previous work, employing time averaged mass spectrometry,@footnote 3@ indicated that BF@sub 2@@super +@ is the dominant ion species in the BF@sub 3@ plasmas, and BF@super +@ is the second most abundant ion species. Due to the short (10 - 50µs) pulse length and low repetition rate (100 - 5000Hz) of the P@super 2@LAD process, the time between the pulses is relatively long so that a time-resolved ion mass-energy measurement is necessary to follow the process before, during and after the pulse period. Time resolved Langmuir probe measurements@footnote 4@ have shown the presence of a cold plasma during the afterglow which may be a key parameter for understanding and controlling the entire process (i.e. charge neutralization, etching, deposition). In this paper, we present time-resolved mass spectrometry data allowing a more complete understanding of BF@sub 3@ P@super 2@LAD processing including the role of negative charges during the afterglow period. @FootnoteText@@footnote 1@D.Lenoble et al., Ion Implantation Technology 2002, Taos, USA.@Footnote 2@R.B. Liebert et al., Ion Implantation Technology 2000, Alpbach, Austria.@footnote 3@B.W. Koo, Z.Fang, S.Felch, Ion Implantation Technology 2000, Alpbach, Austria@footnote 4@Z.Fang et al., Ion Implantation Technology 2002, Taos, US.

3:40pm **PS-ThA6 Gas-Phase Diagnostics and Mechanisms of Energy Transfer in O@sub 2@/NH@sub 3@ Plasmas*, K.R. Kull,*** *D.S. Wavhal, E.R. Fisher,* Colorado State University

Hydrophobic polymeric membranes are used extensively throughout a variety of industrial and biomedical processes. To improve the separation performance, hydrophilic surface modification is required. In this work, we have studied hydrophilic modification of asymmetric porous polyethersulfone membranes using N@sub 2@, NH@sub 3@ and O@sub 2@/NH@sub 3@ plasma treatments. Membrane treatments using 100% N@sub 2@ or 100% NH@sub 3@ plasmas yielded incomplete hydrophilic treatments. In contrast, the O@sub 2@/NH@sub 3@ plasma treatment produced a hydrophilic membrane that retained its hydrophilicity over an extended period after treatment. Examination of the plasma gas-phase composition using optical emission spectroscopy and mass spectrometry revealed the NH radical is present in both the 100% NH@sub 3@ and the O@sub 2@/NH@sub 3@ systems, whereas the OH radical is only observed in the O@sub 2@/NH@sub 3@ plasma. Evidence from other plasma modification systems indicates the OH radical is critical for permanent hydrophilicity using non-polymerizing plasma treatments of polymeric membrane treatments.@footnote 1@ To better understand the chemistry that occurs during these processes, we have used our laser-induced fluorescence based imaging technique to characterize the relative densities of NH and OH and their energy partitioning in these plasmas. The relative densities of both radicals are dependent on the applied rf power (P) and feed gas composition dependent. Interestingly, the rotational temperatures of both species appear nearly independent of P. Surface interactions of NH and OH with membranes, as well as their translational temperatures in the plasma, will be presented and compared to earlier results for NH@sub 2@ radicals in NH@sub 3@ plasma.@footnote 2@ Implications for plasma modification mechanisms will also be discussed. @FootnoteText@@footnote 1@ M. L. Steen, et al., Langmuir 17, 2001, 8156.@footnote 2@ C. I. Butoi, et al.,J. Phys. Chem. B 105, 2001, 5957.

4:00pm **PS-ThA7 The Study of Ion Drift Velocities and Instabilities in Presheaths in Two Ion Species Plasmas***, **X Wang**, E. Ko, N. Hershkowitz,* University of Wisconsin, Madison

The presheath is a region of weak electric field that accelerates ions into the sheath at the plasma boundary. The experiments were performed in multi-dipole DC plasmas with He-Ar gas mixtures (P@sub total@ @>=@ 1.0mTorr, n@sub e@ @>=@ 1x10@super 9@cm@super -3@, T@sub e@ @<=@ 2eV). The concentration of ion species in the two ion species plasmas was determined by measuring ion acoustic wave phase velocity and electron temperature in the bulk region.@footnote 1@ To measure ion drift velocities in the presheath, an ion acoustic wave was launched by both a continuous sinusoidal wave and a pulse, and detected by a cylindrical probe with a boxcar averager. Ion drift velocities were measured in pure Ar plasma. Based on the dispersion relation in the presheath for multi-ion species plasma and phase velocity measurements in He-Ar plasma, the relationship between Ar and He ion drift velocities was determined. Using Ar ion drift velocities from LIF data,@footnote 2@ the He ion drift velocities were determined. In two ion species plasmas, instabilities can be excited by the two ion streams with different drifting velocities that are created in the presheath. Instabilities changing with different partial pressure, positions and discharge current were observed by using a cylindrical probe biased to collect either ion saturation current or electron saturation current and a spectrum analyzer. The frequency of instabilities is ~1.0MHz and wavelength is ~5.0mm compared to ~3.0cm of presheath length. ** Work supported by US DOE grant DE-FG02-97ER54437. @FootnoteText@@footnote 1@A. M. Hala and N. Hershkowitz, Rev. Sci. Instrum. 72, 2279 (2001).@footnote 2@G. D. Severn, Xu Wang, Eunsuk Ko and N. Hershkowitz, Phys. Rev. Lett. 90, 145001 (2003).

4:20pm **PS-ThA8 Ion Collection by a Mach Probe in Flowing Unmagnetized Plasma***, **E. Ko**, X Wang, N. Hershkowitz,* University of Wisconsin, Madison

The measurement of plasma flow along the presheath in unmagnetized plasma is performed using a spherical Mach probe. Ion flow velocity in unmagnetized plasma is examined experimentally and compared to a recent numerical simulation by Hutchinson.@footnote 1@ The spherical Mach probe, which was inspired by Hutchinson's theoretical model, consists of a conducting sphere that has two conducting probe tips, insulated from the sphere and mounted at @theta@ = 0° and 180° with respect to the flow direction. Although the simulation included T@sub i@ = 0.1T@sub e@ ~ 10T@sub e@ and flow velocity v@sub f@ = 0 ~ 3c@sub s@, where c@sub s@ is the sound speed, the laboratory plasma in the presheath was limited to T@sub i@ < 0.1T@sub e@ and v@sub f@ @<=@ 1.0 c@sub s@. The experiment is performed in a multi-dipole DC plasma with Argon pressure ranging from 0.1 to 3mTorr. The upstream and downstream probe tips and the surface of the sphere were simultaneously biased to minimize the probe edge effects, and to obtain a much closer condition to the simulation. This work also examines a previous experiment@footnote 2@ that used the Hudis and Lidsky formula,@footnote 3@ which though shown to be invalid@footnote 4@ still attained results in good agreement with the simulation. *Work Supported by US DOE grant DE-FG02-97ER 54437. @FootnoteText@ @footnote 1@ I. H. Hutchinson, Plasma Phys. Control. Fusion, 44 1953 (2002)@footnote 2@ L. Oksuz, M. A. Khedr, and N. Hershkowitz, Phys. Plasmas, 8 1729 (2001)@footnote 3@ M. Hudis and L. M. Lidsky, J. Appl. Phys., 41 5011 (1970)@footnote 4@ I. H. Hutchinson, Phys. Plasmas, 9 1832 (2002).

4:40pm **PS-ThA9 Novel Plasma Monitoring Scheme by Surface Wave Probe***, **H. Sugai**, H. Kawai,* Nagoya University, Japan*; K. Nakamura,* Chubu University, Japan

A novel and simple technique for measuring the electron density@footnote 1@ and temperature@footnote 2@ of plasma reactors using a surface wave probe (SW probe) is presented. This probe is also called plasma absorption probe as it is based on absorption of surface waves by plasma. The SW probe enables us to measure the local absolute electron density even when the probe surface is soiled with processing plasmas. The technique relies on absorption of surface waves resonantly excited around the probe head at critical frequencies which mainly depend on the electron density. The probe consists of a small antenna connected with a coaxial cable and is enclosed in a tube of dielectric constant @epsilon@@sub d@ inserted in a plasma of electron plasma frequency @omega@@sub p@. A network analyzer feeds a rf signal to the antenna and displays the frequency dependence of the power absorption. The absorption is observed at frequencies slightly above the surface wave resonance frequency, @omega@@sub p@/ (1+ @epsilon@@sub d@),@footnote 1,2@ which allows us to determine the electron density. Use of a pair of SW probes of different sizes enables measurements of both electron temperature and electron density. The measurements were made in a wide range of electron density (10@super 8@ - 10@super 13@ cm@super -3@) and gas pressure (10 mTorr -10 Torr) with high resolutions of space (@DELTA@x~2 mm) and time (@DELTA@t~1 µs). Time-variation of a few percents of electron density is detectable. @FootnoteText@ @footnote 1@H. Kokura, K. Nakamura, I. Ghanashev and H. Sugai, Jpn. J. Appl. Phys. 38, 5262 (1999)@footnote 2@K. Nakamura, M. Ohata and H. Sugai:, J. Vac. Sci. Technol. A21, 325 (2003).

5:00pm **PS-ThA10 Measurement of Absolute Radical and Metastable Species Densities in O@sub 2@ and N@sub 2@ Plasmas using Modulated Beam Appearance Ionization Mass Spectrometry***, S. Agarwal,* University of California, Santa Barbara*; G.W.W. Quax, B. Hoex, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands*; D. Madoudas,* University of Massachusetts, Amherst*; **E.S. Aydil**,* University of California, Santa Barbara

Measurement of radical densities in an electrical gas discharge is important for understanding and improving plasma etching and plasma-assisted deposition processes. We have designed, developed and demonstrated an experimental apparatus for measuring the density of the radicals and electronically excited molecular species in a plasma using modulated beam line-of-sight appearance ionization mass spectrometry (LOS-AIMS). In LOS-AIMS, the species in the plasma are sampled through an aperture on the substrate platen and detected using a quadrupole mass spectrometer (QMS) placed in line-of-sight with this aperture in a three-stage differentially pumped vacuum chamber. Although LOS-AIMS is a versatile tool for measuring absolute radical densities, we show that it requires careful vacuum design and calibration which should take into account various sources of error such as the contribution to the QMS signal from the background gases, the ion mass-to-charge ratio dependence in the sensitivity of the QMS, and space-charge limitations in the QMS ionizer. In addition, collisions within the extracted molecular beam must be taken into account for higher operating pressures in the plasma chamber. Careful consideration of these effects and modulation of the sampled radical beam with a chopper allows the determination of the absolute radical densities, parent molecule concentrations, and the neutral gas temperature near the substrate plane. Specifically, we have measured densities of O and Ar atoms and O@sub 2@ molecules in O@sub 2@/Ar plasma mixtures and N atoms and metastable N@sub 2@ molecules in N@sub 2@ plasmas. In addition, we find that at low pressures, the O@sub 2@ translational temperature is higher than that for Ar. We attribute this difference in Ar and O@sub 2@ translational temperatures to hot O@sub 2@ molecules that are created by O-O recombination reactions on the walls of the plasma chamber which do not equilibrate effectively with Ar atoms at lower pressures.

Semiconductors
Room 321/322 - Session SC+MI-ThA

Ferromagnetic and Dilute Magnetic Semiconductors

Moderator: S.C. Erwin, Naval Research Laboratory

2:00pm **SC+MI-ThA1 Electronic Structure Theory of Mn-doped GaAs***, A. Zunger,* National Renewable Energy Laboratory*; **P. Mahadevan**,* National Renewable Energy Laboratory, India **INVITED**

(1) Orientation dependent ferromagnetism: Models involving the interaction between the transition metal spin and free carriers have conventionally been used to describe ferromagnetism in dilute magnetic semiconductors. In contrast to the expectations of such a model, we find that the GGA calculated energy of the ferromagnetic state for two 3d transition metal (TM) impurities in GaAs show a strong dependence on the crystallographic orientation of the TM pairs. For Mn in GaAs, the ferromagnetic state is strongly stabilized for pairs in the direction. The stabilization is greatest along the directions for which the p-d hybridization matrix elements coupling the Mn atoms are the largest. (2) Interstitial-substitutional complexes: Examining the formation energy of Mn at various lattice sites, we find that Mn at an interstitial (Mn(i)) site could have comparable energy to Mn at a Ga site (Mn(Ga)). Under epitaxial growth conditions, the solubility of both substitutional and interstitial Mn is strongly enhanced over what is possible under bulk growth conditions. The high solubility opens the possibility of Mn atoms forming small clusters. While isolated Mn(i) are hole killers (donors), and should therefore destroy ferromagnetism, complexes such as Mn(Ga)-Mn(i)-Mn(Ga) are found to be more stable than complexes involving Mn(Ga)-Mn(Ga)-Mn(Ga). The former complexes exhibit partial or total quenching of holes, yet Mn(i) in these complexes provides a channel for a ferromagnetic arrangement of the spins on the two Mn(Ga). This suggests that ferromagnetism in Mn doped GaAs arises both from holes due to isolated Mn(Ga)as well as from strongly Coulomb stabilized Mn(Ga)-Mn(i)-Mn(Ga) clusters.

2:40pm **SC+MI-ThA3 Microscopic Valence Band Structure Near Mn and Local Magnetism in Ga@sub 1-x@Mn@sub x@As***, **J. Tang**, M.E. Flatté,* University of Iowa

The microscopic spin-dependent disturbances to the valence band near Mn atoms in Ga@sub 1-x@Mn@sub x@As and the indirect Mn-Mn interaction are studied. The GaAs host is described by a multiband tight-binding Hamiltonian that incorporates spin-orbit interaction, and the Mn impurity is described by a local p-d hybridization and on-site potential. Local spin-polarized resonances within the valence band that significantly enhance the LDOS near the band edge. The quantitative enhancement we calculate is consistent with angle-resolved photoemission and interband magnetoabsorption measurements. We present the hybridization energy for two parallel Mn magnetic moments. The splitting of the acceptor level is highly anisotropic and exceeds 10 meV even if the Mn impurities are separated by as many as 20 Å. This suggests that scanning tunneling spectroscopy can probe the Mn spin orientation and measure the Mn-Mn interaction energy as a function of distance. This work was supported by the ARO MURI DAAD19-01-1-0541.

3:00pm **SC+MI-ThA4 Cross-sectional STM Study of Mn-doped GaAs****, **J.M. Sullivan**,* Naval Research Laboratory*; G.I. Boishin,* Naval Research Laboratory and Nova Research Inc.*; S.C. Erwin, L.J. Whitman, A.T. Hanbicki, B.T. Jonker,* Naval Research Laboratory

When doped with Mn, GaAs exhibits long-range ferromagnetic order at temperatures up to ~150K. It is generally believed that ferromagnetism in GaMnAs is mediated by holes created by the substitution of Mn for Ga. Recent studies have suggested that a substantial amount of Mn is also present at interstitial sites, where Mn acts as a donor, partially compensating the holes and reducing the Curie temperature. To characterize the location and electronic configuration of Mn in device-quality Mn-doped GaAs, we have combined the complementary techniques of cross-sectional scanning tunneling microscopy (XSTM) and density functional theory (DFT). XSTM was used to atomically characterize a GaMnAs film across a single {110} cleavage plane. We used DFT to help interpret our images by theoretically simulating the XSTM image of Mn near the GaAs(110) surface. We considered Mn occurring as substitutionals, interstitials, and substitutional-interstitial complexes; a range of physically plausible charge states was considered for each. Defects in the first four layers near the surface were studied. STM filled-state images were simulated at the level of Tersoff-Hamann theory by integrating the local density of states over an energy window given by the experimental bias voltage. Thus, these complementary techniques allow us to identify Mn-related defects in the GaAs zinc-blende structure. *Supported by the US Office of Naval Research and the Defense Advanced Research Projects Agency.

3:20pm **SC+MI-ThA5 Thin Film Mn/GaAs(100) Interfacial Reactions***, **J.L. Hilton**, B.D. Schultz, C.J. Palmstrom,* University of Minnesota

Although a number of ferromagnetic Mn-based compounds have been epitaxially grown on GaAs, there is a lack of detailed understanding of the interfacial interactions and their effects on spin transport. To date, no detailed Mn/GaAs interfacial reaction studies have been reported. In this study, the interfacial reactions of Mn thin films deposited in-situ on molecular beam epitaxy (MBE)-grown GaAs(100) epilayers are studied. Initial studies involved characterization of ex-situ post-growth anneals of Al(50Å)/Mn(2000Å)/GaAs(100) structures at temperatures of 200, 300, 350, 400, and 500°C for times ranging from 1-30 hours. Prior to annealing, the Mn films on GaAs appear from reflection high-energy electron diffraction and x-ray diffraction (XRD) to be polycrystalline, and Rutherford backscattering (RBS) indicates that no extensive interfacial reactions occur during growth. After annealing at temperatures higher than 200°C, XRD diffraction peaks corresponding to a tetragonal Mn@sub 2@As-like phase and a tetragonal MnGa-like phase are observed. RBS data at both normal and grazing geometries indicate significant Mn-Ga-As reactions occur during anneals in excess of 200°C with the formation of a region with Mn@sub 0.6@Ga@sub 0.2@As@sub 0.2@ composition. Higher temperature anneals result in the dissociation of this region into a MnGa-like region near the sample surface and a Mn@sub 2@As-like region near the GaAs substrate. RBS measurements of the reaction layer thickness for various annealing times at 300°C indicate the interfacial reactions are diffusion controlled. Results from RBS, XRD, and transmission electron microscopy of Al/Mn/GaAs structures will be combined with results from in-situ scanning tunneling microscopy and x-ray photoelectron spectroscopy of 0-20 monolayer Mn coverage studies to determine the nature and behavior of the reactions between Mn, Ga, and As at the metal-semiconductor interface. Supported by ONR, DARPA, and NSF.

3:40pm **SC+MI-ThA6 Cross Sectional Scanning Tunneling Microscopy Studies of Mn Segregation in Ga1-xMnxAs Films***, **J.N. Gleason**, M.E. Hjelmstad, R.S. Goldman, S. Fathpour, S. Ghosh, P.K. Bhattacharya,* University of Michigan

Ga@sub 1-X@Mn@sub X@As is a promising candidate for spintronic applications compatible with conventional GaAs technologies. Theoretical studies have predicted that an increase in disorder of Mn atom positions will lead to a significant increase in the Curie Temperature.@footnote 1@ Therefore, we have investigated the effects of Mn segregation in Ga@sub 1-X@Mn@sub X@As grown by low temperature molecular beam epitaxy using ultra high vacuum cross-sectional scanning tunneling microscopy (XSTM). The heterostructures consist of 10-period superlattices of alternating Ga@sub 1-X@Mn@sub X@As (x=0.5, 2.5 and 5.0%) and Al@sub 0.20@Ga@sub 0.80@As layers, sandwiched between thick p+ GaAs layers. Constant current XSTM images reveal nanometer-sized regions with higher apparent tip height, presumably related to a local increase in the density of states associated with the presence of Mn atoms in Ga@sub 1-X@Mn@sub X@As. In the x=0.5% films, the nanometer-sized bright regions appear relatively dispersed, with ~ 5nm separation. For the x=2.5% and 5% films, agglomeration of the nanometer-sized bright regions is observed, and apparently increases with increasing Mn composition. The apparent Mn clustering does not appear to be affected by the presence of adjacent Al@sub 0.20@Ga@sub 0.80@As superlattices, indicating that any local misfit stress does not act as a sink for Mn accumulation. The apparent Mn clustering is likely due to a long-range attractive potential between Mn atoms, and may be associated with charge carrier screening, similar to earlier GaAs:Zn studies.@footnote 2@ As the Mn composition increases, the free carrier concentration increases, and the screening length decreases. This would in turn lead to a lower self-repulsion of Mn atoms, and an increase in Mn clustering. We will also discuss the effects of annealing on Mn segregation in Ga@sub 1-X@Mn@sub X@As. @FootnoteText@ @footnote 1@M.Berciu et al., Phys. Rev. Lett. 87, 107203 (2001).@footnote 2@P. Ebert et al., Phys. Rev. Lett. 83, 757 (1999).

4:00pm **SC+MI-ThA7 Manipulation of Ferromagnetism by Light in III-V-based Magnetic Alloy Semiconductors and Related Nanostructures***, **H. Munekata**,* Tokyo Institute of Technology, Japan **INVITED**

Because of moderate carrier concentrations (10@super 15@ - 10@super 20@ cm@super -3@), semiconductors and associated hetero- and nano-structures are suitable electronic systems to control both charges and spins by electromagnetic means. Particularly in magnetic semiconductors, manipulation of carrier spins can result in the cooperative and amplified effects through the spin exchange interaction between carrier spin s and local spin S. Those effects would open ways to develop multi-functional devices with low power consumption. One of such precursory demonstrations is the manipulation of magnetism with light in ferromagnetic III-V alloy semiconductors (In,Mn)As and (Ga,Mn)As. In this paper, we discuss the experimental results on (1) photo-generated carrier-induced ferromagnetism in p-(In,Mn)As/GaSb heterostructures, including ultrafast magnetic softening achieved in collaboration with Kono's group in Rice University, (2) collective rotation of ferromagnetically coupled Mn spins and its picosecond spin dynamics in ferromagnetic p-(Ga,Mn)As caused by the illumination with circularly polarized light without a magnetic field (optical spin injection), and (3) light-induced change in magnetic susceptibility at room temperature in GaAs-Fe composite structures, added with the demonstration of optically-controlled micro-cantilevers by Shinji's group of Tokyo Institute of Technology. Works towards room temperature ferromagnetism by other groups will also be reviewed. This work is supported in part by "Semiconductor Nanospintronics (02-)" of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

4:40pm **SC+MI-ThA9 Growth of (Ga,Mn)N: a Diluted Magnetic Semiconductor by Chemical Beam Epitaxy (CBE)**, ***A. Carreno***, *C. Boney, A. Bensaoula,* The University of Houston

The GaN material system is a very promising candidate for the realization of electronic devices based on dilute magnetic semiconductor (DMS) films. The incentive behind DMS materials is the potential to form high-density magnetic memory integrated ICs, semiconductor-based magnetic sensors, magneto-optical devices for communications systems, and other spin-based and photonic-based applications. Many reports have indicated that high doping levels of Mn in GaN lead to ferromagnetic materials with Curie temperatures at or above room temperature. To date (Ga,Mn)N has been fabricated by several epitaxial and non-epitaxial techniques. However, to our knowledge, we are the first to report the epitaxial growth of (Ga,Mn)N by CBE. (Ga,Mn)N has been grown on sapphire substrates using TEG, NH3, and solid Mn as precursors. Very smooth GaMnN films exhibiting bright 2D RHEED patterns have been obtained with Mn concentrations between 0.5-2.0% as determined by EPMA and XPS. XPS depth profiling verifies that the Mn is of uniform concentration throughout the films. In addition to RHEED, the CBE chamber employs two Time of Flight Ion Scattering Spectroscopy techniques, Direct Recoil Spectroscopy (DRS) and Mass Spectroscopy of Recoiled Ions (MSRI). These TOF techniques are used as an in-situ, real time analytical process which allows the surface composition information of film components and impurities to be determined as well as analyzing the structural characteristics based on changes in the relative signal levels with azimuthal rotation of the sample. In these ways DRS/MSRI has been used to detect the incorporation of Mn into the GaN matrix during film growth and from azimuthal data extract the surface periodicity which allows construction of surface structure models for GaN and (Ga,Mn)N surfaces. In addition to available Raman and photoluminescence data, characterization of magnetic properties of the (Ga,Mn)N films is currently under way and will be reported.

Surface Science
Room 327 - Session SS+OM-ThA

Self-Assembled Monolayers
Moderator: L. Hanley, University of Illinois at Chicago

2:00pm **SS+OM-ThA1 Non-dissociative Chemisorption of Methanethiol on Ag(110)- A Critical Result for Self-assembled Layer Formation**, ***J.-G. Lee***, *J. Lee, J.T. Yates, Jr.,* University of Pittsburgh

Three definitive experiments have been performed which show that CH@sub 3@SH does not dissociate upon chemisorption on clean Ag(110). On the clean Ag(110) surface, the adsorption in the first layer occurs at 0.5 ML, producing a (2x1) LEED structure. The undissociated molecule desorbs at ~140 K. Using a 50%-50% mixture of CH@sub 3@SD and CD@sub 3@SH, no evidence of S-H or S-D bond scission by isotope mixing between these molecules is found upon desorption. And finally, when the CH@sub 3@SH molecule is incident on clean Ag(110) surface in the temperature range from 240 K to 400 K, less than 1% of the incident molecules dissociate to produce adsorbed S. In contrast, when a sulfur-poisoned Ag(110) surface is exposed to CH@sub 3@SH, autocatalytic dissociation occurs below 240 K, producing CH@sub 4@, H@sub 2@S and adsorbed S atoms. These results are in striking contrast to the behavior of Cu(110) where CH@sub 3@SH dissociation occurs below 320 K leaving S. These results are of importance in understanding the self assembly of alkanethiol layers on silver where it has been commonly assumed that S-H bond scission occurs at room temperature. This work was supported by DOE-BES.

2:20pm **SS+OM-ThA2 Spectroelectrochemical Studies of Self-Assembled Monolayers of Thiols**, ***I. Thom,*** St Andrews University, Scotland*; M. Buck,* St Andrews University, Scotland, UK

Thiol SAMs provide a convenient route to modify electrodes and to serve as templates for directing electrochemical processes. Towards a rational design of thiol SAMs for electrochemical applications the electrochemically induced desorption and adsorption of thiols are studied in-situ using the combination of electrochemistry and non-linear optical techniques. Potential dependent capacitive and faradaic currents are correlated with the second harmonic signal which probes the S-Au bond formation. Studies of alkane thiols and biphenyl based thiols reveal that this correlation is strongly dependent on the electrolyte, i.e. both the penetration of ions into the layer and the desorption mechanism are affected by the electrolyte. In the ethanol case, a change in the desorption mechanism during multiple potential cycling is observed. While the current continuously decreases with increasing number of cycles, the change of the SHG signal remains essentially unaltered and indicates a change in the faradaic process. This change is explained by a transition from thiolate to disulfide formation upon the desorption of thiols.

2:40pm **SS+OM-ThA3 Photoemission Study of Dodecanethiol on Ag(111) and Au(111)**, ***H. Geisler,*** Xavier University*; J.M. Burst, S.N. Thornburg, C.A. Ventrice,* University of New Orleans*; Y. Losovyj, P.T. Sprunger,* Louisiana State University

Self-assembled monolayers show great promise for use in many technological applications such as in chemical and biological sensing, chemical resists in lithography, corrosion protection, and molecular electronics. However, there are several fundamental properties of these systems that are not well understood. For instance, the adsorption of alkanethiols on Au(111) results in a (@sr@3 x @sr@3)R30° overlayer; whereas, adsorption on Ag(111) results in an incommensurate overlayer even though Au and Ag are isoelectronic and are lattice matched to 0.3%. Although there have been several studies of the geometric structure of thiols on Au(111) and to a lesser extent on Ag(111), there have been very few studies of the electronic structure of these films. Angle-resolved ultra-violet photoelectron spectroscopy studies of the growth of dodecanethiol on Au(111) and Ag(111) have been performed in UHV by vapor deposition. By using vapor deposition, the submonolayer striped phase, full monolayer upright phase, and the multilayer phase can be studied. The monolayer coverage of thiol results in peaks at binding energies of 20 eV, 14 eV, 10 eV, and 7 eV. By comparing the dispersion of the Ag(111) d-band emission for the clean surface to the surface after deposition of a monolayer of thiol, it was determined that there is a loss of order of the Ag surface atoms. Similar measurements for Au(111) reveal that the Au(111) surface remains in an ordered state. This result provides a mechanism for the different adsorption geo metries of alkanethiols on Au(111) and Ag(111). Since there is no ordered template of Ag atoms after thiol adsorption, the van der Waals interaction between the CH@sub 2@ chains dominates, resulting in an ordered, incommensurate overlayer. Measurements of the thiols in the multilayer regime reveal a uniform shift of the thiol peaks to higher binding energy, presumably due to sample charging effects from the insulating nature of these films at 150 K.

3:00pm **SS+OM-ThA4 Short Aromatic Thiols on Cu(111): Initial Adsorption Configuration and the Formation of an Ordered Monolayer**, ***B.V. Rao***, *K.-Y. Kwon, J. Zhang, A. Liu, L. Bartels,* University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial orientation of di-chloro-thio-phenol (DCTP) and S-phenyl-thio-acetate (SPTA), a thio-phenol whose sulfur-bound hydrogen is replaced by an acetyl group. The latter is a common practice in order to protect the thiol group during the synthesis of poly-functional organic molecules. This poster compares the impact of the acetyl substitution on the initial steps of the molecules interaction with a Cu(111) surface. DCTP adsorbs at low temperatures (15K) with the sulfur atom at an on-top site and is able to rotate around it. This results in the observation of a flower shaped species on STM images. There are two chiral adsorption configurations which can be distinguished by STM. In contrast, SPTA adsorbs in a position in which both the phenyl and the second carbon of the acetyl group point upward resulting in a double protrusion in STM images. While tunneling electrons of less than 500meV of either bias can cause the abstraction of hydrogen from the thiol group of DCTP, SPTA is stable beyond 1V in tunneling bias. Increasing the coverage by adsorption at nitrogen temperatures, DCTP forms an ordered monolayer consisting of dimers, both of which have the phenyl group lying flat on the surface. The formation of extended islands of the ordered monolayer requires annealing of the sample beyond liquid nitrogen temepratures. Further increase of the coverage results in pronounced protrusion at defect sites of the ordered monolayer, which we interpret as molecules that point the phenyl ring away from the surface. STM resolution on a film consisting entirely of such species is poor; however, it can confirm that an ordered film is formed.

3:20pm **SS+OM-ThA5 Balance of Structure-building Forces in Monomolecular Films: Terphenyl-substituted Alkanethiolates on Noble Metal Substrates***, **A. Shaporenko,*** Universität Heidelberg, Germany*; M. Brunnbauer, A. Terfort,* Universität Hamburg, Germany*; L.S.O. Johansson,* Karlstad University, Sweden*; M. Zharnikov,* Universität Heidelberg, Germany

The design of versatile monomolecular films relies on detailed knowledge of basic rules governing the packing density and exact arrangement of the molecular constituents in these systems. The most important issue in this connection is the understanding of the interplay between the structure-building headgroup-substrate and intermolecular interactions. To address this issue we have studied self-assembled monolayers (SAM) formed from terphenyl-substituted alkanethiols C@sub 6@H@sub 5@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (TPn, n = 1-6) on Au and Ag substrates. In these systems, strongly interacting terphenyl backbones force a dense molecular packing, which does not fit to the geometry of the metal-S-C bond at certain length of the aliphatic part. We used several complementary experimental techniques such as x-ray photoelectron spectroscopy (XPS), high-resolution XPS, near edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, ellipsometry, and water contact angle measurements to characterize the TPn SAMs. Odd-even changes in the packing density, the tilt angle of the terphenyl moieties, etc have been observed and considered in detail. There changes could be clear correlated with the geometry of the metal-S-C bond, which assumed to be different on Au and Ag. The results imply a predominant role of the headgroup-substrate interaction in the balance of structure-building forces in the aliphatic SAMs and give a practical tool for the fabrication of monomolecular films with desired properties.

3:40pm **SS+OM-ThA6 Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Based Thiol SAMs: A Combined STM and LEED Study***, **P. Cyganik**, M. Buck,* University of StAndrews, UK*; W. Azzam, G. Witte, Ch. Woell,* Ruhr Universitaet Bochum, Germany

Self-assembled monolayers (SAMs) of thiols are promising candidates for nanolithographic applications. Towards a rational design and control down to the length scale reaching molecular dimensions we study SAMs a particular type of thiols which is characterized by a biphenyl unit and an alkane spacer of varying length (CH@sub 3@ (C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5). SAMs adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Our results demonstrate that preparation at elevated temperature results in highly ordered layers with large domains. Whereas the (2@sr@3x@sr@3) structure of the BP3 and BP5 SAMs is similar to that reported previously for other aromatic thiols, SAMs made from BP2 and BP4 exhibit a very different structure. A (5@sr@3x3)rect unit cell containing 8 molecules is found which corresponds to a packing density reduced by 25 % compared to BP3 and BP5. The odd-even effect observed in the molecularly resolved STM images of BPn, therefore, confirms the pronounced influence of the spacer chain on the structure of these biphenyl based SAMs.

4:00pm **SS+OM-ThA7 Mechanism of Nanomolecular Motion Induced by Polarity Change of the Electric Field in the Self-Assembled Monolayers***, **T. Ishida**,* AIST, Japan*; H. Fukushima,* TPRC, SEIKO EPSON Corporation, Japan*; T. Tamaki,* AIST, Japan

We have successfully observed the nanoscale molecular motion induced by polarity change of the electric field by STM, when small amounts of asymmetrical disulfides containing mobile terphenyl moieties were embedded into pre-assembled dodecanethiol SAMs.@footnote 1@ Taking the direction of the dipole moment into account, the thickness of embedded molecular protrusions became larger at the positive bias.@footnote 2@ However, STM experiments revealed that the thickness of the molecular protrusions was larger at the negative bias, contrary to this prediction. STS revealed the higher rectification property at the area of the terphenyl terminated monolayer where also showed the higher electrical conduction at the negative tip bias compared to positive one. The higher electrical conduction at the negative tip bias was likely to retract the STM tip, showing the apparent nanomolecular motion by the polarity change. Next, we investigated the relationship between the higher rectification property and real conformational change. When symmetric disulfide which is not easy to change molecular conformation are embedded into pre-assembled dodecanethiol SAMs for the comparison, both the rectification property and apparent molecular motion were not observed. In addition, when the STM tip was directly attached to asymmetric disulfides, rectification property was not observed in STS. Thus, we concluded that the conformational change is the influential factor to induce the higher rectification property. @FootnoteText@@footnote 1@ T. Ishida, H. Fukushima, T. Tamaki and H. Tokumoto, Jpn J. Appl. Phys. in press. @footnote 2@ H. Fukushima and T. Tamaki J. Phys. Chem. B106 7142(2002).

4:20pm **SS+OM-ThA8 The Reaction of Tetrakis(dimethylamino)titanium with Self-Assembled Monolayers Possessing -OH, -NH@sub2@ and -CH@sub3@ Terminal Groups***, **A.S. Killampalli**, P.F. Ma, J.R. Engstrom,* Cornell University

Organic materials are playing an increasing role in modern microelectronic devices--beyond their traditional role as photoresists. New areas include their application as low-@kappa@ dielectrics. Interfaces between organics and metals are also of interest, including in fields such as molecular electronics. To date, almost all work concerning the formation of organic-metal interfaces on pre-existing organic layers has involved metal thin films deposited by (elemental) evaporation. In the work described here we examine an alternative approach to the formation of inorganic-organic interfaces, namely, via the use of organo-transition metal complexes. Here we study the reaction of the titanium precursor, tetrakis(dimethylamino)titanium (TDMAT), with model organic surfaces [self-assembled monolayers (SAMs) terminated by -OH, -NH@sub2@ and -CH@sub3@ groups] using X-ray photoelectron spectroscopy (XPS). Trichlorosilane self-assembled monolayers have been formed on SiO@sub2@ surfaces that, in selected cases, were subjected to additional chemical conversion steps. Prior to insertion into vacuum these layers were characterized using AFM, ellipsometry and contact angle measurements. Exposure of these surfaces to TDMAT was carried out in a custom-designed ultrahigh vacuum chamber equipped with facilities for XPS and quadrupole mass spectrometry (QMS). In selected cases, angle resolved XPS (ARXPS) was used to probe the spatial extent of reaction of the precursor. Among the SAM surfaces studied, the -OH terminated SAM exhibits the highest reactivity, followed by the -NH@sub2@ and -CH@sub3@ terminated SAMs, in that order. ARXPS results reveal that TDMAT reacts primarily at the top of the -OH terminated SAM, while the reaction on the -CH@sub3@ terminated SAM is actually with underlying reactive regions at the SAM/SiO@sub2@ interface. Additional results concerning the reaction of TDMAT with these monolayers, including modeling of the adsorption kinetics, will be presented.

4:40pm **SS+OM-ThA9 Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using Near-Edge X-ray Absorption Fine Structure***, **T.M. Willey**[1],* University of California, Davis and Lawrence Livermore National Lab*; A.L. Vance, T. van Buuren, C. Bostedt, B.R. Hart, R.W. Meulenberg, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Laboratory*; C.S. Fadley,* Lawrence Berkeley National Laboratory

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure reorientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH@sub 2@)@sub 15@COOH) a long-chain molecule with strong

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

chain-chain interactions and thioctic acid (S@sub 2@(CH@sub 2@)@sub 2@CH(CH@sub 2@)@sub 4@COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO- vs. COOH.) In addition, we will present initial results on ordering and attachment in amino-terminated alkanethiols on gold, and preliminary results using functional groups in switching interlocking molecules on surfaces.

5:00pm **SS+OM-ThA10 Self Assembled Monolayers on Microelectronic Copper Thin Film for Prevention of Corrosion*, Y.S. Tan,*** National University of Singapore, Singapore*; M.P. Srinivasan, S.O. Pehkonen,* National University of Singapore*; Y.M. Chooi,* Chartered Semiconductor Manufacturing Ltd., Singapore

Abstract: Self-assembled monolayers of dodecanethiol (DT), Mercaptobenzothiazole (MBT), Benzotriazole (BTA) and Imidazole (IMD) were formed by adsorption on the surface of copper thin film used in the ultra large-scale integrated circuits. The films were characterized by X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FTIR) Spectroscopy and contact angle measurements. The corrosion inhibitive behaviours of these organic monolayers were investigated in aerated 0.5 moldm@super -3@ H@sub 2@SO@sub 4@ solutions by means of Electrochemical Impedance Spectroscopy (EIS) and polarization techniques. The presence of the monolayers reduced corrosion by blocking the copper surface from the dissolved oxygen in the acid medium. The relative inhibition efficiencies of these inhibiting agents in preventing copper oxidation is found to be in the order of: DT > MBT > BTA > IMD. The effectiveness of the inhibitors increased with temperature, concentration of the inhibitors and immersion time in the solution. An adsorption model was proposed on the basis of the variation of impedance with inhibitors' concentration.

Surface Science
Room 328 - Session SS-ThA
Oxide Reactions and Catalysis

Moderator: A. Klust, Tulane University

2:00pm **SS-ThA1 Atomic Understanding of Strong Nanometer-Thin Metal/Alumina Interfaces and the Making of Nanoscale Island and Film Catalysts*, D.R. Jennison,*** *T.R. Mattsson,* Sandia National Laboratories

Chambers, Droubay, Jennison, and Mattsson [Science 297 (2002) 827] recently reported room temperature laminar growth of Co deposited in vacuum from an evaporation source on fully hydroxylated but otherwise clean @alpha@-Al@sub 2@O@sub 3@(0001). We extend this work to a number of metals using density functional (DFT) calculations. The exothermicity of the suggested core reaction, 2OH@super -@ + M => H@sub 2@ + 2O@super 2-@ + M@super 2+@, where M represents any metal, is investigated for Cr, Fe, Ni, Cu, Mo, Ru, Rh, Pd, and Al. We find that this reaction is strongly exothermic for most metals. However, while Rh is slightly endothermic, it has a sufficient heat of adsorption to react immediately upon contact. The behavior of Cu cannot be determined within the current accuracy of DFT. Pd is strongly endothermic, suggesting noble metals will not react. By first-principles molecular dynamics simulations of Rh, we confirm a substantial likelihood for direct "hot" reactions driven by the heat of adsorption, as originally proposed. However, Rh has two reaction barriers, indicating more complex kinetics than with Co. Now 1-2 ML films may be made and also nano-islands with steps, both having potential catalysis applications. 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.

2:20pm **SS-ThA2 Potassium Adsorption on Thin Film Cerium Oxide and Its Effect on Supported Rhodium Activity@footnote 1@*, D.R. Mullins,*** Oak Ridge National Laboratory

We have examined the adsorption of K on CeO@sub 2@ thin films and its effect on the adsorption of CO on Rh supported on the CeO@sub 2@. The K saturation coverage, i.e. the maximum coverage achievable before the onset of multilayer desorption, is ca. 1 x 10@super 15@ cm@super -2@. This is about twice what has been observed on Rh(111). It is similar to the CeO@sub 2@(111) surface density of 0.8 x 10@super 15@ cm@super -2@. The K exhibits three distinct desorption states near 450K, 600 K and 700 K. The K 2p core-level photoemission does not indicate a significant change in binding energy or the presence of multiple K states as a function of annealing temperature and coverage. CO dissociates when adsorbed on Rh on reduced CeO@sub X@. It is of interest to determine whether charge transfer from K to CeO@sub 2@ will also cause CO dissociation on Rh supported on K/CeO@sub 2@. CO desorbs from Rh on fully oxidized CeO@sub 2@ below 500 K and shows little evidence of O exchange with the ceria. The desorption is similar to CO on Rh(111). When K is present, the CO desorption occurs between 600 K and 700 K and shows considerable O exchange with the support. The high temperature desorption is similar to what was observed on K/Rh(111) which was ascribed to an interaction between the K and the CO. The high temperature desorption and O exchange are also similar to what has been observed for dissociated CO on Rh supported on reduced CeO@sub X@. For the system CO/Rh/K/CeO@sub 2@, there is no evidence of CO dissociation as indicated by the C 1s photoemission. The C 1s photoemission does indicate the formation of surface carbonates. Carbonates were not observed on either K/Rh(111) or Rh/CeO@sub X@. @FootnoteText@ @footnote 1@Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

2:40pm **SS-ThA3 The Interaction of Methyl Iodide with Surface Defects on UO@sub 2@(100)*, J. Stultz,*** *S.A. Joyce, M.T. Paffett,* Los Alamos National Laboratory

Actinide materials undergo thermal and non-thermal reactions with adsorbed molecules resulting in chemical transformations leading to degradation and gas generation. In most handling and processing scenarios actinide materials readily oxidize forming an actinide oxide interface. Evidence suggests that unique chemistry occurs and may possibly be driven by surface defect sites at these oxide interfaces. To characterize these interactions and possibly quantify surface defect sites, the thermal reactivity of CH@sub 3@I with a well annealed and sputter defected UO@sub 2@(100) surfaces was investigated. XPS results indicate CH@sub 3@I undergoes dissociative adsorption on UO@sub 2@(100) at 300K in which I reacts and adsorbs selectively at defect sites leaving little or no residual carbon on the surface. Semi-quantification of surface defects was achieved by analysis of the XPS results for moderately high surface defect densities. Low temperature TPD results indicate mono and multilayer CH@sub 3@I desorption characteristics similar to that seen for other metal oxide systems. Additionally, low intensity features in the TPD data suggest trace levels of oxidation of residual surface carbon to form formic acid. LA-UR-03-2698.

3:00pm **SS-ThA4 Thermal and Radiation-Induced Chemistry of Water on Uranium Dioxide Surfaces**, *J. Stultz, M.T. Paffett,* ***S.A. Joyce,*** Los Alamos National Laboratory

Most plans for the disposition of surplus nuclear materials involve storage in sealed containers where the evolution of gases from reactions of adsorbed water could present both pressure and flammability hazards. In order to better understand the relative importance of the thermal- and radiation-induced chemistry, we have studied the interactions of water on single crystals of uranium dioxide. Temperature programmed desorption and electron stimulated reaction/desorption are used to examine the chemistry. In the absence of radiation, water adsorbs/desorbs molecularly on nominally pristine oxide surfaces with a binding energy of only a few kcal/mole greater than water with itself. The strength of this interaction is large enough to indicate that UO@sub 2@ surfaces handled outside the driest of environments will be covered with water. External low energy electron irradiation is used to simulate the effects of radiolytic chemistry induced by decay particles. The principle neutral gaseous radiolytic products are H@sub 2@, O@sub 2@, and water. The relative yields are strongly dependent on temperature and coverage. Ion desorption, which is often sensitive to minority species, indicates that surface hydroxyls, presumably formed at defect sites, are stable up to high temperatures (~ 600K).

3:20pm **SS-ThA5 Gas Sensing Mechanism of SnO@sub 2@*, M. Batzill,*** *B. Katsiev,* Tulane University*; A. Chaka,* National Institute of Standards and Technology*; U. Diebold,* Tulane University

Stannic oxide is widely used as a gas sensing material for reducing and oxidizing gases. Variations in the surface oxygen concentration of metal-oxide gas sensors play an important role for explaining their response to a change in the surrounding gas phase. Here we show for different low index SnO@sub 2@ surfaces that non-stoichiometric surface terminations are favored at a low oxidation potential of the environment (e.g. UHV conditions). Under such conditions the low-energy (110) surface forms complex surface reconstructions in order to accommodate the loss of surface oxygen. The (101) and (001) surfaces, on the other hand, retain bulk terminations for both stoichiometric and reduced surfaces. The stability of these surfaces is explained on ground of the dual valency of Sn (SnII and SnIV) and the rutile-structure of SnO@sub 2@ that allow the (001) and (101) surfaces to attain a Sn@super 2+@O@super 2-@ stoichiometry by removal of bridging oxygen atoms. The surface structures have been determined by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). For reduced surfaces, angle resolved UPS was employed to characterize the dispersion of the surface electronic states. The variation of the surface composition has been measured by temperature programmed ion scattering spectroscopy. The experimental results are verified by density functional theory calculations that show the stability of different surface phases as a function the oxygen chemical potential. This variable surface composition accompanied by a change in the electronic structure is proposed to be the fundamental process of the gas sensing mechanism for SnO@sub 2@.

3:40pm **SS-ThA6 Photoinduced Reaction Dynamics of Halocarbon Adlayers on the Fe3O4 (111)-(2x2) Selvedge of Fe2O3 (0001)***, **G.G. Totir**, Y. Le, R.M. Osgood, Jr.,* Columbia University

Electron transfer reactions on surfaces play a key role in electrocatalysis and in photoinduced processes in surface-adsorbate systems. More recently, interest in understanding the reactivity of iron oxides toward halogenated hydrocarbons has been stimulated by applications in catalysis and environmental decontamination procedures. We used time-of-flight (TOF) and temperature programmed desorption (TPD) to study the electron transfer reaction dynamics and photochemistry of halocarbons on surface reconstructed single crystal hematite, Fe2O3 (0001). For example, TPD spectra recorded at various coverages of methyl iodide adsorbed at 100 K on the magnetite, Fe3O4, termination of single crystal hematite, indicate a rich surface chemistry, with multiple desorption events, similar to results previously obtained for other adsorbates on the same surface. Furthermore, angle-resolved TOF results for monolayer coverage of methyl iodide on Fe3O4 (111)-(2x2) indicated that the methyl fragments produced from dissociative electron attachment were ejected at an angle of ~ 0o with respect to the surface normal. Post-irradiation desorption spectra for methyl iodide and carbon tetrachloride on the magnetite surface, and results discussing adsorbate orientation and coverage dependence will be presented.

4:00pm **SS-ThA7 Photo-oxidation of Trimethyl Acetic Acid on the Surface of TiO@sub 2@(110)***, **M.A. Henderson**, J. Szanyi,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas, Austin

TiO@sub 2@ has received considerable attention for its use as a photocatalyst in the destruction of organics. Complexities associated with microcrystalline TiO@sub 2@ (e.g., identification of surface active sites and intermediates) often hamper mechanistic study of the step-by-step conversion of organics into CO@sub 2@. In an attempt to address mechanistically the photo-oxidation of organics on TiO@sub 2@, we employ rutile TiO@sub 2@(110) as a model photocatalyst and trimethyl acetic acid (TMAA) as a model organic. A saturation exposure of TMAA at 300 K results in dissociation of the acid O-H bond to form bidentate trimethyl acetate (TMA) and OH groups at the bridging anion sites. In TPD, recombination of TMA and OH to form parent occurs between 300 and 550 K, along with water from OH combination and some TMA decomposition to isobutane and isobutene. However, the majority of the TMA adlayer decomposes to CO and isobutane/isobutene at 650 K. UV exposure was performed at 110 K in order to capture intermediates during photolysis, subsequently analyzed in TPD. UV exposure in the absence of O@sub 2@ results in rapid conversion of the species responsible for the 300-550 K TPD states into acetate groups. In contrast, the TMA species responsible for the 650 K TPD states are converted into isobutene/isobutene and CO@sub 2@ by cleavage of the C-COO bond. Inclusion of O@sub 2@ does not affect the rate of acetate formation, but accelerates the conversion of the 650 K TMA into isobutene/isobutane. Evidence has been found for the continued photo-oxidation of the C@sub 4@ daughter products into C@sub 3@ species. These reactions do not appear to be wavelength dependent for photons with energies in excess of the TiO@sub 2@ bandgap. Based on these results, we propose that products of hole trapping on TMA depend on the structural environment of the adlayer, and that a limited amount of electron trapping permits some degree of photochemistry in the absence of O@sub 2@.

4:20pm **SS-ThA8 The Origin of Photo-induced Hydrophilicity on TiO@sub2@ Surfaces: Photo-generation of Surface Oxygen Vacancies or Photo-oxidation of Adsorbed Organics?***, **J. Szanyi**, M.A. Henderson,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas, Austin

Since the discovery of the photocatalytic nature of TiO@sub2@ in the 1970s, significant efforts have been made to understand both the properties of the oxide material itself and the catalytic processes that occur on its surfaces. In recent years the photo-induced hydrophilic nature of TiO@sub2@ has been discovered and studied. The hydrophilic behavior continues after removal of the light, but gradually degrades to the pre-irradiation conditions. Most of the original work from Japan suggests that hydrophilicity and photo-oxidation of surface organic contaminants are unrelated properties of TiO@sub2@. They propose UV generated oxygen defect sites on the TiO@sub2@ surface as the origin of hydrophilicity. In turn, the oxidation of oxygen vacancies by O@sub2@ in the air has been proposed as the mechanism for the slow degradation of hydrophilicity of a TiO@sub2@ surface. In order to understand the origin of photo-induced hydrophilicity of TiO@sub2@, we have studied the adsorption of water on a clean and trimethyl acetic acid covered TiO@sub2@(110) surface under carefully controlled experimental conditions. TPD of H@sub2@O suggests that irrespective of the presence or absence of vacancies, water wets the TiO@sub2@ surface as evidenced by the sequential filling of monolayer, second layer and multilayer states as a function of increasing coverage. On the other hand, the monolayer water TPD state is absent for water adsorbed on a TiO@sub2@(110) surface pre-saturated with trimethyl acetate (TMA) species, formed from decomposition of the acid. Exposure of the TMA adlayer to UV light in 5x10@super-6@ torr O@sub2@ results in nearly complete photo-oxidation of the organic and restoration of the ability of the surface to directly bind water. In this presentation, based on these molecular-level UHV studies, we propose that the origin of photo-induced hydrophilicity on TiO@sub2@ surfaces is likely due to photo-oxidation of adsorbed organics that create a hydrophobic monolayer.

4:40pm **SS-ThA9 The Adsorption and Reaction of NO on Single Crystal Titanate (TiO@sub 2@ and SrTiO@sub 3@) Surfaces***, **C.H.F. Peden**, S. Azad, M.H. Engelhard, M.A. Henderson, J. Szanyi, L.-Q. Wang,* Pacific Northwest National Laboratory

The control of NOx (NO and NO@sub 2@) emissions from combustion processes, including vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion), where the need is to selectively reduce NOx with a reductant in a large background of the competing oxidizing species, O@sub 2@. A wide variety of oxide materials, including zeolites, are known to be effective for selective catalytic reduction of NOx from the exhaust of 'lean-burn' engines.@footnote 1@ As such, there has been much interest for some time in determining the kinetics of adsorption and surface reactions of NO and NO@sub 2@, as well as identifying the composition and structure of the mechanistically important adsorbed NOx species on this class of catalytic materials. In this presentation, we will discuss selected results from our ongoing studies aimed at addressing some of the considerable remaining uncertainties about these processes.@footnote 2@ In particular, we will compare and contrast the results of our temperature programmed desorption (TPD) and x-ray photoemission spectroscopy (XPS) studies of NO adsorption on single crystal TiO@sub 2@ and SrTiO@sub 3@ surfaces. Both weakly adsorbed NO and the reaction product, N@sub 2@O, were observed in TPD from TiO@sub 2@(110). The N@sub 2@O is formed from an 'NO-like' species identified with XPS. However, NO is the only desorption product from a SrTiO@sub 3@(100) surface. @FootnoteText@ @footnote 1@M. Shelef and R.W. McCabe, Catal. Today 62 (2000) 35. @footnote 2@The work was carried out at Pacific Northwest National Laboratory (PNNL) and funded by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Divisions of Chemical Sciences and Materials Sciences. Experiments were performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility located at PNNL and supported by the DOE's Office of Biological and Environmental Research.

5:00pm **SS-ThA10 An FTIR Study of Methanol, Water and Acetic Acid on MgO(100) Under Ambient Conditions***, **M.C. Foster**,* University of Massachusetts

We have investigated the interactions occurring between the MgO(100) surface and a series of small molecules, namely water, methanol and acetic acid. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. The adsorbate of interest is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. Photometry then allows for the quantitative determination of adlayer coverages from absorbance measurements using a modified Beer-Lambert Law. The substrates have also been inspected with atomic force microscopy (AFM) both before and after each series of experiments. The interactions of these adsorbates with MgO(100) under room temperature conditions and pressures on the order of 10 Torr vary from physisorbed, as is the case with methanol all the way up to dissociatively chemisorbed, as is the case with acetic acid resulting in the formation of magnesium acetate under these experimental conditions.

Thin Films

Room 329 - Session TF-ThA

In-Situ / Ex-Situ & Real-Time Monitoring

Moderator: R.A. Lukaszew, University of Toledo

2:00pm **TF-ThA1 Thin-film Cavity Ringdown Spectroscopy (tf-CRDS) for Ultra-sensitive and Direct Detection of Defect-related Absorptions in a-Si:H Thin Films***, **I.M.P. Aarts**[1], B. Hoex, A.H.M. Smets, R. Engeln,* Eindhoven University of Technology, The Netherlands*; M. Nesládek,* Limburgs Universitair Centrum, Belgium*; W.M.M. Kessels, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

We have explored the applicability of cavity ringdown spectroscopy with respect to the measurement of small, defect-related absorptions in thin films. First of all, the validity of the method has been confirmed by rigorous studies on the issues that arise when placing an optical transparent substrate inside the high-finesse optical cavity: it has been found that the stability of the cavity, the build-up time of the electromagnetic field inside the cavity as well as the changes in output signal are not significantly affected by the substrate. Furthermore, the losses caused by surface scattering induced by the sample's surface roughness have been estimated employing surface morphology data obtained from atomic force microscopy. It is shown that surface scattering will eventually limit the absorption sensitivity of the technique, which is as good as 10@super -7@ per pass. Subsequently, as a proof-of-principle, measurements have been performed on several samples of hydrogenated amorphous silicon (a-Si:H) thin films in a broad spectral range (0.7 - 1.7 eV) using an optical parametric oscillator laser. The absorption values of the a-Si:H films of various thickness (5 - 1000 nm) have been corrected for interference effects that have been modeled in a straightforward but complete manner. The optical absorption spectra obtained revealed good agreement with conventional transmission-reflection and photothermal deflection spectroscopy (PDS) measurements and the spatial distribution as well as the bulk and surface defect densities in the a-Si:H thin film have been determined. From the results, it can be concluded that tf-CRDS is an ultra-sensitive absorption technique that does not require any calibration. The technique is therefore very promising for a broad range of thin film research fields and currently experiments are carried out to detect ultra-low doping levels of rare earth metals in silicon and to apply the technique real time during film growth of a-Si:H.

2:20pm **TF-ThA2 Quasi-Real Time in-situ FT-IR Spectroscopy of Doped and Undoped SiO@sub 2@ Deposition from TEOS / Ozone Chemistry***, J.E. Crowell,* ***L.D. Flores,*** University of California, San Diego

Application of quasi- real time in-situ infrared spectroscopy to the chemical boundary layer (CBL) region formed during atmospheric pressure chemical vapor deposition is investigated for silicate glass deposition from TEOS / Ozone, and upon addition of phosphorus and boron dopants. The CBL-FT-IR methodology provides direct chemical measurement of the deposition intermediates formed upon dopant addition allowing for measurement of both film forming precursors and film formation processes. Similarly, CBL difference spectroscopy (CBL-DS) provides a sensitive measurement of the time needed for attainment of steady state reactor conditions after introduction or switching of reagents. Partial least squares Beer's law quantitative methods applied to the isolated form of ethoxysilanol (3737 cm@sup -1@) show that its concentration is reduced by a factor of 2 during growth of PSG under steady state conditions. We have developed a PLS methodology to quantitate reactive chemical mixtures of TEOS and ozone and found the chemical kinetics to be independent of added phosphite (i.e. [k@sub TEOS@/k@sub OZONE@]@sub PSG@ ~ [k@sub TEOS@/k@sub OZONE@]@sub USG@). Considering the ca. 2.8-fold enhancement in deposition rate observed upon phosphorus addition along with the measured reduction in gas phase isolated silanol groups illustrates that gas phase ethoxysilanol species are the main film deposition intermediates in equilibrium with SiO@sub 2@ film growth. This result shows that real time CBL-DS is a powerful methodology to determine the chemical mechanisms of film growth as well as the associated chemical kinetics of gas phase processes responsible for their growth. Spectroscopic differences and comparisons for PSG, BSG, and BPSG film growth and the associated intermediates will additionally be made.

2:40pm **TF-ThA3 Numerical Analysis of the Three-phase Problem in Optical Diagnostics***, **K.F. Flock**, D.E. Aspnes,* North Carolina State University

One of the major unsolved problems in optical diagnostics is the practical simultaneous determination of n, k, and t, i.e., the real and imaginary parts of the complex refractive index and the thickness, respectively, of a depositing film, ideally at the monolayer or near-monolayer level. This capability is particularly important for purely sample-driven feedback control of deposition processes such as OMCVD. For very thin layers analysis can be done in principle within the three-phase (substrate/overlayer/ambient) model, since the underlying substrate, no matter how complicated, can be represented approximately as a pseudodielectric function and the material deposited between measurements can be considered uniform in composition. Current optical diagnostic tools, such as our PDA-based polarimeter, return three pieces of information, i.e., the p- or s-polarized reflectance and the phase and amplitude of their ratio, and hence are well suited for this approach. Wavelength-by-wavelength analysis of electrochemical modulated-reflectance data, a related application, has been done previously in the three-phase model with marginal results. Here, we use a simple analytic approach to investigate correlations among n, k, and t to gain better insight into the nature of these solutions. We find that the correlation among the three parameters would be exact if the power reflectance were an analytic function. This explains the high sensitivity to experimental uncertainty, which in wavelength-by-wavelength applications would require accuracies of the order of 1 part in 10@super 6@ for consistent results. We present a method that circumvents this difficulty by taking advantage of spectral dependences. Applications discussed include the determination of n, k, and t for sub-nm-scale layers of Ga and AlAs on GaAs.

3:00pm **TF-ThA4 Mapping Epitaxial Interfaces with Ultrabright X-rays***, **R. Clarke,*** University of Michigan, Ann Arbor **INVITED**

A new direct structure determination technique, Coherent Bragg Rod Analysis (COBRA), has been developed@footnote 1@ that reveals the atomic structure of epitaxial thin films and interfaces with sub-Angstrom resolution. The measurements take advantage of the high brilliance of x-ray synchrotron radiation from undulator beam lines at the Advanced Photon Source, Argonne National Laboratory. In this presentation we will describe the capability of COBRA to reveal subtle details of the interface structure that cannot be accessed by existing structural methods. The method will be illustrated by several examples drawn from our recent work on epitaxial oxide films, including perovskite ferroelectric heterostructures. This work is carried out in collaboration with Y. Yacoby (Hebrew University, Jerusalem), R. Pindak (NSLS), and E. Stern (University of Washington) and is funded by the U.S. Department of Energy, Basic Energy Sciences, and by FOCUS, a National Science Foundation Frontiers of Physics Center. @FootnoteText@ @footnote 1@ 1. Direct determination of epitaxial interface structure: Gd2O3 passivation of GaAs, Y. Yacoby, E.Stern, J. Cross, D. Brewe, R. Pindak, D. Walko, E. Dufresne and R. Clarke, Nature Materials 1, 99-101 (2002).

3:40pm **TF-ThA6 Real Time X-ray Monitoring of Ta Film Thickness, Phase, and Texture Evolution during Sputter Deposition***, **D. Windover,*** Rensselaer Polytechnic Institute*; S.L. Lee,* ARDEC, Benet Laboratories*; T.-M. Lu,* Rensselaer Polytechnic Institute

This work focuses on X-ray reflectivity and diffraction techniques for real time monitoring of thin film deposition inside a sputtering system. An X-ray transparent, beryllium, cylindrical chamber was constructed to allow for diffraction and reflection from the multiple geometries necessary for X-ray characterization methods. A magnetron sputter head with varying target-sample distances was used as the deposition source. In this study, tantalum was deposited on silicon substrates. Fast X-ray diffraction and texture information was collected using a position sensitive area detector. Fast X-ray reflectometry was collected using an energy dispersive silicon detector.

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[1] **TFD Student Award Winner**

Examples of thickness, phase, and texture monitoring are presented. We conclude with a discussion on the advantages and potential limitations of the characterization approaches and their applicability to real time monitoring in deposition systems.

4:00pm **TF-ThA7 Epitaxial Growth of Nanostructured Metal/Metal Oxide Thin Films by Ultrahigh Vacuum In-situ TEM*, M. Yeadon,*** IMRE, Singapore*; J. Yu,* National University of Singapore, Singapore*; W. Tian, H.P. Sun, X.Q. Pan,* University of Michigan*; C.B. Boothroyd,* IMRE, Singapore*; R.A. Lukaszew,* University of Toledo*; R. Clarke,* University of Michigan, Ann Arbor **INVITED**

The structure and properties of metal: metal oxide systems are of substantial importance in applications ranging from magnetic storage and spintronic devices to supported catalysts. In some metal/oxide systems it is possible to achieve epitaxial growth and the properties of the films may strongly depend on the interfacial structure as well as their growth mode. Using a modified ultrahigh vacuum transmission electron microscope (the MERLION system), we have investigated the nucleation and growth of Ni thin films on electron transparent metal oxide substrates. The system is equipped with solid source electron beam evaporators together with gas injection capability, all within the polepiece of the electron microscope which has a base pressure of 1.5x10@super -10@Torr. The talk will focus on the early stages of nucleation and growth. Real-time video recordings of the observed microstructural evolution will be presented. Some results from related in-situ experiments involving the growth of other thin films and nanostructured materials will also be presented.

4:40pm **TF-ThA9 Growth of Epitaxial Two-dimensional Layers of Indium on Si(100) by Femtosecond Pulsed Laser Deposition*, M.A. Hafez,*** *M.S. Hegazy, H.E. Elsayed-Ali,* Old Dominion University

The growth of high quality epitaxial metal films on Si is of interest to device technology. Pulsed laser deposition (PLD) produces energetic species, which result in the increase of the sticking coefficients and adatom surface mobility enhancing epitaxial growth. Compared to longer laser pulses, femtosecond (fs) laser pulses significantly alter the processes associated with ablation. Epitaxial growth of thin films by fsPLD has been previously reported. Heteroepitaxial growth of indium on Si(100)-(2x1) substrates is performed under ultrahigh vacuum (base pressure low 10@super -9@ Torr) with a Ti:sapphire laser (130 fs) at wavelength of 800 nm. Reflection high-energy electron diffraction (RHEED) is used during the deposition to study the growth dynamics and the surface structure of the grown films. Morphology of the indium films is examined by ex-situ atomic force microscopy (AFM). At a substrate temperature of ~145 °C, indium was initially found to grow two-dimensionally, and then three-dimensional islands were formed. Epitaxial indium thin films are found to grow at a deposition temperature of ~400 °C, which have a 3x4 structure as observed from the RHEED pattern. The RHEED analyses and intensity oscillations show that indium films grow with two-dimensional layers and the AFM reveals two-dimensional nucleation islands. Growth modes and nucleation of indium films at different deposition conditions are discussed.

5:00pm **TF-ThA10 Real-time Observation of Initial Stages of Copper Film Growth on Silicon Oxide using Reflection High-energy Electron Diffraction*, J.T. Drotar,*** Rensselaer Polytechnic Institute

We have studied, in real time, the evolution of a thin (less than 200 Å) copper film deposited onto an oxidized silicon surface using reflection high-energy electron diffraction (RHEED). We show that quantitative measurements of island size and shape as functions of time are possible and the results are presented. While the film texture is initially random, texture competition leads to an absence of the low energy (111) and (200) oriented grains for later times. It is also found that the film surface is composed of facets that increase in size with time. This behavior is explained in terms of facet coalescence.

Vacuum Technology
Room 323 - Session VT-ThA

Industrial Vacuum Applications

Moderator: N.T. Peacock, MKS Instruments

2:00pm **VT-ThA1 The Role of Outgasssing, Outdiffusion and Desorption in Vacuum Coating*, D.M. Mattox,*** Management Plus Inc. **INVITED**

The role of vacuum technology in the vacuum coating industry has changed significantly in the last 30 years. Previously the objective of producing a vacuum was to attain the best possible vacuum in the shortest time possible. In recent years to this goal has been added the requirements of establishing specific partial pressures of inert and reactive gases and vapors, generating uniform plasma environments and controlling the gas flow and gas distribution in the processing system. The vacuum systems are of ten required to handle toxic and corrosive gases and to tolerate fine particles generated in the processing. The increasing use of polymer substrates and rolls of films (webs) has increased the demands imposed for handling outgassing and desorption during vacuum processing. This paper will describe some of the problems and solutions used not only to address the problems of outgassing and desorption but also to minimize the problems by proper system design and substrate treatments in the vacuum system.

2:40pm **VT-ThA3 Pumping Characteristics of Metal Films in a Vacuum Glass Vessel: Experimental and Theoretical Issues*, A. Bonucci,*** *C. Carretti, G. Longoni, R. Giannantonio, M. Urbano,* SAES Getters SpA, Italy

The evaluation of the pumping characteristics of metallic films deposited onto glass surfaces in a vacuum environment is a very important issue for several industrial and research applications. Many years ago, an optimized experimental setup was established to measure the pumping characteristics of barium films inside Cathode Ray Tubes (CRTs). However, some technological limitations, related both to the particular experimental configuration and to the materials used, prevented the possibility to extend this approach to a more general case, including adsorbing materials different from barium deposited onto surfaces having a geometry different from that of a CRT. The progress in vacuum technology makes today possible to use a large variety of components to assemble an experimental vacuum apparatus. Moreover, the availability of powerful computational tools allows to design the best experimental configuration for any specific purpose. In this work, a new approach to the study of the pumping characteristics of an adsorbing film in a vacuum is discussed. An improved experimental configuration is here first described and a mathematical method, based on the angular coefficients approach, able to suitably calculate the pressure distribution inside a vacuum vessel, is proposed. The agreement between the experimental and the theoretical results obtained in the simple case of a gettering surface deposited onto spherical glass bulbs having different dimensions is finally discussed.

3:00pm **VT-ThA4 Vacuum Thermal Insulation - Inventions for the Future*, V. Nemanic,*** Jozef Stefan Institute, Slovenia **INVITED**

The innovative application of vacuum in a gap between two bottles is attributed to Sir James Dewar in 1892. The underlying technical innovations followed through numerous patents that have often driven the remarkable progress in different fields. An examination of the past century of progress is indeed an exciting venture which manifests the state of the art of contemporary vacuum science and technology. The review of operational principles, main technical difficulties and future trends of developments are presented for: 1) cryogenic scientific instrumentation, where the insulating value of the single gap is improved by insertion of multiple reflectors. This was first done in the mid of the last century offering the lowest thermal flux in "super insulated" cylindrical vessels. Well proven solutions in this field seems to have an impact on potential storage of liquid hydrogen as it can become the automotive fuel of the future. 2) everyday thermos bottles became in last few years light and durable by replacing the glass wall with the thin stainless steel. This valuable change did not affect the price, but manifests better evacuation methods and application of new getters. 3) evacuated insulating flat elements with high insulating value are an efficient alternative for polymer foam panels. Longevity sets still very strict requirements for selection of highly porous filler material, as well as for envelope tightness and permeation rate. Anyhow, vacuum panels are already built in energy efficient home appliances and will soon spread in cargo containers and buildings. 4) transparent and translucent vacuum glazing were proposed for over a century in improving concepts in patents. Beside a still limited application in passive solar energy capture elements, the commercial vacuum window glazing, with point supported two sheets of glass, appeared in the last five years. Today performances may be thus optimistically envisioned for tomorrow.

3:40pm **VT-ThA6 A Comparison of Chamber Conductance Calculations Using CFD and a Thermal Radiation Analogy*, L.A. Gochberg,*** Novellus Systems

The design of semiconductor vacuum chambers often requires that overall chamber conductance be optimized. In high-density plasma (HDP) chemical vapor deposition (CVD) systems for dielectric deposition in STI applications, a high chamber conductance will promote lower chamber pressures over the wafer. These lower pressures can enhance the ability to perform high aspect ratio dielectric gapfill on the wafer. Flow modeling is routinely used in the design of such CVD systems, employing either Monte Carlo methods or Navier-Stokes solvers (CFD) using slip boundary conditions. In this work, a thermal radiation analogy to free molecular flow is used in place of a collisionless Monte Carlo computation for two different HDP-CVD chamber configurations. Modeling results show that with either the thermal radiation analogy approach, or the CFD approach, chambers with centrally-mounted pedestal chamber designs perform significantly better from a conductance/pressure perspective than do cantilever- mounted pedestal designs. Also, the thermal radiation analogy model approach allows complex 3D chambers to be modeled quickly with general-purpose, commercially available CFD codes. This CFD approach is preferable in industrial environments as opposed to using Monte Carlo methods, which require the use of a separate software modeling approach that is not available commercially, and is difficult to use for complex 3D geometries.

4:00pm **VT-ThA7 CFD Analysis of a 2D Model of a Gaede Drag Pump in Viscous and Slip Flow Regime***, **S. Giors,*** Varian Vacuum Technology, Italy*; F. Subba,* Politecnico di Torino, Italy

Experimental analysis on a uniform and a tapered Gaede pumps were already performed in Varian in 2002 and the results presented at AVS 49th Intl. Symposium.@footnote 1@ The experimental results assessed both compression and pumping speed performances of those pumps and showed some weaknesses of the Couette-Poiseuille 1D model, developed a few years ago by Helmer and Levi to describe the Gaede stage behaviour and to be used as a design tool.@footnote 2@ A 2D model of the Gaede pump, based on Navier Stokes equations, is now developed and validated against experimental results. A commercial CFD code is used to simulate the pumping performance of a single stage Gaede pump (the uniform one in the experiment) in the viscous regime, for different operating conditions, with and without throughput, in order to assess both compression and pumping speed performances, as well as to improve the general understanding of the physics of Gaede pumps within the limitations of a 2D model. The possibility of extending the Navier Stokes model at low pressure, through slip flow boundary conditions is also explored, and the lower pressure limit found for the resulting model by comparison of the numerical results with the experiment. Validation against experimental results has shown some weakness of the pure 2D model, and ideas to include some 3D effects (e.g. the radial leak path) into the 2D model are proposed for future developments. @FootnoteText@@footnote 1@ S. Giors, R. Gotta, J.C. Helmer, "Experimental analysis of Tapered Gaede pumps", AVS 49th Intl. Symposium oral presentation, Denver CO, November 2002.@footnote 2@ J. C. Helmer, G. Levi, "Transition gas flow in drag pumps and capillary leaks", J. Vac. Sci. Technol. A 13(5), 2592-2599, Sep/Oct 1995.

4:20pm **VT-ThA8 Characteristics Evaluation Practice of Predictable Performance Monitoring for Low Vacuum Dry Pumps in the Semiconductor Production Line***, **J.Y. Lim,*** Korea Research Institute of Standards and Science, Korea*; W.S. Cheung,* Korea Research Institute of Standards and Science*; J.H. Joo,* Sungwon Edwards Ltd., Korea*; Y.W. Kim,* Samsung Electronics Co. Ltd., Korea*; W.G. Sim,* Hannam University, Korea*; K.H. Chung,* Korea Research Institute of Standards and Science

The early prediction system of performance fluctuation for low vacuum dry pumps in the semiconductor process line has been issued since devastating malfunctions or characteristics degradations of dry pumps due to mainly chemical byproducts during the production processes have been occasionally reported in Samsung Electronics. This motivation drove implementing central monitoring system (CMS) to the production facilities. CMS, however, is not a single condition monitoring or a prediction analysis method, but an overall monitoring program with historical performance data only. To compromise with this issue, the real time, in-situ characteristics evaluation system for two Edwards iH600 dry pumps has been established at the Ti/TiN chemical vapor deposition system in the Samsung Electronics production line #10, in which system pump malfunction or degradation mostly happens. The real time data in Samsung Electronics and the experimental reference data from the KRISS characteristics evaluation system@footnote 1@ have been thoroughly compared each other and analyzed to ascertain if there exist unusual degradation symptoms such as in pumping speed, power consumption, vibration, noise, etc. The integrated data at the actual process pressure range of about 1 to 10 mbar and experimental measurement rage of about 100 to 10@super -3@ mbar are time-synchronized with respect to the inlet pressure in a scientific manner of coincidence. In this recent work, we report the first significant results of the method of characteristics synchronization between the laboratory and process line in the way of the pump malfunction or degradation symptom to be clearly diagnosed and positively protected during the production process. @FootnoteText@@footnote 1@J.Y. Lim, S.H. Chung, W.S. Cheung, K.H. Chung, Y.H. Shin, S.S. Hong, W.G. Sim, Expanded Characteristics Evaluation for Low Vacuum Dry Pumps, AVS 49th International Symposium, November 4, 2002, Denver, CO, USA.

4:40pm **VT-ThA9 An Alternative-voltage Penning Cell for Low-voltage Vacuum Gauges and Other Applications***, **S.A. Cherenshchykov,*** National Science Centre "Kharkov Institute of Physics and Technology", Ukraine

A two-anode Penning cell with cold cathodes was researched. Due to additional source of a variable voltage used as power source, it becomes possible to ignite and to support the discharge at significantly lower voltage. This phenomenon was observed in a wide range of pressures (from 5 Pa up to 10@-6@ Pa). The reduction of Penning discharge voltage was up to 20 volts at the pressure value of 0.3 Pa and up to 300 volts when pressure was the lowest. The discharge current decreased together with pressure. The discharge current irreproducibility at the pressure of 10@-5@ Pa was not worse than 12 %. The current of existing discharge in magnetic field increased in many times under effect of additional variable voltage. It is supposed that efficiency of ionization of low-pressure gas will increase under affect of variable voltage. These discharge properties can make the basis for perfection of devices that use the Penning cell and other discharge magnetic cells (such as full and partial pressure gauges, leak detectors, ion pumps, ion sources and hot plasma sources). The new properties of the discharge can promote expansion of its application area, in particular, on sources of vacuum ultra-violet and soft x-ray radiation and polarized charged particles. The working model of the vacuometer was created based on such discharge. This vacuometer can unite all the advantages of magnetic discharge vacuometer and hot-cathode ionizing vacuometer. Besides it could be cheaper, is safer from the point of view of explosion possibility. Its power consumption and the heat dispersion on its gauge are almost hundred times lower. In addition, it can be smaller in volume and weight in comparison with analogues.

Applied Surface Science
Room 324/325 - Session AS-FrM
SIMS

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

8:20am **AS-FrM1 Static ToF-SIMS - A VAMAS Interlaboratory Study, 2002***, **I.S. Gilmore**, M.P. Seah,* National Physical Laboratory, UK

The first VAMAS static SIMS inter-laboratory study was conducted by NPL in 1996.@footnote 1@ That study included 21 static SIMS instruments with a wide variety of spectrometer types. Results indicated that, whilst repeatabilities could be as good as 1%, they were on average only 10%. Additionally, the equivalence of data between all the different instruments was improved by a factor of 4 by use of a relative instrument transmission function RISR.@footnote 1@ In 2002, the second VAMAS static SIMS inter-laboratory study was conducted, this time restricted to time-of-flight instruments which now dominate static SIMS analysis. The principal objectives are (i) to determine the repeatability of instruments, (ii) to determine the reproducibility of between laboratories, (iii) to evaluate variations in spectral response between different types of SIMS instruments and, optionally, (iv) instrument compatibility with G-SIMS@footnote 2@ may also be tested. Data have now been received from 31 laboratories (10 with G-SIMS data) from 16 countries. Three reference materials were used in this study, a thin spin cast polycarbonate film, a thin layer of polystyrene oligomers on silver and PTFE. A protocol for analysis was supplied to each laboratory. Relevant details of the protocol will be discussed. Excellent repeatabilities have been demonstrated with over 90% of participants achieving average repeatabilities of better than 5% and 30% of participants with better than 1.5%. The reference materials give an average repeatability of 2% over 27 laboratories. This shows a considerable improvement from the average repeatability of 10% in the former study. An analysis of the results and the issues of conducting both SSIMS and G-SIMS using different instruments will be presented. @FootnoteText@ @footnote 1@ I S Gilmore and M P Seah, Surf. Interface Anal., 29 (2000) 624.@footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000) 465.

8:40am **AS-FrM2 TOF-SIMS with Polyatomic Primary Ion Bombardment: A Comparison Between Different Projectiles***, **R. Möllers**, F. Kollmer, D. Rading, M. Terhorst, E. Niehuis,* ION-TOF GmbH, Germany*; R. Kersting, B. Hagenhoff,* Tascon GmbH, Germany

In the past TOF-SIMS has been established as an analytical technique for the chemical characterization of surfaces. In particular the simultaneous detection of atomic as well as molecular ions, and the ability to obtain these information laterally resolved, makes this technique well suited for the analysis of structured molecular surfaces. Recently it was shown that polyatomic primary ion bombardment (e.g. SF@sub 5@@super +@, C@sub 60@@super +@, Au@sub n@@super +@-clusters,...) leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub-µm range. In this presentation we will continue our systematic investigation on the influence of different primary ion species, including monoatomic as well as polyatomic primary ions, on secondary ion parameters such as yield Y, damage cross section @sigma@, efficiency E = Y/@sigma@, and useful lateral resolution @DELTA@l. Those parameters have been evaluated for a variety of different sample materials and sample preparations. Also the effect of different primary ion energies (4 to 25 keV) will be issued. The results from this investigation will be expanded by examples from routine analysis in a commercial service laboratory.

9:00am **AS-FrM3 Characterisation of Peptides Using TOF-SIMS with Polyatomic Primary Ion Bombardment***, K. Pfitzer, E. Tallarek, R. Kersting, **B. Hagenhoff**,* TASCON GmbH, Germany

In the 80s of the last century it could be shown that the optimum sample preparation for SIMS of peptides under monoatomic primary ion bombardment is a monolayer preparation on noble metal substrates.@footnote 1,2@ Yields from thick overlayers turned out to be distinctly lower compared to the monolayer preparation. Although many applications were possible by this type of preparation, information could not be gained from biological material directly where peptides or proteins are embedded in thick organic matrices. Now, the use of polyatomic primary ions offers new opportunities. Under such primary ion bombardment conditions molecular ions can be emitted with high secondary ion formation efficiency also from thick organic layers. Efficiency enhancement factors can reach up to 3 orders of magnitude.@footnote 3@ We have applied Ga@super +@, Au@sub 1@@super +@, Au@sub 2@@super +@, Au@sub 3@@super +@ as well as Au@sub 5@@super +@ bombardment to several peptides. The peptide masses varied from 1000u up to 3500u. Variations of the chemical structure could be tested by varying the number of basic and acidic side chains. The samples were prepared as monolayers on noble metal substrates, as thick overlayers (powders, thick layers spin coated from solutions) as well as mixed into nitrocellulose. The results show that polyatomic primary ion bombardment indeed allows to desorb peptides efficienctly from thick layers. Progress can therefore be expected for SIMS imaging of peptides and proteins in biological matter. @FootnoteText@ References: @footnote 1@ A. Benninghoven; J. Vac. Sci. Technol. A3 (3), (1985), 451 @footnote 2@ D. van Leyen, D. Greifendorf, A. Benninghoven in: A. Benninghoven, A. M. Huber, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS VI); John Wiley & Sons, Chichester, 1988, 679 @footnote 3@ D. Stapel, M. Thiemann, B. Hagenhoff, A. Benninghoven, in: A. Benninghoven, P. Bertrand, H. N. Migeon, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS XII); John Wiley Sons, Chichester, 2000, 255

9:20am **AS-FrM4 SIMS Quantification for Depth Profiling: Overview, Recent Results for Surfaces and Insulators, and Current Problems***, **F.A. Stevie**, C. Gu, A. Pivovarov, D.P. Griffis,* North Carolina State University*; J.M. McKinley,* NanoSpective*; H. Francois-Saint-Cyr,* University of Central Florida **INVITED**

This paper provides an overview of quantification for SIMS depth profiling and presents recent results illustrating the importance of surfaces, matrix variations, and insulators on the quantification process. Quantification is complicated by the orders of magnitude variation of secondary ion yields over the periodic table and significant variation of these ion yields for different matrices. Since practical methods for calculation of elemental sensitivity factors using theoretical methods do not exist, a standard for each element in the matrix in which it is contained is required. However, only a few standards with high accuracy have been produced. Despite these limitations, measurement precision less than 1% can be achieved. Using ion implant standards, quantification can be achieved at surfaces, within multilayered samples, at interfaces, and in bulk materials. Implantation through a removable layer provides a known quantity at a surface that can be used as a standard by many analytical techniques. Multiple layers require an understanding of each layer. A study of O2+ SIMS analysis of TaN/Ta barrier penetration by Cu shows the low secondary ion yield in the barrier compared with the SiO2 and Si regions complicates interpretation. Insulators present additional problems due to sample charging. Analysis of thin insulating films can be performed by using electrons with energy sufficient to penetrate the layer thus rendering the layer conductive. Magnetic sector SIMS analysis of GaN structures can be aided by the use of molecular secondary ions accompanied by the maximization of mass spectrometer secondary ion energy bandpass. Adequate O- primary beam density can be obtained to provide depth profiles in bulk insulators. Many aspects of quantification using SIMS still require additional study. It is difficult to extend the information from one matrix to another, and analysis of insulators such as porous low-k dielectrics present special problems.

10:40am **AS-FrM8 SIMS Backside Depth Profiling of Test Pads on PMOS Patterned Wafers***, **E.S. Windsor**, J.G. Gillen, P.H. Chi,* National Institute of Standards and Technology*; J.A. Bennett,* International Sematech

In semiconductor electronics, the diffusion of elements from one layer to another can lead to poor performance or device failure. Interlayer diffusion is of particular interest in process design where experimentation with films of varying composition and thickness is common. In this study, we investigate a patterned PMOS wafer containing hafnium oxide as an experimental gate dielectric. The question arises as to whether boron from the overlying polysilicon layer has diffused through the dielectric down into the silicon substrate below. We use Secondary Ion Mass Spectrometry (SIMS) to investigate possible boron diffusion because of the high analytical sensitivity and excellent depth resolution of the SIMS technique. Front-side SIMS analyses of these patterned wafers can be limited by: (1) difficulty sputtering patterned (non-planar) surfaces, (2) initial or sputter induced topography of the sample surface and (3) degraded depth resolution caused by ion mixing when sputtering from high to low concentrations of the element(s) of interest. To minimize these effects, it is often desirable to sputter (analyze) from the backside of the wafer. Backside analysis requires the removal of the majority of the silicon substrate (final substrate thickness less than 1 micron). This is accomplished by mechanical grinding and polishing. Since the features of interest (test pads in this study) can not be observed from the backside, they must be marked from the front side prior to mechanical preparation. Marking is accomplished by ion sputtering, and we sputter both holes and raster craters. Holes mark the features of interest while the larger raster craters are used to aid thickness determinations and adjust planarity during mechanical preparation. Also investigated are factors that limit the usefulness of mechanical backthinning preparation such as polished surface roughness and sample polishing planarity.

11:20am **AS-FrM10 Development and its Application of Multiple as Delta Layer Si Reference Thin Film for Shallow Junction SIMS Profiling*, D.W. Moon,*** Korea Research Institute of Standards and Science, South Korea*; H.K. Kim, K.J. Kim,* Korea Research Institute of Standards and Science*; H.K. Shon, J.Y. Won, J.C. Lee,* Samsung Advanced Institute of Technology, Korea*; F. Toujou,* Matsushita Technoresearch, Inc., Japan

To meet the demand for shallow junction SIMS profiling, the surface transient Si sputtering effect should be corrected in addition to the improvement of depth resolution. With low energy grazing incident ions, the SIMS depth resolution could be improved better than 1 nm. For the correction of the surface transient effect, we report that multiple As delta-layer Si thin films characterized with HRTEM and MEIS can be used as a reference thin film. With the reference thin films, the depth scale shift in the surface transient region can be calibrated under each analysis condition. For low energy O@sub 2@@super +@ and Cs@super +@ ion bombardment, the average Si sputtering yield in the first surface 5 nm layer can be 50~70% higher than that in the steady state for typical incidence angles around 45°. However, for incidence angle above 60°, the surface transient effect enhanced significantly with the increase of the sputtering yield up to 150% and the extension of the surface transient region up to 15 nm for low energy Cs@super +@ bombardment. Preliminary understanding for the enhanced surface transient effect will be discussed.

Biomaterial Interfaces
Room 318/319 - Session BI+PS-FrM
Plasma Methods for Bio-interfaces

Moderator: E.R. Fisher, Colorado State University

8:20am **BI+PS-FrM1 Precision Chemical Control of Plasma Deposition for Smart Biosurfaces*, B.D. Ratner,*** University of Washington **INVITED**

In recent years, methods have evolved to deposit thin organic films from plasma environments that exhibit good control of chemistry along with the uniformity and substrate adhesion expected from plasma deposition. Three examples will be presented illustrating chemical control with special application to biomaterials. (1) Poly(N-isopropyl acrylamide) (pNIPAM) exhibits a solubility transition at 32 Â°C in an aqueous environment. When grafted onto a solid substrate, the pNIPAM phase transition produces a "smart" surface with strongly varying physical properties switchable with small temperature changes. Cells adhere and grow on ppNIPAM at 37Â°C and detach from the surface at room temperature. The ppNIPAM surfaces are non-toxic and excellent for cell growth. A microheater array can spatially control cell attachment to a ppNIPAM-treated chip. This suggests possibilities for cellomic and proteomic devices. (2) Since plasma environments destroy complex biomolecules, a new instrument has been constructed that combines electrospray ionization with plasma treatment of surfaces to produce a fast, efficient, flexible means to treat the surfaces of biomaterials with active biomolecules. The system has been successful in depositing intact, chemically bound hyaluronic acid (HA) onto plasma-activated stainless steel surfaces. (3) Poly(L-lactic acid) (PLLA) has been widely applied in tissue engineering scaffolds or for delivery of bioactive molecules, as it breaks down in the body to lactic acid, a component of the normal metabolism The pulsed plasma deposition techniques has been used to form thin PLLA coatings using cyclic lactide monomer. Such films degrade in a phosphate buffer solution.

9:00am **BI+PS-FrM3 Investigation of Organic Monomers in Plasma-induced Chemical Micropatterning*, G.Sh. Malkov,*** *M.L. Godek, D.W. Grainger, E.R. Fisher,* Colorado State University

Plasma-enhanced chemical vapor deposition (PE-CVD) of organic films is a valuable technique for the surface modifications of polymeric biomaterials. Recently, plasma-based methods have been developed for the fabrication of chemical micropatterns, which have a number of applications, including production of multianalyte biosensors, diagnostic tests, DNA microchips, and genomic arrays. The generation of micropatterns by means of the plasma deposition of organic compounds through a transmission electron microscope (TEM) grid mask has been reported.@footnote 1@ Here, we have created various high fidelity micron-scale patterns of different chemistries using inductively coupled pulsed RF plasma deposition through a TEM grid with the following monomers: acrylic acid, N-vinyl-2-pyrrolidinone, 2-hydroxyethyl methacrylate, N-vinylformamide, allylamine, and hexylamine on PS coated with plasma deposited, highly hydrophobic fluorocarbon materials. SEM images of the patterned surfaces will be demonstrated. Physico-chemical properties of deposited polymeric materials were characterized using angle-resolved XPS, FTIR, spectroscopic ellipsometry, and static contact angle measurements on unpatterned samples, which were plasma treated under identical plasma conditions. Directed cell attachment studies have also been performed. NIH 3T3 fibroblast cells were used to test the cell adhesion and viability on the various patterned surfaces. PS coated with FC is biologically inert: cells do not adhere on this surface. In contrast, cells proliferate well on surfaces functionalized with organic monomers. Other cell culture experiments and biomolecule patterning will be discussed. @FootnoteText@@footnote 1@ N.A. Bullet, R.D.Short et al. Surface and Interface Analysis. 2001, 31, 1074-1076.

9:20am **BI+PS-FrM4 Combining Pulsed RF Plasma Polymer Coatings with Avidin-Biotin Chemistry for On-Probe Affinity Capture Mass Spectrometry*, G.R. Kinsel,*** *M. Li, R.B. Timmons,* University of Texas at Arlington

Matrix assisted laser desorption / ionization mass spectrometry (MALDI-MS) has become a powerful analytical tool for the characterization of proteins. As the effectiveness of the MALDI method has advanced, the need for high-speed isolation and purification of targeted proteins in complex mixtures (e.g. culture media, serum or urine) has increased. The approach described in this presentation focuses on the use of RF plasma polymer coated MALDI probes as platforms for introduction of avidin/biotin chemical modifications. Pulsed RF plasma deposition of allyl amine or vinyl carboxylic acid directly on the MALDI probe surface is used to produce amine modified and carboxylic acid modified surfaces, respectively. Control of the functional group density is achieved through changes in the duty cycle of the pulsed RF plasma. Both amine and carboxylic acid functionalized plasma polymer modified probe surfaces have been investigated as platforms for attachment of avidin or biotin. Testing of the surfaces for peptide/protein isolation based on the targeted properties is performed using various laboratory prepared control mixtures and mixtures obtained from biological sources. In all cases selective capture of the targeted protein/peptide was evaluated through the acquisition MALDI mass spectra using a Bruker BiFLEX linear MALDI TOFMS or a laboratory-constructed linear MALDI TOFMS. Data has been obtained from both avidin and biotin surfaces demonstrating the efficacy of these modified MALDI probe surfaces for achieving on-probe bioselective isolation of target compounds.

9:40am **BI+PS-FrM5 Chemical Modifications of PVC Endotracheal Tubes by RF-Oxygen Glow Discharge Pre-functionalization and NaOH/AgNO@sub 3@ Wet Treatments to Reduce Bacterial Adhesion*, D.J. Balazs,*** *K. Triandafillu,* Swiss Federal Inst. of Tech., Switzerland*; P. Wood,* Univ. Hospital of Geneva, Switzerland*; Y. Chevolot,* Goemar Laboratories, France*; C. van Delden,* Univ. Hospital of Geneva, Switzerland*; H. Harms, C. Hollenstein, H.J. Mathieu,* Swiss Federal Inst. of Tech., Switzerland

The use of silver as an antibacterial agent can be traced back to ancient times, and is currently used in several medical applications.@footnote 1@ Bacterial colonization of intubation tubes is responsible for 90% of all nosocomial pneumonia cases, 40 % of which lead to death, despite aggressive antibiotic therapy.@footnote 2@ We have developed an approach based on the surface modification of medical grade poly(vinyl chloride) (PVC) to create an anti-colonization surface, rich in silver ions. The modification consists of an oxygen plasma treatment, followed by a two step wet treatment in sodium hydroxide (NaOH) and silver nitrate (AgNO@sub 3@) solutions. XPS analysis and contact angle measurements were used to investigate the chemical nature and surface wettability of the films following each step of the modification. Saponification with NaOH of esters, like those of PVC plasticizers was determined to be a simple, irreversible method of hydrolysis, producing sodium carboxylate and phthalate salts. Following a subsequent in incubation in the AgNO@sub 3@ solution, XPS showed evidence of a replacement reaction that produced a surface rich in silver ions. The potential of wet treatments that incorporate silver as a germicidal agent was demonstrated in bacterial and biofilm studies, using various P. aeruginosa strains. The native and O@sub 2@ pre-functionalized PVC surfaces submitted to the wet treatments exhibited a

100% reduction in initial bacterial adhesion. The efficacy of the wet treatment to reduce colonization over a longer period was demonstrated as 7-logarithmic drop in biofilm population at 24h and an 8-logarithmic reduction at 72 h, as compared to native PVC substrates. @FootnoteText@@footnote 1@ R.O. Darouiche, (1999) Clin. Infect. Dis. 29, 1371-1377. @footnote 2@ J.L. Vincent, D.J. Bihari, et al., (1995) JAMA 274: 639-644. .

10:00am **BI+PS-FrM6 PECVD Growth and Ion Beam Modification of Polymer Films with Patterned Surface Charge Properties***, **A. Valsesia**, M. Manso, G. Ceccone, D. Gilliland, F. Rossi,* Joint Research Centre, Ispra, Italy

The performance of polymer films in biomedical devices such as DNA arrays and other biosensors depends greatly on the ability to control their surface properties. In fact, surface features determine the ability of the polymer to immobilize a target biomolecule or to give this molecule an orientation towards adsorption. Plasma enhanced chemical vapor deposition (PECVD) of Polymers is an attractive way to produce this kind of films due to the high rate of functional groups obtained at energies ensuring film stability. The density of functional groups can be modified by an Ion Beam Modification. If this last treatment is performed through a mask, the surface remains with regions expressing different responses to chemical groups and environmental free charges (i.e. ions in solution). In this work we have studied the properties of two polymers with contrasted surface charge behavior. Allylamine (AlA) and Acrylic Acid (AcA) films were studied in parallel by Fourier transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) outlining the changes occurred during plasma polymerization and ion beam modification. These spectroscopic results were correlated with wetting and surface charge behavior by performing contact angle and Z-potential measurements. Their stability and ability for protein adsorption was evaluated by using a quartz crystal microbalance (QCM-D). The possible interference with topographic features has been tested by observing the films in an atomic force microscope, which was further used to monitor electric fields in buffer solutions. From these results we conclude that the combination of PECVD and ion beam modification is an effective way for the growth of polymer films with controlled properties for bio-sensing applications.

10:20am **BI+PS-FrM7 Growth of Biodegradable Thin Films by Methods of Pulsed Laser Deposition***, **J.M. Fitz-Gerald**, A.L. Mercado, L. Zhigilei, R. Johnson, C.L. Fraser,* University of Virginia*; J.D. Talton,* Nanotherapeutics, Inc.

Poly(DL-lactide-co-glycolide) (PLGA) is a biodegradable polymer with application in many areas of biomedical field ranging from contact lenses to sustained drug release formulation. In this research thin films (25 nm - 5 microns) of PLGA were deposited onto Si and NaCl wafers, in addition, a specific class of particulate materials (inhaled steroids) ranging from 1-5 microns in size were coated for in-vitro testing. All coatings were processed by both conventional pulsed laser deposition (PLD) and matrix-assisted pulsed laser evaporation (MAPLE) techniques. Film morphology, chemical structure, and decomposition effects were characterized by scanning electron microscopy (SEM), Fourier transform infrared infrared spectroscopy (FTIR), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and in-vitro dissolution.

10:40am **BI+PS-FrM8 Study of RGD Peptide and Fibronectin Adsorption on Polymer Surfaces Micropatterned by Cold Plasma and Ion Beams***, **C. Satriano**,* University of Catania, Italy*; M. Manso,* Joint Research Centre, Ispra, Italy*; N. Giamblanco,* University of Catania, Italy*; G. Ceccone, D. Gilliland, F. Rossi,* Joint Research Centre, Ispra, Italy*; G. Marletta,* University of Catania, Italy

Thin films of polycaprolactone (PCL) and polyhydroxymethylsiloxane (PHMS) were patterned by Ar@super +@ ions beams or cold microwave Ar plasmas through Ni masks. The dimensions of the patterns stripes and pitches were typically between 30 and 100 µm. In the case of Ar@super +@ irradiation, the two ion energies of 50 keV and 0.5 keV were used, with fluences ranging from 1x1014 to 5x1015 ions/cm@super 2@. For plasma irradiation, the samples were placed on a grounded or RF biased sample holder (-50V), for different times. The surface structure and composition changes were characterized by spatially resolved X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface roughness on the micro- and nanometer scale was determined by Atomic Force Microscopy (AFM). The surface charge and dispersive/polar forces distribution were determined by Zeta Potential (ZP) and Surface Free Energy (SFE) measurements respectively. Finally the change of thickness and visco-elastic properties of the films was investigated by the Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) technique. The adsorption of RGD peptide sequences and fibronectin was investigated as a function of the different treatment parameters, including ion energy and dose. The in-situ kinetics of adsorption and modeling of the viscoelastic properties of the adsorbed layers were studied by using QCM-D technique, while the chemical structure and lateral distribution of the adlayers were characterized ex situ by Small Spot XPS, ToF-SIMS Imaging measurements and AFM. The results showed that selective patterning of the adsorbed peptide and fibronectin could be achieved mainly in connection with the polar to dispersive ratio of the surface free energy. In particular, the surface modification seems to affect also the morphology adlayers.

11:00am **BI+PS-FrM9 Chemical Modification of a Three-dimensional Tissue Engineering Polymeric Scaffold by Low-temperature Radio-frequency Plasma Treatment***, **S. Kumar**,* University of South Australia, Australia*; R.St.C. Smart,* University of South Australia*; D.J. Simpson,* University of South Australia and Seoul National University, Korea

The technique of low-temperature radio-frequency plasma has been employed for the chemical modification of Osteofoam, a three-dimensional polymeric (PLGA) tissue engineering scaffold material. The chemical modification in question was aimed at coating Osteofoam with a thin layer of silica, both on its surface as well as in its bulk. For this, Osteofoam cubes of dimensions 12 mm x 12 mm x 12 mm were treated with the plasma generated using tetraethoxysilane (TEOS) as the main precursor. The chemical modification thus achieved was investigated and quantified using the X-ray photoelectron spectroscopy technique, revealing the presence of silica both on the surface as well as in the bulk of Osteofoam samples. The XPS data also suggest that the plasma process developed and employed by us is relativley more efficient at modifying the sample surface than its bulk.

11:20am **BI+PS-FrM10 Deposition of Amine Containing Films from Hyperthermal Silazane and Allyl Amine Ions***, A. Choukourov, H. Biederman,* Charles University, Czech Republic*; E. Fuoco, S. Tepavcevic, **L. Hanley**,* University of Illinois at Chicago

Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces. We have previously shown that fluorocarbon and siloxane ions can be employed for the growth and modification of organic thin films on polymer, semiconductor, and metal surfaces.@footnote 1-3@ These films are often similar in chemical composition to plasma polymers, due at least in part the presence of large, hyperthermal positive ions in many plasmas. This work deposits beams of mass-selected 5 - 200 eV silazane and allyl amine ions onto aluminum and silicon substrates. Silazane and allyl amine ions are produced by electron impact ionization of 1,3-divinyltetramethyldisilazane and allyl amine, respectively. These ion-deposited films are analyzed by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy. Chemical functionalization prior to XPS analysis permits the unique identification of primary and secondary amine groups. Secondary amine containing films are shown to form at low silazane ion energies whereas the higher ion energies lead to formation of more inorganic, silico-carbo-nitride-like films. Primary amines are produced by allyl amine ions at various energies. Films grown by allyl amine ion deposition are compared with those produced by plasma polymerization of allyl amine. Effects of film aging in air are also discussed. @FootnoteText@ @footnote 1@L. Hanley and S.B. Sinnott, Surf. Sci. 500, 500 (2002). @footnote 2@P.N. Brookes, S. Fraser, R.D. Short, L. Hanley, E. Fuoco, A. Roberts, and S. Hutton, J. Elec. Spect. Rel. Phenom. 121, 281 (2001).@footnote 3@E.R. Fuoco and L. Hanley, J. Appl. Phys. 92, 37 (2002).

11:40am **BI+PS-FrM11 Plasma Chemistry of Allylamine for the Deposition of Nitrogen-Containing Organic Films***, **D.C. Guerin**,* Naval Research Laboratory, National Research Council*; V.A. Shamamian, R.T. Holm,* Naval Research Laboratory

We studied the chemistry of an allylamine/argon plasma for the deposition of nitrogen-containing organic films. We used in situ mass spectrometry to determine the identity of the molecular ion flux to the deposition surface. Our investigation showed that under the span of powers interrogated (30-100 W) the identity of the ion flux did not substantially change. The total ion current to the deposition surface increased linearly with plasma power. However, the molecular ion mass distribution changed with the plasma pressure. In lower-pressure plasmas, the predominant ions were generated by electron-impact ionization reactions. At higher pressures ions generated by ion-molecule reactions dominate the flux to the surface. We used appearance potential mass spectrometry to confirm the creation of NH@sub 3@ as a by-product of the ion-molecule reactions. The resulting films were characterized optically. The deposition rates were highly dependent on the plasma power. However, the indicies of refraction were similar for the conditions studied. Infrared spectroscopy of the films showed that different plasma conditions resulted in only small changes in film structure. We determined that the film deposition mechanism was not controlled by plasma-ion chemistry. This contrasted with earlier results involving a saturated monomer. However, the film structure was highly dependent on the film thickness. The N-H signal increased greatly in the thicker films. Fluorescamine tagging of the amine groups in the films showed that the primary amine concentration was not well correlated to the intensity of the N-H stretch in the infrared spectra.

Magnetic Interfaces and Nanostructures
Room 316 - Session MI+SC-FrM

Semiconductor Spin Injection

Moderator: S.A. Chambers, Pacific Northwest National Laboratory

8:20am **MI+SC-FrM1 Ferromagnetic Nano Fe-Germenide Particles in MBE-grown Ge-Fe*, R. Goswami,*** Geo-Centers Inc.*; G. Kioseoglou, A.T. Hanbicki, B.T. Jonker, G. Spanos,* Naval Research Laboratory

Ferromagnetic-semiconductors (FMSs) have attracted considerable attention due to the coexistence of semiconductor properties and long-range ferromagnetic (FM) order in these materials. Recently, ferromagnetic order was reported in alloy thin films based on Ge, which provides a simple host lattice to explore the fundamental origins of FM order. A relatively high Curie temperature,120 K, has been experimentally observed in a Ge-3.3at.% Mn film grown epitaxially on GaAs. It has been theoretically predicted very recently that Ge with Fe atoms in the lattice will be ferromagnetic semiconductors and the Curie temperature will increase as a function of Fe concentration. To date, relatively little attention has been paid to understanding the fine scale microstructural evolution within Ge-Fe thin films. It is well known that the microstructure plays a vital role in dictating the ferromagnetic properties. Fe-Ge contains different phases with magnetic properties ranging from ferromagnetic Fe to antiferromagnetic FeGe@sub2@. The purpose of the present investigation is to elucidate the phase transformations and overall microstructural evolution in epitaxial Ge- 4at.% Fe thin films deposited on (100) GaAs substrates at three different temperatures, 150°, 250° 400 ° C, in order to better understand magnetic properties in these materials. The equilibrium phases at this composition (4%Fe) are Ge with negligible amount of Fe and antiferromagnetic FeGe@sub2@. We have observed for all cases that nano-particles of ferromagnetic- Fe@sub3@ Ge@sub2@ form uniformly in a crystalline Ge-matrix. The particle size was observed to decrease with the substrate temperature. We demonstrate that a supersaturated Ge-Fe solid-solution forms initially from the vapor phase resulting in the solid state precipitation of this metastable ferromagnetic- germanide. This work was supported by the Office of Naval Research and DARPA.

8:40am **MI+SC-FrM2 Epitaxial Ferromagnet on Ge(111)*, C. Zeng,*** The University of Tennessee*; J.R. Thompson,* The University of Tennessee and Oak Ridge National Laboratory*; L.C. Feldman,* Vanderbilt University and Oak Ridge National Laboratory*; S.C. Erwin,* Naval Research Laboratory*; H.H. Weitering,* The University of Tennessee and Oak Ridge National Laboratory

The difficulty of injecting spin-polarized electrons into a semiconductor is a major bottleneck in spintronics research. There are two ways to realize spin injection. One of these is to fabricate a ferromagnetic-metal/semiconductor heterostructure; the other is to use a dilute magnetic semiconductor (DMS) as the spin aligner. The former method does not work well, mainly because of the large conductivity mismatch between the ferromagnetic metal and semiconductor. The latter method is limited by the low Curie temperature, T@sub c@ of DMS. We have developed a novel interface with good potential for spin injection, namely an epitaxial ferromagnetic Mn@sub 5@Ge@sub 3@ film on Ge(111). The Mn@sub 5@Ge@sub 3@ films are fabricated by depositing Mn and subsequent annealing, or by codeposition of Mn and Ge. Mn@sub 5@Ge@sub 3@(001)//Ge(111) epitaxy relationship is verified by X-ray diffraction results, due to the small lattice mismatch. STM images display (@sr@3x@sr@3)R30° honeycomb structure, which perfectly agrees with the theoretical image of the Mn terminated Mn@sub 5@Ge@sub 3@ (001) surface. RBS and ion-channeling experiments confirmed the stoichiometry and epitaxy of the film. Magnetic measurements reveal a T@sub c@ of about 295 K. The easy axis is in-plane which is most likely due to the shape anisotropy. The multiplet splitting of the Mn 3s core level in XPS indicates an average magnetic moment of 2.6 µ@sub B@ per Mn atom, which is in almost perfect agreement with the spin-resolved band structure calculations and SQUID measurements. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

9:00am **MI+SC-FrM3 Tunnel Spin Injection from a Ferromagnetic Metal into a Semiconductor Heterostructure*, A.T. Hanbicki,*** *O.M.J. van 't Erve, R. Magno, G. Kioseoglou, C.H. Li, R.M. Stroud, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, R. Mallory, M. Yasar, A. Petrou,* SUNY at Buffalo **INVITED**

Significant effort has been made to incorporate ferromagnetic metals into semiconductor spintronic devices because they offer high Curie temperatures, low coercive fields, and a ready source of spin polarized electrons. Recently it has been shown that the key to efficient spin injection from a metal into a semiconductor heterostructure is a sufficient interface resistance.@footnote 1@ Tunnel barriers have been a common way of satisfying this criterion, and there are a number of recent experimental successes with Schottky contacts, thin metal oxides, and AlAs. We will review the state of the art of spin injection from an Fe Schottky contact into an AlGaAs/GaAs spin-LED. A Schottky barrier at the Fe/AlGaAs interface can serve as an effective tunnel contact if the doping profile of the semiconductor near the interface is engineered to produce a narrow depletion width. In this system, we have successfully injected polarized electrons and obtained electron spin polarizations ranging from 13% to 32% in the GaAs QW,@footnote 2@ where quantum selection rules directly link the measured circular polarization and the electron spin population. We report here recent efforts to characterize transport properties and the physical structure of this interface, and correlate them with the measured spin polarizations. To determine the dominant transport mechanism, we have analyzed the transport process using the Rowell criteria. The parabolic G-V curves and the temperature dependence of the zero-bias resistance demonstrate that single step tunneling is the dominant transport mechanism. The I-V data show a clear zero-bias anomaly and phonon signatures providing further evidence for tunneling. Preliminary data suggest that roughness and Fe segregation at the spin injecting interface suppresses spin injection. @FootnoteText@ This work was supported by the DARPA SpinS program and ONR@footnote 1@E.I. Rashba, PRB 62 (2000)@footnote 2@A.T. Hanbicki, et al., APL 80 (2002); APL 82 (2003).

9:40am **MI+SC-FrM5 Spin Injection Across (110) Interfaces: Fe/GaAs(110) Quantum Well Spin-LEDs*, C.H. Li,*** *A.T. Hanbicki, G. Kioseoglou, O.M.J. van 't Erve, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, R. Mallory, M. Yasar, A. Petrou,* SUNY Buffalo

Spin-LEDs can be used to reliably measure spin injection efficiency via the quantum selection rules subject to the limits imposed by the ratio of spin to radiative lifetimes. However, to date they have been implemented only in (001) oriented GaAs or InGaAs quantum wells (QWs), where the spin lifetime is shorter, resulting in an underestimate of spin injection efficiency. Recent work has shown that the spin lifetime is longer in (110) GaAs QWs, and increases with temperature.@footnote 1@ In this study we investigate spin injection in (110) oriented spin-LED QW structures to take advantage of this, and to explore the effects of band structure and the non-polar interface on spin injection. AlGaAs/GaAs LEDs have been grown on (110) substrates by molecular beam epitaxy at 450 oC and an As/Ga flux ratio of 20. Atomic force microscopy shows excellent surface morphology with a RMS roughness less than 0.5 nm. Photoluminescence is dominated by the QW excitonic emission with a linewidth of 8 meV. Initial electroluminescence results using a tailored Fe Schottky tunnel barrier injector show that a 10% spin polarization in the GaAs QW has been achieved due to injection across the Fe/AlGaAs(110) interface. The temperature dependence of the polarization, as well as comparison with (001) oriented samples and first principles theory will be presented. @FootnoteText@ Supported by DARPA, ONR, and NSF. @FootnoteText@@footnote 1@Y. Ohno et. al., PRL 83, 4196 (1999).

10:00am **MI+SC-FrM6 Electrical Spin Injection from Ferromagnetic Metal/Tunnel Barrier Injectors into AlGaAs/GaAs Quantum Well Structures*, X. Jiang,*** Stanford University*; R. Shelby,* IBM Almaden Research Center*; R. Wang,* Stanford University*; R. Macfarlane,* IBM Almaden Research Center*; G. Solomon, J. Harris,* Stanford University*; S. Parkin,* IBM Almaden Research Center

Electrical injection of highly spin-polarized electrons into semiconductors is an essential component for the operation of spintronic devices. In this talk, we present a study of electrical spin injection into semiconductors from injectors comprised of ferromagnetic metals and tunnel barriers. An AlGaAs/GaAs quantum well structure is used to optically detect the spin-polarization of the injected electrons in the semiconductor. Large polarization of the electroluminescence from the quantum well is observed. The bias dependence and temperature dependence of the electroluminescence polarization will be discussed. This work is supported by DARPA.

10:20am **MI+SC-FrM7 Efficient Electrical Spin Injection in GaAs: A Comparison Between Different Spin Sources*, P. Van Dorpe*, *V.F. Motsnyi, Z. Liu, W. Van Roy, G. Borghs, J. De Boeck,* IMEC, Belgium **INVITED**

Electrical spin injection in semiconductors remained elusive for a long time. Recently however, break-throughs have been accomplished in the field. It appeared that tunnel injection of spin polarized electrons from ferromagnetic metals provides an efficient way for spin injection, even at room temperature. We will quantitatively compare different spin sources for spin injection in GaAs, based on tunnel injection from ferromagnetic materials. The injected spin polarization is assessed in a (Al,Ga)As-based spin-LED, using the Oblique Hanle Effect@footnote 1@ as the analysis technique. The first material combination that we successfully applied for spin injection is a CoFe/AlOx based tunnel injector where the AlOx provides a stable tunnel barrier between the ferromagnetic material and the GaAs. We have shown injected spin polarizations which exceed 24% at 80K and 12% at room temperature.@footnote 2@ A second spin source we examined uses the native Schottky barrier between GaAs and an epitaxially grown ferromagnetic metal as tunnel barrier. NiMnSb, MnAs and MnSb have been used and will be compared for their spin injection properties. Finally the results of electron spin injection from a (Ga,Mn)As-based Zener diode will be discussed. The spin polarized holes in (Ga,Mn)As are transferred to electrons in GaAs by Zener tunnelling and create a spin polarization in GaAs of at least 50% at LHe temperature. The results on electrical spin injection regularly show an interesting dependence on the applied bias. This dependence will be shown and discussed in terms of doping and band structure. @FootnoteText@@footnote 1@V.F. Motsnyi et al, Appl. Phys. Lett. 81, 265 (2002) @footnote 2@P. Van Dorpe et al, Jpn. J. Appl. Phys., Part 2 42, L502 (2003) Acknowledgements : SPINOSA (IST-2001-33334), FENIKS(GR5D-CT-2001-00535).

11:00am **MI+SC-FrM9 Electrical Spin Injection from a Ferromagnetic Metal Into a Semiconductor: Schottky vs Al@sub 2@O@sub 3@ Tunnel Barriers*, O.M.J. van 't Erve*,** *A.T. Hanbicki, C.H. Li, G. Kioseoglou, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, R. Mallory, M. Yasar, A. Petrou,* SUNY Buffalo

Efficient injection of spin-polarized electrons from a metal into a semiconductor requires a high resistance interface contact such as a tunnel barrier.@footnote 1@ The natural Schottky tunnel barrier which forms at the Fe/AlGaAs interface provides highly efficient spin injection, and a polarization of more than 32% has been measured in a GaAs quantum well detector.@footnote 2@ The pseudo-triangular shape and high interface doping level of the Schottky tunnel contact are factors which are quite different from those encountered for the canonical rectangular barrier typically formed from Al@sub 2@O@sub 3@. It is therefore of interest to compare the characteristics and performance of an Al@sub 2@O@sub 3@ tunnel barrier with the Fe/AlGaAs Schottky barrier in essentially identical MBE-grown device structures. The Al@sub 2@O@sub 3@ barrier is formed on top of an AlGaAs/GaAs spin-polarized light-emitting diode (spin-LED) by multi-step in situ natural oxidation of thin evaporated Al layers. A ferromagnetic metal layer is evaporated on top of this tunnel barrier and provides the spin-polarization of the injected electrons. We measure the spectral features, intensities and polarization of the electroluminescence from the surface emitting spin-LEDs, and compare these directly with similar data for the Fe Schottky contact and with literature to obtain insight into various aspects of the spin injection process. @FootnoteText@ This work was supported by the DARPA SpinS program, ONR, and NSF. @footnote 1@ E. I. Rashba, Phys. Rev. B 62, R16267 (2000).@footnote 2@ A.T. Hanbicki et al, Appl. Phys. Lett. 82 (9 June 2003).

11:20am **MI+SC-FrM10 Electrical Spin Injection from CdCr@sub 2@Se@sub 4@ into AlGaAs/GaAs Spin-LED*, G. Kioseoglou*,** *A.T. Hanbicki, C.H. Li, O.M.J. van 't Erve, R. Goswami, G. Spanos, B.T. Jonker,* Naval Research Laboratory*; R. Mallory, M. Yasar, G. Itskos, A. Petrou,* SUNY at Buffalo

Ferromagnetic semiconductors (FMS) provide an opportunity to control spin dependent behavior and study spin injection and transport in semiconductor heterostructures. Much of the effort has focused on III-Mn-V p-type FMS, where the ferromagnetism is mediated by holes. Since electron transport is the basis for high frequency and low power operation, an n-type FMS grown epitaxially on a device quality substrate is especially attractive. Recent work demonstrated epitaxial growth of n-type CdCr@sub 2@Se@sub 4@, a chalcogenide spinel FMS, on GaAs(001) and GaP(001).@footnote 1@ The measured conduction band offsets indicate a staggered band alignment conducive to electron transport from the CdCr@sub 2@Se@sub 4@ into the AlGaAs.@footnote 2@ We present here spin polarized electron injection from CdCr@sub 2@Se@sub 4@ into an AlGaAs/GaAs LED structure. The circular polarization due to spin injection from the CdCr@sub 2@Se@sub 4@ reaches a maximum value of 6% at B = 0.5T, and mimics the hard axis magnetization determined by SQUID magnetometry measurements. In contrast to previously studied ZnMnSe and Fe contacts in which injection of predominantly m@sub j@ = -1/2 electrons was observed, for CdCr@sub 2@Se@sub 4@ the majority of the injected electrons are in the m@sub j@ = +1/2 state. TEM reveals that the existing interfaces are highly defected, a factor known to limit spin injection.@footnote 3@ Efforts to increase the spin injection efficiency are focused on improving the interface, the contact resistance and electrical properties of CdCr@sub 2@Se@sub 4@. Ga, an n-type dopant in CdCr@sub 2@Se@sub 4@, was introduced in a @delta@-doping configuration, and results on new LED structures with improved electrical characteristics and interface morphology will be presented. @FootnoteText@ This work was supported by DARPA SpinS program, ONR, and NSF. @footnote 1@Y.D. Park et al., Appl. Phys. Lett. 81, 1471 (2002). @footnote 2@H.B. Zhao et al, Appl. Phys. Lett. 82, 1422 (2003). @footnote 3@R. Stroud et al, Phys. Rev. Lett. 89, 166602 (2002).

11:40am **MI+SC-FrM11 Chemical Intermixing and Spin Injection in Fe/AlGaAs Schottky Barrier SpinLEDs*, R.M. Stroud*,** *A.T. Hanbicki, G. Kioseoglou, O.M.J. van Erve, C.H. Li, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, R. Mallory, M. Yasar, A. Petrou,* SUNY Buffalo

Injected spin polarizations ranging from 13% to 32% have been measured for Fe/AlGaAs Schottky barrier spin-polarized light emitting diodes spinLEDs.@footnote 1@ Transmission electron microscopy studies of these devices show evidence for diffusion of the Fe into the underlying AlGaAs. High-resolution images indicate an expansion of the AlGaAs (100) plane spacing near the interface by up to 15% and a change in contrast. The Fe diffusion is confirmed by energy-dispersive x-ray spectroscopy and Z-contrast imaging. The thickness of the intermixing region estimated from lattice images inversely correlates with the injected spin polarization, ranging from 0.8 nm +/- 0.3 nm for the 32% spin polarization sample up to 1.6 nm +/- 0.3 nm for the 13% spin polarization sample. Spin scattering in this intermixing region may explain the reduction in the injected spin polarization. This work was supported by ONR and the DARPA SpinS program. @FootnoteText@ @footnote 1@Hanbicki, et al., APL 80 (7): 1240-1242 (2002).

Nanometer Structures
Room 317 - Session NS+BI-FrM

Nanotechnology and Biology

Moderator: R.J. Hamers, University of Wisconsin-Madison

9:40am **NS+BI-FrM5 Interaction of Fluorescent Molecules with Metallic Nanoparticles Mediated by Biospecific Interactions*, V.H. Perez-Luna*,** *K. Aslan, I. Severcan,* Illinois Institute of Technology

Metallic nanoparticles affect the emission characteristics of fluorophores located in their proximity. Here we exploit this strong influence in a system where gold nanoparticles are functionalized with biotin. Preparation of biotinylated gold nanoparticles is performed in the present of a nonionic surfactant to ensure their stability. The interaction of these biotinylated gold nanoparticles with Alexa488-labeled anti-biotin in solution was studied by optical absorption spectroscopy and fluorescence spectroscopy. It was found that reduction or enhancement of fluorescence emission could result when Alexa488-labeled anti-biotin interacted with biotinylated gold nanoparticles. This depended on the surface coverage of biotin groups, the concentration of antibody and the concentration of biotinylated gold nanoparticles. Introduction of soluble biotin to dissociate the bound antibodies from the surface of the nanoparticles reversed the signals observed previously. These observations can be explained in terms of the competing effects that metallic nanoparticles can have on emission of fluorescence. Quenching of fluorescence can occur when the fluorophores are in close proximity to the metallic surfaces. However, metallic nanoparticles can also enhance the excitation intensity due to concentration of the incident field in the vicinity of the nanoparticles.

Additionally, metallic surfaces can also provide additional pathways for radiative decay of the fluorophores. These concepts will have important implications for novel materials in fluorescence detection.

10:00am **NS+BI-FrM6 Real-Time, Label Free Biosensing using Immobilized Gold Nanoparticles: Influence of Nanoparticle Size on Sensor Performance***, **N. Nath**, A. Chilkoti,* Duke University

We recently demonstrated a label-free optical sensor to quantify biomolecular interactions in real-time that exploits the surface plasmon resonance effect exhibited by noble metal nanoparticles (nanoSPR). The sensor monitors changes in the extinction spectrum of a monolayer of gold nanoparticles on glass as a function of biomolecular binding. We have previously shown that 13 nm diameter gold nanoparticles can monitor the binding of streptavidin to biotin with a detection limit of 16nM. The performance of the biosensor is controlled by the size, shape and dielectric constant of the metal nanostuctures, and their interparticle spacing. As a first towards optimization of the nanoSPR sensor, we investigated the size of gold nanoparticles on sensor performance. Monodisperse gold nanoparticles were chemically synthesized with diameters ranging from 12 nm to 50 nm. The extinction spectrum of the monolayers of gold nanoparticles of all sizes exhibited both a red shift as well as an increase in the extinction at peak wavelength as a function of bulk solution refractive index. However, sensitivity, defined as change in extinction per unit change in bulk refractive index, increases with an increase in particle size and reaches a maximum value of 1.42 for a particle size of 39 nm. Second, the sensing volume of the immobilized gold nanoparticles, defined as the distance from the surface within which a bulk refractive index change will result in a change in the optical signal, increases with particle size and peaks for 39 nm diameter nanoparticles. Based on these results, an optimized sensor was fabricated using 39 nm gold nanoparticles, and its detection limit for biotin-streptavidin binding was found to be ~1 nM. NanoSPR on a chip is attractive for biosensing because of simple solution based assembly and ability to measure extinction spectrum using widely available UV-vis spectrophotometers.

10:20am **NS+BI-FrM7 Ultrasensitive Nanowire Sensor for Drug Discovery and Medical Diagnostics***, **W. Wang**,* Harvard University

Semiconductor nanowires represent a novel class of nanostructured materials with a wide range of future applications from molecular electronics to biotechnology. Using appropriate fabrication procedures, our group has previously demonstrated that field-effect transistors (FETs) made from p-type Si nanowires possess electronic characteristics exceeding that of conventional planar devices. This outstanding electronic property makes nanowire FETs ideal transducers in a sensor system with label-free, real-time detection capability. Furthermore, sensors made from Si nanowires offer additional advantages over other type of sensors including the ease to differentially modify many nanowires for multiplexed sensing, the potential to be very small and inexpensive, and most importantly the unparalleled extreme sensitivity to the point where single molecule detection is possible. With successful chemical modification to covalently immobilize biological receptors onto the surface of nanowires, we showed that a nanowire FET can be configured into a nano-scale sensor and the binding of charged ligands to the receptors generates specific electrical responses in a quantitative manner. We first applied this strategy to develop a sensitive detector for prostate cancer by measuring the levels of PSA, a marker for prostate cancer. The sensor was shown to detect PSA as low as 0.025 pg/ml (7fM). In addition to medical diagnostics, the combined advantages of label-free detection and extreme sensitivity offer a unique opportunity to configure the nanowire sensors into a drug discovery platform. Using Abl kinase/ATP/Gleevec as a model pathological system (in chronic myeloid leukemia), we have demonstrated the possibility to visualize drug action, or small molecule/protein interactions in real time. Lastly, because of the high sensitivity inherent to the nanowire sensors, individual binding/unbinding events of single molecules can be resolved electrically.

10:40am **NS+BI-FrM8 Nanopores in Ultrathin MOS-compatible Membranes for Electrical Detection of DNA***, **T. Kim**, J. Heng, V. Dimitrov, C. Ho,* University of Illinois at Urbana-Champaign*; A. Kornblit, F. Klemens, J. Miner, W. Mansfield, C. Pai, T. Sorsch,* New Jersey Nanotechnology Consortium*; G. Timp,* University of Illinois at Urbana-Champaign

We are developing a revolutionary type of silicon integrated circuit that incorporates MOS technology with an on-chip nano-pore mechanism for directly sensing the electrical activity of bio-molecules such as ions, proteins or DNA. The electronic detection of biological analytes could have several advantages over the conventional scheme, fluorescent microscopy, which is used so prevalently in biology to discriminate the experimental outcomes. For example, if each analyte has a characteristic signature, then an electronic biosensor could facilitate the analysis of the data by eliminating the need for sensitive dyes, thereby improving the dynamic range for detection. We have recently discovered a method to produce ~1-2nm diameter pores (a size comparable to the secondary structure of a protein) in membranes made from materials such as Si, SiO@sub 2@, and Si@sub 3@N@sub4@ that are compatible with MOS fabrication technology. We have adopted this method to create nano-pores spanning a high quality ~2-5nm thick SiO@sub 2@ membrane that constitutes part of the gate electrode in a Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET) amplifier. Here, Hwe report on the fabrication of nanometer-scale pores in MOS compatible materials using a high voltage, tightly focused electron beam, and on time-resolved measurements of the transport of 100bp to 1500bp DNA through a range of pore diameters (2-8nm) and membrane thicknesses (2-30nm).

11:00am **NS+BI-FrM9 Electrically Switchable Nanostructured Superhydrophobic Surfaces***, **J.A. Taylor**,* New Jersey Nanotechnology Consortium*; T.M. Schneider, S. Yang,* Bell Laboratories, Lucent Technologies*; A. Kornblit,* New Jersey Nanotechnology Consortium*; T.N. Krupenkin,* Bell Laboratories, Lucent Technologies

Dynamically switchable nanostructured surfaces are investigated. Behavior of liquids on these surfaces is studied both experimentally and theoretically. Three major states of a liquid drop on these surfaces are demonstrated. The states include highly mobile rolling ball, immobile droplet, and complete wetting state. The transitions between these states were dynamically induced by applying a voltage between a liquid and a nanostructured substrate. Droplet contact angle was measured as a function of applied voltage and nanostructured layer geometry. The obtained results show quadratic dependence of the cosine of the contact angle on voltage, which is in good agreement with the typical electrowetting behavior. The details of interaction of liquids with the nanostructured layer were investigated using SEM technique. The proposed approach potentially allows novel methods of manipulating microscopically small volumes of liquids. This includes essentially frictionless liquid transport, the ability to selectively immobilize the droplets at any given time or position, as well as dynamic control over the penetration on liquids through the nanostructured layer. The obtained results potentially open new and exciting opportunities in microfluidics, chemical microreactors, bio/chemical detection, thermal management of microelectronics, bio-optics, and many other areas.

11:20am **NS+BI-FrM10 Engineering Information Processing in Biological Systems***, **R.H. Blick**,* University of Wisconsin-Madison **INVITED**

The key aspect of this work is to present methods for understanding and engineeringinformation processing in nanoscale biological systems. The systems we are focusing on are nanometer-sized ion channels integrated in high frequency circuits. The ion channels are embedded in bilipid membranes, which are brought to microstructured glass chips for direct transport measurements. Recording the passage of ions is successfully performed and first results on high-frequency response are shown.

Plasma Science and Technology
Room 315 - Session PS-FrM

Plasma-Surface Interactions: Etching

Moderator: H. Blom, Uppsala University, Sweden

8:20am **PS-FrM1 Multidimensional Plasma Sheaths and Resulting Ion/Fast Neutral Distributions on the Substrate Surface***, **D.J. Economou**, D. Kim,* University of Houston

Multidimensional plasma sheaths are encountered in diverse processes including plasma immersion ion implantation, extraction of ions (or plasma) through grids, MEMS fabrication, neutral beam sources, and plasma contact with internal reactor parts (e.g., wafer chuck edge). The sheath may become multidimensional when: (a) plasma is in contact with surface topography, and the size of the topographical features is comparable to the plasma sheath thickness, or (b) the surface is flat but inhomogeneous, i.e., a conducting surface next to an insulating surface. In either case, the flux, energy and angular distributions of energetic species incident on the substrate are of primary importance. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface. A two-dimensional fluid/Monte Carlo simulation model was developed to study multidimensional sheaths. The radio frequency (RF) sheath potential evolution, and ion density and flux profiles over the surface were predicted with a self-consistent fluid simulation. The trajectories of ions and energetic neutrals (resulting by ion neutralization on surfaces or charge exchange collisions in the gas phase) were then followed with a Monte Carlo simulation. Ion flow and energy and angular distributions of ions and energetic neutrals bombarding a surface with a trench will be reported in detail and compared with experimental data. Results for a flat but inhomogeneous surface will also be reported. @FootnoteText@ Work supported by the National Institute of Standards and Technology, National Science Foundation and Sandia National Laboratories.

8:40am **PS-FrM2 Study of Gas Phase Fluorocarbon Chemistries in a Modified Gaseous Electronics Conference Plasma Reactor Using Fourier Transform Infrared Spectroscopy and Ellipsometry***, **B. Zhou**, E.A. Joseph, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

Fluorocarbon chemistries of CF@sub 4@ plasmas during dry etching are studied in the modified Gaseous Electronics Conference (mGEC) Reference cell, using Fourier Transform Infrared (FTIR) spectroscopy. These measurements are enhanced by the use of a multi-pass White cell with capabilities up to 40 passes. The flexible design of the mGEC reactor allows us to study the effect of the dimensions, materials and wall conditions of a plasma reactor on the gas phase and surface phase chemistries, as well as the interactions between them. Three sets of inner walls with diameters of 20.3, 40.6, and 61 cm are used and the wall temperature can be raised above 100°C. The gap between the quartz window and chuck can be varied from 2.7cm to 18 cm. For a 5 cm gap, the IR spectra show that the concentrations of CF@sub 2@ and CF@sub 3@ radicals and etch products such as SiF@sub 4@ and COF@sub 2@, are strongly dependent upon the bias voltage. The concentration of CF@sub 2@ radicals is raised by about an order of magnitude to 10@sup 13@ cm@sup -3@ when the chuck self-bias voltage is changed from 0 to -40V. In addition, the concentration ratio of CF@sub 2@ to CF@sub 3@ increases as the bias voltage is made more negative due to an increased etch rate and increased consumption of F atoms. These gas phase measurements will also be compared with etch rate measurements using in-situ spectroscopic ellipsometry. Finally, the experimental data will be compared with simulation results using HPEM.@footnote 1@ This work is supported by a grant from NSF/DOE, CTS-0078669. @FootnoteText@ @footnote 1@ D. Zhang and M. J. Kushner, "Surface Kinetics and Plasma Equipment Model for Si Etching by Fluorocarbon Plasmas", J. Appl. Phys. 87, 1060 (2000).

9:00am **PS-FrM3 Measurement and Modeling of Plasma Feature Etching***, **H.H. Sawin**[1],* Massachusetts Institute of Technology **INVITED**

This paper reviews the progress in the understanding of plasma surface interactions. The understanding of the surface kinetics of plasma surface interactions is critical in the efficient development of plasma processes. Our fundamental understanding of plasma-surface interactions has in large part been based on beam experiments in which the flux from a plasma process is synthesized by a combination of beams. The use of beams rather than a plasma source allows the independent control of the beam fluxes. The measurement of polysilicon etching in fluorine and chlorine plasmas has been particularly successful because of its relatively simple discharge chemistry; however, the inclusion of product and polymer deposition during the etching process has typically not been included in kinetic models. The etching of dielectric materials with fluorocarbon gases is much more complex because of the large number of ions and neutral species that must be considered. The use of beams generated from complex plasmas that produce multiple products can be used to better represent the fluxes; however, these studies sacrifice some independence in the control of the fluxes. Based on the kinetic measurements and kinetic models developed from the beam studies, feature profile evolution has been modeled using several approaches, especially Monte Carlo techniques that allow the inclusion of all known kinetics. Deposition processes in which the surface is covered with a material of a single composition is particularly easy as the surface chemistry is does not vary with time or feature position. In etching processes, the surface kinetics are known to be a function of the composition of the feature position and is more complicated since the surface composition varies. In addition, for the deposition of “polymer film” onto the surface during etching to be included for direction etching processes, the polymer film thickness and composition must be tracked as the simulation proceeds.

9:40am **PS-FrM5 The Influence of Ion Implantation on the Poisoning Mechanism During Reactive Magnetron Sputtering***, **D. Depla**, R. De Gryse,* University Ghent, Belgium

During reactive sputter deposition, the interaction of the plasma with the target surface strongly influences the deposition process and the deposited layer characteristics. Besides chemisorption of the active species on the target surface, reactive ions become implanted in the target subsurface region. An analytical model is proposed describing the effect of ion implantation on the poisoning mechanism during reactive magnetron sputtering. We assume that the target can be described by a mixture of the original target material and the compound material formed by reactive ion implantation. The target is subdivided into three regions :i) the surface region, ii) the subsurface region and iii) the bulk region. The sputter removal of the compound material from the target surface region is balanced by the compound formation by reactive ion implantation in the subsurface and bulk region. The steady-state solution shows a small but abrupt change of the deposition rate. The abrupt change in deposition rate is accompanied by a much larger abrupt change of the target condition in the subsurface region. Moreover, a narrow hysteresis region is found. Several experimental results can be easily explained from this analytical model. As this analytical approach neglects several aspects of the sputtering process, e.g. knock-on effects, recoil mixing, range shortening, we have also simulated this process using TRIDYN. More specific, the influence of reactive ion implantation during the reactive sputtering of Al in Ar/O2 is simulated.@footnote 1@ The results of these simulations confirm not only the basic ideas described by the analytical model, but a quite good agreement between both models is found. @FootnoteText@ @footnote 1@Z.Y. Chen, A. Bogaerts, D. Depla, I. Ignatova, Nucl. Instr. And Meth. B, accepted for publication.

10:00am **PS-FrM6 The Role of Chamber Dimension in Fluorocarbon Etching of SiO@sub 2@ and its Effects on Gas and Surface-Phase Chemistry***, **E.A. Joseph**, B. Zhou, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas - Dallas*; B.E. Gnade,* University of North Texas

The influence of plasma-wall interactions in a CF4 discharge and their symbiotic effect on processing of SiO2 has been explored as a function of chamber dimension using a modified gaseous electronics conference (mGEC) reference cell. By varying chamber wall diameter, 20-66 cm, and source-platen distance, 4 - 6 cm, the etch behavior of SiO2 and the resulting gas-phase chemistry change significantly. Results from in-situ spectroscopic ellipsometry show significant differences in etch characteristics, with etch rates as high as 700nm/min and as low as 150nm/min for the same self-bias voltage. Etch yields however remain unaffected by the chamber size variations. Fluorocarbon deposition rates are also highly dependent on chamber dimension and vary from no net deposition to deposition rates as high as 450 nm/min. Significant shifts in gas-phase properties such as electron density and electron temperature, as determined by Langmuir probe, are also measured while gas-phase in-situ multi-pass Fourier Transform Infra-Red spectroscopy (FTIR) is used to corrleate CF2, CF3 and CF4 gas-phase densities to CFx overlayer thickness and stoichiometry measured by x-ray photoelectron spectroscopy (XPS) and grazing angle total internal reflection (GATIR-FTIR). @FootnoteText@ This work is supported by a grant from NSF / DOE, CTS-0078669.

10:20am **PS-FrM7 Molecular Dynamics Simulations of Silicon in Fluorocarbon Plasmas: Role of the Fluorocarbon Film as an Etchant Source***, **D. Humbird**, D.B. Graves,* University of California at Berkeley*; X. Hua, G.S. Oehrlein,* University of Maryland, College Park

We use MD simulations to examine fluorocarbon (FC) ions and radicals impacting Si and compare these simulations to new experimental results. During FC plasma etching of Si, Oehrlein and coworkers observe changes in surface chemistry as ion energy is increased above the threshold necessary for etching, and/or when a large fraction of the impinging ions are Ar@super +@. The F/C ratio of the film decreases and Si-C, C-C, and Si-F bonds all increase in number with the onset of etching. These results were interpreted to mean that F is driven from the FC film into the underlying Si, creating etch products. In simulations of Si etching with CF@sub x@@super +@ species with and without Ar@super +@, we observe a change in the composition of the FC film as the ion energy increases from a depositing to an etching level. The FC film formed at lower energy is comprised almost entirely of C-F@sub x@ groups. At higher energy (>50 eV), Si etching commences, C-F@sub x@ groups are greatly reduced, and SiF@sub x@ bonds form. The FC film becomes stratified, with Si-C at the surface of the film, and Si-F (the etch precursor) underneath. These results are in excellent agreement with XPS measurements of Si samples etched by FC plasmas. Oehrlein and co-workers concluded from their measurements

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[1] **AVS 50th Anniversary Invited Speaker**

that the FC film contains the etchant F. The simulations confirm that F can reach the Si by way of the FC film. We identify the mechanisms for ion-induced redistribution of F between the FC film and substrate.

10:40am **PS-FrM8 Surface Kinetics Study of Silicon Oxide Etching with Fluorocarbons Plasmas***, **O Kwon**, H.H. Sawin,* Massachusetts Institute of Technology

Fluorocarbon plasma for silicon oxide etching is a complicated system involving many ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity to photoresist. For a better understanding of the process it is necessary to have an appropriate physical model to describe the surface kinetics including simultaneous etching and deposition. We developed a surface kinetic model using ABACUSS II, a modeling environment and simulator. In the modeling we included the effect of both neutral and ion fluxes to the surface, sticking probabilities, surface composition, sputter etching reactions, ion enhanced chemical etching reactions and neutral-to-ion flux ratio. We demonstrated this model by applying it to various systems such as silicon etching with chlorine/fluorine plasma, silicon oxide etching with chlorine/fluorine plasma and silicon oxide etching with fluorocarbon plasma. This model was verified using measured etching yield data determined by quartz crystal microbalance (QCM) in conjunction with plasma neutral and ion concentrations/fluxes determined by mass spectrometry.

11:00am **PS-FrM9 Integrated Modeling of Etching, Cleaning and Barrier Coating PVD for Porous and Conventional SiO@sub 2@ for Fluorocarbon Based Chemistries@footnote 1@***, **A. Sankaran**, M.J. Kushner,* University of Illinois at Urbana-Champaign

The modeling of process integration of advanced materials for interconnect wiring can provide insights to methods to optimize the process. This is particularly true for nontraditional materials, such as porous silica. In this work we discuss the modeling of the process integration steps of etch, clean and barrier coating for porous SiO@sub 2@ using a feature profile simulator coupled to a plasma equipment model. Results will be discussed for ICP and MERIE reactors for etching of conventional and porous SiO@sub 2@ for C@sub 2@F@sub 6@, CHF@sub 3@ and C@sub 4@F@sub 8@ in mixtures with Ar and O@sub 2@. The etch step is followed by the stripping of the residual fluorocarbon polymer layer and of the photoresist. The cleaned features then receive a barrier coating by IMPVD. Etch rates and profiles for interconnected and closed pore networks will be presented. In general, larger molecular weight fluorocarbon gases produce more polymerizing fluxes to the substrate leading to thicker polymer films and hence slower etch rates. Polymer build-up due to opening of large pores and interconnected pore networks leads to slower etching. Increasing O@sub 2@ during the etch step reduces polymer buildup but also erodes the photoresist, resulting in less taper (possibly bowing) due to the broader view angles of the incident ion fluxes. Removal of polymer from the pores during the clean step, particularly when interconnected, is problematic. Conformal metal films (for the barrier layer) on porous substrates are more difficult to achieve for larger pores and higher interconnectivities due to shadowing of ion fluxes caused by the complex pore morphology. @FootnoteText@ @footnote 1@ Work supported by Semiconductor Research Corporation SEMATECH and National Science Foundation.

11:20am **PS-FrM10 Analysis of ILD Sidewall Damage during Photoresist Removal Post Single and Dual Damascene Processing***, **N.C.M. Fuller**, T.J. Dalton, M.E. Colburn, S.M. Gates,* IBM T.J. Watson Research Center*; R. Dellaguardia,* IBM Microelectronics Division

The introduction of CVD and SOD low-@kappa@ organosilicate (OSGs) materials for 90 nm and beyond CMOS back end of the line (BEOL) technologies presents several process challenges. One such challenge is the minimization of ILD sidewall damage during photoresist removal post single and dual damascene processing. The determination of the composition, thickness, and probable mechanism of formation of the damaged layer is critical to its control, prevention, and/or removal and, thus, device performance, functionality, and reliability. To these ends, experimental measurements including XPS and TEM/EELS were performed to characterize the damaged layer formed on an OSG and a porous OSG material exposed to various strip chemistries in a commercial plasma etching tool. These results will be presented.

Semiconductors
Room 321/322 - Session SC+NS-FrM
Low Dimensional Structures and Amorphous Silicon

Moderator: A.C. Gossard, University of California, Santa Barbara

8:20am **SC+NS-FrM1 Self-Organized Template Formation for Quantum Dot Ordering***, **R. Noetzel**,* Eindhoven University of Technology, The Netherlands **INVITED**

The realization of semiconductor quantum dot arrays and networks in well-defined lateral arrangements is essential for the development of future quantum functional devices. We have successfully created these kinds of networks by self-organized anisotropic strain engineering of (In,Ga)As/GaAs templates for the ordering of InAs quantum dots by local strain recognition: On GaAs (100) substrates, during molecular beam epitaxy of a strained (In,Ga)As/GaAs superlattice, elongated (In,Ga)As quantum dots develop into very uniform and long quantum wire arrays with a well-defined lateral periodicity. Quantum wire formation relies on the anisotropic adatom surface migration and In desorption during annealing of the layers of elongated quantum dots after capping with a thin GaAs layer. The accumulation and improvement of the uniformity of the generated anisotropic strain field in superlattice growth provides a well-defined template for the ordering of InAs quantum dots grown on top in one-dimensional arrays. On high-index GaAs (311)B substrates, strain induced growth instability of (In,Ga)As layers occurs to from a matrix of closely packed cells. The related strain distribution constitutes a uniform template for the full control of InAs quantum dot nucleation in a two-dimensionally connected network. Excellent structural perfection and optical properties are established for these ordered InAs quantum dot arrays by atomic force microscopy, high-resolution X-ray diffraction, and photoluminescence spectroscopy. Temperature dependent photoluminescence measurements reveal efficient carrier transfer from the templates, which themselves are distinct one- and zero-dimensional quantum nanostructure arrays, to the quantum dots and within the quantum dot arrays. Hence, self-organized anisotropic strain engineering provides a unique route for the realization of well-defined and functional quantum dot arrays and networks of high quality.

9:00am **SC+NS-FrM3 Self-Assembly of Nanostructures in GaAs/InAs and GaAs/GaSb Multilayer Structures***, **C.A. Pearson**, C. Dorin, J. Mirecki Millunchick, Y. Chen, B.G. Orr,* University of Michigan, Flint

Reproducibly obtaining regular arrays of phase-separated material is a promising way to acquire low dimensional structures such as quantum dots or wires. Short period superlattice (SPS) structures, where each layer is approximately one or two monolayers thick, can spontaneously phase separate under certain growth conditions resulting in compositional modulations. The appearance of lateral composition modulation is correlated to roughening of the surface front. To further elucidate this progression, in situ scanning tunneling microscopy (STM) was used to examine SPS structures at integral and fractional periods, where one period consists of 2 monolayers (ML) of GaAs followed by 2 ML of InAs or GaSb. For both integral and fractional periods, the surfaces are quite distinct. The as-grown InAs surface is decorated with anisotropic islands that exhibit a (2x4) reconstruction upon a terrace with a (nx3) reconstruction. The GaAs terminated surfaces are characterized by flat mesa structures surrounded by deep trenches. With increasing number of periods, both surfaces evolved towards greater long scale roughness. Furthermore, the islands (InAs terminated) or trenches (GaAs terminated) become larger and show a preferential lateral arrangement with a characteristic separation in the [110] direction of ~20 nm, which corresponds to the modulation wavelength observed using other techniques. Similar results are also observed in the GaAs/GaSb structure where islanding of GaAs is observed in a GaSb matrix. These results are consistent with continuum perturbation models that predict the coupling of morphological and compositional instabilities under the appropriate circumstances.

9:20am **SC+NS-FrM4 Tuning of the Electronic Properties of Self-assembled InAs/InP(001) Quantum Dots by Rapid Thermal Annealing and Low-energy Ion Implantation***, **C. Dion**,* École Polytechnique de Montréal, Canada*; C. Nì Allen, S. Raymond, P.J. Poole,* National Research Council, Canada*; F. Schiettekatte,* Université de Montréal, Canada*; R.A. Masut, P. Desjardins,* École Polytechnique de Montréal, Canada

We have investigated the effect of post-growth rapid thermal annealing on the low temperature photoluminescence (PL) spectra of self-assembled InAs/InP(001) quantum dots (QD) grown by chemical beam epitaxy (CBE) and metal-organic vapor phase epitaxy (MOVPE). Annealing temperatures

T@sub a@ and times t@sub a@ ranged from 650 to 800 °C and 30 to 210 s, respectively. As-grown samples are characterized by a broad emission peak centered near 800-900 meV arising from the e1-hh1 transition of an ensemble of QDs and a narrow peak near 1100 meV from radiative recombination in the wetting layer. Detailed analysis of the QD PL emission reveals that it is composed of up to 9 peaks corresponding to families of dots emitting at different energies. A blueshift of the QD transitions, resulting from intermixing, is observed upon annealing. It increases with T@sub a@ and t@sub a@; blueshifts of up to 90-100 meV are obtained for annealing time of 210s at 800 °C. While the PL emission energies of the various QD families shift at different rates upon annealing, their width remains constant. This behavior is consistent with inhomogeneous broadening dominated by monolayer height fluctuations in InAs/InP(001) dots. In order to obtain larger blueshifts, we studied the effect of introducing point defects into thick InP cap layers, either by growing InP at low temperature or by implanting P at energies sufficiently low to insure that the InAs QDs are not damaged. Such point defects, located far from the QDs, dramatically increase diffusion rates; shifts of up to 250 meV have been obtained following annealing at 765 °C for 90 s.

9:40am **SC+NS-FrM5 Anisotropic Stress Relaxation and Ordering of InAs/GaAs Quantum Dot Superlattices***, **W. Ye**, M. Reason, X. Weng, R.S. Goldman,* The University of Michigan

Recently, self-assembled quantum dot (QD) superlattices (SLs) have shown significant promise for a wide range of electronic and optoelectronic device applications. In general, self-assembled QD formation is driven by the elastic relaxation of stress via island nucleation. The vertical stacking of QDs is often explained by the preferred nucleation of islands at strain energy minima directly above buried dots. However, the mechanisms of lateral ordering of QD arrays are the subject of continued debate. For example, anisotropic lateral alignment of QDs has been observed in a number of materials systems. A significant remaining question concerns the relative effects of buffer layer patterning and anisotropic stress relaxation on this lateral QD alignment. Therefore, we have examined the patterning effects of buffer layers, as well as the stress relaxation process during the growth of stacked QDs. Our QD SLs consisted of 2.6 ML InAs and 5 nm GaAs grown by molecular beam epitaxy at 500°C. Prior to QD deposition, GaAs buffer layers were grown at 580°C and/or 500°C. During QD growth, reflection high energy electron diffraction (RHEED) reveals a streaky to spotty pattern transformation, typical of the Stranski-Krastanov (S-K) growth mode transition. However, simultaneous wafer curvature measurements using multi-beam optical stress sensor (MOSS) reveal that stress relaxation occurs after the S-K growth mode transition is complete. Ex-situ atomic force microscopy measurements indicate a preferential alignment of QDs along the [-110] direction. This anisotropic alignment is enhanced as the number of SL periods increases and may be due to pre-patterning by the 500°C buffer layer. We will discuss the relative roles of buffer layer patterning and anisotropic stress relaxation on QD ordering. This work was supported in part by DOE (Photovoltaics Beyond the Horizon Program), ARO (MURI Program), and NSF (Nanoscale Exploratory Research Program).

10:00am **SC+NS-FrM6 Ge Island Nucleation on Large-Miscut Si(001) Surfaces***, **K. Ohmori**, Y.L. Foo, S. Hong, J.G. Wen, J.E. Greene, I. Petrov,* University of Illinois at Urbana-Champaign

We study self-organized growth of Ge nanostructures on Si surfaces with large off-[001]-axis miscut as a function of the tilt angle @theta@ and in-plane azimuth angle @phi@ with respect to the [100] direction. The off-axis surfaces were fabricated using focused ion beam (FIB) to precisely pattern a variety of structures such as trenches, concave cones, and square-pyramids on Si(001) surfaces. During the FIB processing, the Si(001) substrates were covered with 200-nm-thick protective SiO@sub 2@ films. A 50-nm-thick Si buffer layer was grown at 800°C by ultrahigh vacuum gas-source molecular beam epitaxy using Si@sub 2@H@sub 6@ precursor prior to Ge deposition at 600°C using Ge@sub 2@H@sub 6@. The nominal thickness of the Ge layer is about 7 ML. Diverse Stranski-Krastanov growth modes (Ge domes, elongated islands, and nanowires) were observed as a function of @theta@ and @phi@, which we attribute to differences in anisotropic-strain relief mechanism. While on a vicinal (001) surface (@theta@ = 0.3°), dome-shaped Ge islands with a density of 30.9 µm@super -2@ are formed, the island density increases by 30% on a surface with @theta@ = 5° for all @phi@-values . In the range of @theta@ = 10 to 20°, elongated island shapes emerge in directions near @phi@ = 45 n° (n = 1, 3, 5, 7), while at @phi@ = 90 n° (n = 0, 1, 2, 3) island nucleation is suppressed. With @theta@ @>=@ 25°, Ge nanowires with a length of about 2 µm are formed on planes with @phi@ = 45 n° ± 15° (n = 1, 3, 5, 7).

10:20am **SC+NS-FrM7 Bond-Centered Hydrogen in Amorphous Silicon: New Infrared Studies***, **J.-F.T. Wang**,* Vanderbilt University*; G. Lüpke,* The College of William and Mary*; L.C. Feldman, N.H. Tolk,* Vanderbilt University

Recent infrared absorption spectroscopy measurements taken at 77 K on initially hydrogen free amorphous silicon following hydrogen implantation at low temperature, exhibit an absorption line associated with the bond-centered (BC) hydrogen local vibration stretching mode at 1993 cm-1. This line, newly observed in amorphous silicon, appears at the same wavelength seen in crystal silicon following hydrogen implantation at LN temperatures.@footnote 1,2@ These results indicate that the bond-center (BC) hydrogen defect structure can form in amorphous silicon as well. The experimental data give insight into recent molecular dynamic simulations involving hydrogen's role in the amorphous-to-nanocrystalline phase transition in amorphous silicon.@footnote 3@ In both the crystalline and amorphous case, the 1993 cm-1 line disappears when the samples are annealed to room temperature. However only in the crystalline silicon case does the migrating hydrogen reappear in other IR-active defect sites.@footnote 1,2@ @FootnoteText@ @footnote 1@M. Budde, G. Lüpke, C. Parks Cheney, N. H. Tolk, and L. C. Feldman, Phys. Rev. Lett. 85, 1452 (2000). @footnote 2@B. Holm, K. Bone Nielsen, and B. Bech Nielsen, Phys. Rev. Lett. 66, 2360 (1991). @footnote 3@Saravanapriyan Sriraman, Sumit Agarwal, Eray S. Aydil & Dimitrios Maroudas, Nature (London) 418, 62 (2002).

Surface Science

Room 327 - Session SS1-FrM

Catalysis IV: Reactivity of Complex Systems

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am **SS1-FrM1 Surface Chemistry of Carburization and Embrittlement of Fe***, **D.E. Jiang**[1], E.A. Carter,* University of California, Los Angeles

High temperature and pressure, as well as reactive gases such as CO and H@sub 2@S, erode steel. Experimental observations of eroded steel show that carburization and embrittlement are potential causes for the erosion. We investigate the surface chemistry behind this problem via spin-polarized periodic density functional theory. In this talk, we will discuss C and H adsorption on Fe(110) and C and H diffusion into and through bulk Fe. Static properties including site preference, solution enthalpies, and adsorption energies, are predicted with increasing system size and compared with experiment. For adsorption, different 2-dimensional structures will be compared. Barriers for diffusion of C and H into and through bulk Fe will be presented. Our predictions generally agree very well with experiment, though we do make some predictions which suggest further experimental studies. C and H show very different behavior both in bulk Fe and on Fe(110). For example, H prefers the tetrahedral site in bulk Fe, while C prefers the bulk octahedral site. H prefers the quasi three-fold site on Fe(110), while C prefers the long bridge site. Our study provides a clear picture of structures and energetics of C and H in bulk Fe and on Fe(110).

8:40am **SS1-FrM2 Surface Science Studies of Tungsten Carbides as Potential Electrocatalysts***, **M.B. Zellner**, H.H. Hwu, J.G. Chen,* University of Delaware

The purpose of this research is to examine the feasibility of tungsten carbides as direct methanol fuel cell (DMFC) and hydrogen fuel cell electrocatalysts. The motivation to study tungsten carbides stems from the fact that current fuel cells require the use of Pt/Ru anodes, which are expensive and easily poisoned by CO. The successful development of tungsten carbide electrodes as Pt/Ru substitutes can therefore positively influence the commercialization of DMFC and hydrogen fuel cell systems. The reactions of CH@sub 3@OH, H@sub 2@O, H@sub 2@ and CO over tungsten carbide surfaces are studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Thus far, investigations on the C/W(111) and Pt/C/W(111) have been completed. The results show that the carbide surfaces possess characteristics critical to the potential application as DMFC and hydrogen fuel cell anodes. In particular, these surfaces are highly active toward the decomposition of CH@sub 3@OH and H@sub 2@O, and are able to desorb CO at relatively low temperatures. In order to bridge the materials gap from model surfaces to realistic systems, thin films of WC and W@sub 2@C have been deposited on carbon paper and glassy carbon substrates by

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

means of PVD to be tested as electrocatalysts for hydrogen oxidation. Electrochemical testing on the PVD electrocatalysts is currently underway.

9:00am **SS1-FrM3 Chemical Properties of Bimetallic and Metal Carbide Surfaces by Theoretical and Experimental Studies***, **J.R. Kitchin**, M.A. Barteau, J.G. Chen,* University of Delaware

The optimal catalyst balances the adsorption energies of all surface species involved, ensuring adequate concentrations of important intermediates, while preventing poisoning by strongly bound intermediates. Multi-component catalysts, such as transition metal carbides and bimetallic catalysts, are one solution to these problems, as the adsorption properties of molecules can be tuned by the composition of the catalyst. However, it is difficult to know a priori how the chemical properties of a particular carbide or bimetallic catalyst will be modified relative to the parent metals. Advances in Density Functional Theory (DFT) now allow many of these systems to be explored from first principles with desktop computers. We have used DFT to calculate electronic properties and adsorption energies of small molecules and atoms on idealized bimetallic and carbide catalyst surfaces. These electronic properties were then used to establish correlations with experimental data and the calculated adsorption energies. For example, we calculated the electronic structure and adsorption energy of H atoms (HBE) on 13 different monolayer, bimetallic catalyst surfaces and showed a near linear correlation between the calculated HBEs and the surface d-band center of the catalyst. We have calculated the surface d-band centers of more than 25 other monolayer, bimetallic combinations and some carbide surfaces. Using the HBE/d-band correlation established above we could use these calculations to predict promising new bimetallic catalysts with desirable H and CO binding energies. These correlations, along with a growing database of calculated d-band centers for bimetallic and carbide catalysts, should be considered a starting point for the rational design of bimetallic and carbide catalysts with desired chemisorption properties.

9:20am **SS1-FrM4 HREELS Measurements of Iodine Vibrations on Cu(111) and Cu(221)***, **D. Sung**, A.J. Gellman,* Carnegie Mellon University

Density functional theory calculations have shown that iodone atoms adsorb at the tops of the step edges on stepped Cu single crystal surfaces. In order to try to corroborate this prediction, we have measured and compared vibrational frequencies of iodine atoms adsorbed on the flat Cu(111) surface and the stepped Cu(221) surface using High Resolution Electron Energy Loss Spectroscopy (HREELS). Energy losses at 136 cm@super -1@ and 235 cm@super -1@ are observed on both surfaces. We assign these two frequencies to in-plane and out-of-plane vibrations of iodine on the (111) terrace sites. On a stepped surface one would expect the in-plane mode perpendicular to the step edge to be higher in frequency than the in-plane mode on the Cu(111) surface, if the atom is adsorbed at the bottom of the step edge. It would be expected to appear at a lower frequency if the atom is adsorbed at the top of the step edge. On the Cu(221) surface, an additional peak appears at 80 cm@super -1@, corresponding to the vibration of iodine adsorbed on the step edges of Cu(221). The fact that this new mode is at a lower frequency than the in-plane mode on the Cu(111) surface is consistent with the expectation that the iodine atom is adsorbed at the top of the step edge. The experimental results are consistent with the theoretical prediction that iodine atoms adsorb at the top of the step edges on the Cu(221) surface.

9:40am **SS1-FrM5 Elucidating the Origin of Low-Temperature Reactivity of the Ni-Pt Bimetallic System***, **N.A. Khan**, J.G. Chen,* University of Delaware

Bimetallic surfaces possess unique physical, chemical and electronic properties unlike those of either parent metal. These surfaces have generated considerable interest as novel catalytic materials with higher reactivities and selectivities. As catalysts, they are used in numerous applications, such as fuel cells, hydrotreating (bimetallic sulfides and carbides) and hydrogenation catalysts. In our research, we have studied the Ni/Pt(111) and Pt/Ni(111) model bimetallic systems. We have found that the 1 ML Ni/Pt(111) surface demonstrates a low-temperature hydrogenation reaction pathway not present on either pure metal surface. DFT and LEIS studies indicate that this reaction pathway may be a result of Ni diffusing into the Pt(111) subsurface layers. In order to further study the interaction between Pt and Ni and the chemical properties of these bimetallic surfaces, we have also investigated the low-temperature reaction pathway on Pt/Ni(111). TPD studies reveal that the hydrogenation chemistry on the 1 ML Pt/Ni(111) surface is almost identical to that of the 1 ML Ni/Pt(111), revealing that the chemistry is independent of the order of metal deposition, i.e. Ni/Pt(111) or Pt/Ni(111). We will also demonstrate the strong correlation between model Ni-Pt surfaces and supported Ni-Pt bimetallic catalysts.

10:00am **SS1-FrM6 Surface Reactions of Co-Adsorbed CH@sub 2@I@sub 2@ and CF@sub 3@I on Ag (111)***, **K. Adib**, H. Piao, J. Hrbek,* Brookhaven National Laboratory*; W. Huang, J.M. White,* University of Texas at Austin

Synchrotron X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) have been used to study the surface reactions of sequentially coadsorbed CH@sub 2@I@sub 2@ and CF@sub 3@I on Ag (111). When adsorbed separately on Ag (111), CH@sub 2@I@sub 2@ and CF@sub 3@I molecules undergo C-I bond cleavage at temperatures as low as 100 K to produce adsorbed CH@sub 2@ and CF@sub 3@, respectively, as well as I adatoms. In the case of CH@sub 2@I@sub 2@, upon subsequent thermal annealing of the surface, the dissociatively adsorbed CH@sub 2@ fragments may subsequently recombine and desorb primarily as C@sub 2@H@sub 4@. In the case of sequential co-adsorption in the submonolayer regime, the CF@sub 3@ and CH@sub 2@ fragments recombine to desorb as CF@sub 2@CH@sub 2@. Synchrotron XPS results indicate the presence of a surface bound species formed recombinatively in the temperature range of 200-250 K confirming that the CF@sub 2@CH@sub 2@ desorption is a two-step process. The first step involves methylene insertion to produce a surface bound species (CF@sub 3@CH@sub 2@) that can be detected by XPS. The second step involves fluoride elimination and the desorption of CF@sub 2@CH@sub 2@ as detected by TPD.

10:20am **SS1-FrM7 Probing the Chemistry of CH@sub 3@I on Pt-Sn alloys***, **E.C. Samano**,* CCMC-UNAM, Mexico*; C. Panja, N.A. Saliba, B.E. Koel,* USC

Adsorption and reaction of CH@sub 3@I (methyl iodide) on Pt(111) and the (2x2) and (@sr@3x@sr@3)R30° Sn/Pt(111) surface alloys was investigated primarily by using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). CH@sub 3@I adsorbs molecularly on Pt(111) at 100 K, and 34 % of the adsorbed CH@sub 3@I monolayer decomposes during heating above 200 K in TPD. Competition occurs during heating within the chemisorbed layer between hydrogenation to produce methane and dehydrogenation that ultimately leads to adsorbed carbon. Alloying Sn into the Pt(111) surface decreases the heat of adsorption and the amount of decomposition of CH@sub 3@I. Alloyed Sn slightly reduces the CH@sub 3@I adsorption bond energy from 13.4 kcal/mol on Pt(111) to 11.4 kcal/mol on the (2x2) alloy with @theta@@sub Sn@ = 0.25 and 9.3 kcal/mol on the (@sr@3x@sr@3)R30° Sn/Pt(111) alloy with @theta@@sub Sn@ = 0.33. More notably, the Sn-Pt alloy surface strongly suppressed CH@sub 3@I decomposition. Only 4% of the adsorbed CH@sub 3@I monolayer decomposed on the (2x2) Sn/Pt(111) surface, and no decomposition of CH@sub 3@I occurred on the (@sr@3x@sr@3)R30° Sn/Pt(111) surface during TPD. Methane was the only hydrocarbon desorption product observed during TPD. These results point to the importance of adjacent "pure Pt" three-fold hollow sites as reactive sites for CH@sub 3@I decomposition. Finally, we note that CH@sub 3@I, and presumably the other short-chain alkyl halides, are not reactive enough on Pt-Sn alloys to serve as convenient thermal precursors for preparing species small alkyl groups such as CH@sub 3@(a) for important basic studies of the reactivity and chemistry of alkyl groups on Pt-Sn alloys. Another approach is required such as the use of a CH@sub 3@-radical source or non-thermal activation of adsorbed precursors via photodissociation or electron-induced dissociation (EID).

10:40am **SS1-FrM8 A Model Catalyst with Selectivity Controllable Functions: the Effects of Thickness Extensional Resonance Oscillation on the Catalytic Activities for Ethanol Decomposition of Thin AgAu Film Alloy Deposited on a Ferroelectric z-cut LiNbO@sub 3@ Crystal***, **N. Saito**, Y. Sato, Y. Yukawa, H. Nishiyama, Y. Inoue,* Nagaoka University of Technology, Japan

In an attempt to design a heterogeneous catalyst that has artificially controllable functions for catalytic reactions, we have employed the resonance oscillation (RO) of acoustic wave generated on a poled ferroelectric crystal and demonstrated that the thickness extension mode resonance oscillation (TERO) has the ability to change the reaction selectivity over thin metal catalysts deposited on a z-cut LiNbO@sub 3@ crystal.@footnote 1@ The effects of TERO are suggested to have strong influences on the electronic states of metal catalysts, and it is particular interesting to apply the TERO for alloy catalysts consisting of more than one component surface metal atom with different electronic structures. In the present study, we investigated the TERO effects on catalytic ethanol decomposition on AgAu alloy catalysts. The AgAu alloy catalysts were prepared by consecutive deposition of Au and Ag, followed by heat treatment at high temperature enough to allow the metal phases to diffuse and to uniformly mix each other. In catalytic run on a Ag catalyst, the TERO increased ethylene activity without changes in acetaldehyde, indicating that the TERO activate only ethylene production on a single Ag metal surface. On the other hand, the TERO with AgAu catalysts increased the activity for acetaldehyde significantly. The activity enhancement increased with increasing Au content, passed through a maximum at 80% and decreased sharply. Laser Doppler measurement showed that lattice displacement generated by the TERO became the smallest at the same Au content (80%) as that where the TERO effect on the activity for acetaldehyde was the highest. This indicates that the nature and strength of Ag-Au bonds plays in an important role in the TERO-induced activity enhancement. Similar results were also observed for AgCu alloys. The mechanism of different TERO effects between Ag and Ag-based metal alloys is discussed. @FootnoteText@ @footnote 1@ N.Saito and Y.Inoue, J.Phys.Chem.B, 107/9, 2040(2003).

11:00am **SS1-FrM9 Different Changes in Work Function of Low- and High-index Cu Surfaces with Lattice Displacement in Surface Acoustic Wave Propagation***, **H. Nishiyama**, N. Saito, Y. Inoue,* Nagaoka University of Technology, Japan

Surface acoustic wave (SAW) generated on a poled ferroelectric crystal by applying rf electric power has been demonstrated to markedly enhance the catalytic activity of thin polycrystalline metal (Ag, Pd, Ni, Cu) films for different kinds of the metal-catalyzed reactions such as ethanol decomposition, ethanol and CO oxidation. The enhancement of the catalytic activity and the changes in the selectivity with SAW suggest that the SAW could affect the work function of the catalyst metal surfaces. To confirm the view, in the present study, photoelectron emission spectroscopy (PEEM) was employed, since photoemission characteristics are directly related to the work function of the metal surfaces. Thin Cu metal films treated by either annealing or sputtering have been used, and their atomic scale surface structures were inferred by the characteristic CO stretch frequency obtained in infrared reflection absorption spectroscopy (IRAS). It was shown that annealing gave rise to a Cu(111)-like low index plane mainly, whereas sputtering produced a large density of step sites and high index planes such as (311) and (211). The different SAW effects on the low- and high-index Cu surfaces were observed: the SAW propagation decreased the PEEM intensity for the low-index plane such as Cu(111), whereas it increased the PEEM intensity for the high index planes and step sites. The results indicated that the SAW enhanced the work function of a densely packed Cu surface and reduced that of a less packed Cu surface with coordinatively-unsaturated metal atoms. Dynamic and vertical lattice displacement by SAW was proved to have prominent structure-sensitive effects enough to change the electronic structures of the metal surface.

Surface Science
Room 328 - Session SS2-FrM
Oxide Surfaces and Interfaces

Moderator: R.L. Kurtz, Louisiana State University

8:20am **SS2-FrM1 Desorption Induced by Electronic Transitions (DIET) from a Lunar Sample and a Model Mineral Surface****, **B.V. Yakshinskiy**, T.E. Madey,* Rutgers University

We report recent results on an investigation of source mechanisms for the origin of alkali and alkaline earth atoms in tenuous planetary atmospheres, with focus on non-thermal processes (photon stimulated desorption (PSD), electron stimulated desorption (ESD), and ion sputtering). Whereas alkaline earth oxides (MgO, CaO) are far more abundant in lunar samples than alkali oxides (Na@sub 2@O, K@sub 2@O), the atmosphere of the Moon contains easily measurable concentrations of Na and K, while Ca and Mg are undetected there; traces of Ca have recently been seen in the Mercury's atmosphere (10@super -3@ of Na). Our experiments have included ESD, PSD and ion sputtering of alkali atoms from model mineral surface (amorphous SiO@sub 2@) and from a lunar basalt sample obtained from NASA. A comparison is made between ESD and PSD efficiency of monovalent alkalis (Na, K) and divalent alkaline earths (Ba, Ca). We find that bombardment of the alkali covered surfaces by ultraviolet photons or by low energy electrons (E > 4 eV) causes desorption of "hot" alkali atoms. This results are consistent with the model developed to explain our previous measurements of sodium and potassium desorption from a silica surface:@footnote 1,2@ electron- or photon-induced charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. A two-electron charge transfer to cause desorption of divalent alkaline earth atoms is a less likely process. A striking reversible temperature-dependent variation of PSD and ESD yields of alkalis from the lunar sample is found; these data have important implications for models of tenuous planetary atmospheres. The data support the suggestion that PSD by UV solar photons is a dominant source process for alkalis in the tenuous lunar atmosphere. @FootnoteText@ * supported in part by NASA@footnote 1@ BVY TEM, Nature (1999) 400, 642@footnote 2@ BVY TEM, Surf. Sci.(2003) 528, 54.

8:40am **SS2-FrM2 Temperature Dependence of the Noncommutative Valence Band Offset at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@ Epitaxial Heterojunctions***, **J.R. Williams**, S.A. Chambers,* Pacific Northwest National Laboratory

The valence band discontinuity at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@ interfaces in epitaxial heterojunctions grown on @alpha@-Al@sub 2@O@sub 3@ (0001) substrate has been measured as a function of deposition temperature. A prior study, conducted at a given temperature, showed a noncommutative band offset of -0.3 ± 0.1 and +0.7 ± 0.1 eV in this system when the top layer is Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@ respectively. This was attributed to an interface dipole that presumably depends on the growth sequence. In this study deposition temperatures of 500°C to 850°C have been investigated, and preliminary results show that this noncommutative band offset is largely independent of deposition temperature. This is an unexpected result, as the interface dipole is expected to change with deposition temperature due to interfacial mixing. Specifically we find that the binding energy difference between the Cr 3p and Fe 3p shallow core levels remains at 11.85 ± 0.08 eV (12.36 ± 0.20 eV) for structures with Fe@sub 2@O@sub 3@ (Cr@sub 2@O@sub 3@) as the top layer, and that these values are independent of deposition temperature. RHEED analysis of these structures shows that in all cases the Fe@sub 2@O@sub 3@ layer is unstrained, while the Cr@sub 2@O@sub 3@ layer is strained to match the lattice parameter of Fe@sub 2@O@sub 3@. This work was supported by U.S. DOE BES Department of Chemical Sciences.

9:00am **SS2-FrM3 Electronic Structure at the Fe@sub 3@O@sub 4@/NiO Interface@footnote 1@***, **H.Q. Wang**, W. Gao, E.I. Altman, V.E. Henrich,* Yale University

The interfacial electronic structure between the metallic ferrimagnet Fe@sub 3@O@sub 4@ and the insulating antiferromagnet NiO has been investigated in the heteroepitaxial system Fe@sub 3@O@sub 4@ (100)/NiO (100) by growing from submonolayer to multilayer films of NiO (100) on single-crystal Fe@sub 3@O@sub 4@ (100) substrates. The lattice mismatch in this system is only 0.55 %, and excellent superlattice structures have been grown previously by other groups. The presence of tetrahedral Fe@super 3+@ ions lying above the plane of O anions and octahedral Fe cations on Fe@sub 3@O@sub 4@ (100) results in unusually short Fe-Ni cation-cation distances in the stoichiometric interface structure with rocksalt NiO. The Fe@sub 3@O@sub 4@ surface prior to growth is characterized by LEED, RHEED and STM; both the (1x1) and (@sr@2x@sr@2)R45° surface reconstructions have been studied. The NiO growth morphology is measured with STM. The electronic structure is monitored versus overlayer thickness by using UPS, XPS, Auger and EELS spectroscopies, which were chosen because they sample several monolayers (ML) into the substrate/overlayer structure. The overlayer thickness dependence of spectral features is then used to separate interfacial states from those of the substrate and the overlayer film. The evolution of the density-of-states in the O 2p-Fe 3d-Ni 3d band has been observed during the first few ML of NiO deposition. Changes occur across the entire band (from E@sub F@ to about 12 eV below E@sub F@). For NiO layers thicker than about 3 ML, the overlayer electronic structure is essentially that of bulk NiO. @FootnoteText@ @footnote 1@This research was partially supported by U.S. Department of Energy Grant DE-FG02-00ER45844; and NSF equipment grant DMR-0075824.

9:20am **SS2-FrM4 Understanding Fermi Level Pinning of SiO on GaAs(001)-(2x4)***, **D.L. Winn**, M.J. Hale, A.C. Kummel,* University of California, San Diego

Scientists have been trying to develop a metal oxide semiconductor field-effect transistor (MOSFET) with GaAs in an effort to reduce standby power and gate leakage. In order to fabricate this device, it is important to understand the chemistry and physics at the oxide/semiconductor interface. It has been reported that a common cause of Fermi level pinning is the liberation of As, resulting from oxides bonding to Ga atoms on the surface. This has been directly observed using STM to monitor the reactions of O and O@sub 2@ on GaAs(001)-(2x4). In contrast, we have shown that SiO pins the Fermi level but does not liberate As when it is deposited on the GaAs(001)-(2x4) surface. Scanning tunneling microscopy (STM) images show that SiO inserts into the As dimers. SiO bonds in both trough and row dimers with a very small minority of the SiO molecules inserting into As-Ga backbonds. Using scanning tunneling spectroscopy (STS), we have observed that ~5% of a monolayer of SiO pins the Fermi level on GaAs(100)-(2x4) at mid-band gap. This is consistent with the SiO absorbates withdrawing charge from the surface As atoms, causing charge on the As atoms to grossly deviate from the charge on bulk As atoms.

9:40am **SS2-FrM5 Surface Phase Transitions Upon Reduction of WO@sub 3@(100) Thin Films***, **M. Li**, E.I. Altman, A. Posadas, C.H. Ahn,* Yale University

The evolution of surface morphology and reconstructions induced by reducing epitaxial WO@sub 3@(100) thin films grown on LaAlO@sub 3@(100) was studied using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). When the WO@sub 3@(100) surface was annealed in either O@sub 2@ or NO@sub 2@ at 620 K, the surface was predominantly covered by a p(2x2) reconstruction with a low density of elongated (1x1) islands. Raising the annealing temperature to 800 K led to a net reducing environment even in the presence of O@sub 2@ or NO@sub 2@. Under these conditions, the surface was dominated by a two domain p(4x2)/p(2x4) reconstruction, although a few small patches of the p(2x2) surface could still be detected. Further annealing at 800 K in oxygen led to the appearance of p(3x2) domains on the p(4x2) dominated surface and a more diffuse p(4x2) LEED pattern. The surface was exclusively populated by a p(3x2) reconstruction upon annealing in UHV above 800 K while a p(3x2) LEED pattern could also be observed. After further annealing in UHV above 800 K, (1x1) islands appeared on the surface and the p(3x2) LEED pattern became more diffuse. The (1x1) area increased with annealing time in UHV and eventually exclusively (1x1) terminated terraces with straight steps due to crystallographic shear planes were observed. The STM images of the p(4x2) and p(3x2) surfaces were dominated by 0.1 nm deep troughs separating bright rows with 4x and 3x spacings respectively between rows. The appearance of the rows was sensitive to the imaging bias with a 2x periodicity along the rows seen at high biases and a 1x periodicity at low biases. These results could be explained by a structural model based on incomplete (1x1) terraces that form as reduced W@super 3@ ions migrate from the surface into the bulk.

10:00am **SS2-FrM6 First Principles Calculations of the ZrO@sub 2@ (100)/Ni(111) Interface***, **J. He**, S.B. Sinnott,* University of Florida*; E.C. Dickey,* Pennsylvania State University

We report on first principle calculations of the equilibrium geometries, interfacial energies, and work of separation for the O- and Zr-terminated Ni(111)/cubic-ZrO@sub 2@(100) interfaces. The approach is density functional theory using the generalized gradient approximation combined with nonlocal, norm-conserving and ultrasoft pseudopotentials. The polar ZrO@sub 2@ surface slab is non-stoichiometric to remove artificial electric fields. Consequently, while the work of separation is relatively straightforward to calculate, determination of the interfacial energies depends on the chemical potentials of the system. The manner in which the oxygen and zirconium chemical potentials are calculated will be discussed. The results show the way in which the preferred termination, and thus the interfacial structure, depends on oxygen partial pressure. These results are helpful to better understand the nature of the bonding at metal-ceramic interfaces and to predict the atomistic structure and stoichiometry of the equilibrium interface at various environmental conditions. This work is supported by the NSF (DMR-9976851).

10:20am **SS2-FrM7 In situ-STM Experiments at Elevated Temperature (475K) on Growth, Atomic and Electronic Structure of Thin NiO Films on Ag(001)***, **Ch. Hagendorf**, H. Neddermeyer,* Martin-Luther-University, Germany

New results will be presented on the growth behaviour as well as atomic and electronic structure of thin NiO films on Ag(001) by using scanning tunneling microscopy (STM) and spectroscopy (STS) at elevated temperatures. NiO films were deposited with a thickness of up to 3 monolayers by evaporation of Ni in an O@sub 2@ atmosphere of 10@super -6@ mbar. Deposition and heating of the NiO films were followed by in situ-STM measurements which allowed us to identify the various stages of the growth mode. A (1x2) reconstruction is observed at substrate temperatures of less than 475 K and submonolayer coverages. They show a transition to (1x1) double layer NiO(001) after completion of the first monolayer. Only the latter one exhibits a pronounced bias dependent contrast reversal.@footnote 1@ The electronic structure of Ag(001), NiO(001) and the NiO precursor has been mapped using I(V)-STS at elevated temperatures and will be discussed in reference to results obtained on CoO /Ag(001).@footnote 2@ At coverages of more than one double layer areas with metallic behaviour are identified using STS. This indicates the formation of Ag islands in a height of several monolayers by segregation. @FootnoteText@@footnote 1@ Th. Bertrams et al., J. Vac. Sci. Technol. B 14 (1996), 1141.@footnote 2@ Ch. Hagendorf et al., Surf. Sci. (2003), in press.

10:40am **SS2-FrM8 Low Temperature Oxidation of Nitrided Surfaces***, **J. Torres**, C.C. Perry, S.J. Bransfield, D.H. Fairbrother,* Johns Hopkins University

The oxidation of transition metal nitride coatings is an important process because the resultant oxidized interface plays a crucial role in determining the interfacial properties of these materials as well as their durability in extreme environments. The oxidation of iron nitrides, in particular, has received little attention despite its importance as a magnetic coating in the recording industry. In the present study, X-ray Photoelectron Spectroscopy (XPS), Reflection Absorption Infrared Spectroscopy (RAIRS) and Mass Spectrometry (MS) were used to probe the low temperature (< 150 K) oxidation of nitrided iron surfaces exposed to oxygen and water. By carrying out the reactions at these low reaction temperatures, new pathways and intermediates have been identified. During the exposure of nitrided iron surfaces to oxygen, iron oxynitride (Fe@sub x@N@sub y@O@sub z@), nitrosonium ions (NO@super +@) as well as nitrite(nitrito) and iron oxide(hydroxide) species were observed. Upon prolonged oxygen exposures, nitrate species were formed in the oxidized overlayer indicative of an O-insertion mechanism into the iron nitride lattice, a process that has not been observed in previous studies of nitride oxidation. In contrast to oxygen, the reactivity of nitrided iron surfaces towards water was limited to the production of adsorbed N-O species and iron oxide(hydroxide). No molecular nitrogen was produced during reactions with oxygen or water in contrast to oxidation studies on other transition metal nitrides. Upon annealing the oxidized overlayer from 150 K to 600 K, nitrogen desorbs exclusively as nitric oxide (NO) between 250-400 K, leaving a surface film of iron oxide on top of the iron nitride.

11:00am **SS2-FrM9 Surface Characteristics of the Remote Plasma-treated ITO***, **S. Kim**, H. Seo,* Hanyang University, Korea*; Y. Kim,* Pusan National University, Korea*; K. Kim, Y. Tak,* LG Electronics*; H. Jeon,* Hanyang University, Korea

Indium tin oxide (ITO) is an essential material in fabrication of organic light emitting devices (OLEDs). ITO functions as a hole injector into organic material and the injection efficiency is influenced by the work function of ITO anode surface. Work function of the ITO surface primarily depends on carbon and oxygen concentration. Particularly, carbon contaminants of ITO surface should be removed as much as it could be, because it results in the defect of bonding structure and increases in the sheet resistance of ITO. We investigated the removal of surface carbon contaminants using the oxygen and hydrogen plasma and examined the change of chemical composition and electrical properties of ITO after plasma treatments. ITO film was coated on glass to a thickness of about 1600â„« and had a sheet resistance of about 10 â„¦/â–¡. And these ITO glass specimens were not pre-cleaned before plasma cleaning to demonstrate effects using plasma treatments only. The remote RF plasma cleaning chamber and the surface analysis system were connected each other by an ultra-high vacuum transfer system for the in-situ analysis. The carbon residues were almost removed below the detection limit of XPS after remote plasma cleaning at 50W. In XPS analysis for Sn3d@sub 5/2@, Two peaks were completely resolved. These resolved peaks indicated respectively Sn@super 2+@ and Sn@super 4+@. The peak intensity of Sn@super 4+@ was reduced on ITO surfaces which was treated by plasma. Work function on ITO surface increased by oxygen plasma treatment and decrease by hydrogen plasma treatment. It also showed that the oxygen concentration affected much more than carbon contamination at the work function of the ITO surfaces. @FootnoteText@ @footnote 1@H. Y. Yu, X.D. Feng, D. Grozea, and Z. H. Lu, R. N. S. Sodhi, A-M. Hor and H. Aziz, Appl. Phys. Lett., 78, 2595-2597 (2001).

11:20am **SS2-FrM10 Temperature Dependent Water Adsorption on BSCCO Single Crystal***, **X.F. Hu**, D.A. Human, C.J. Hirschmugl,* University of Wisconsin-Milwaukee

Infrared Reflection adsorption spectroscopy and Temperature Programmed Desorption studies of water adsorption on the surface normal to ab-plane of BSCCO single crystal reveal the molecular adsorption of water. The monolayer and multilayer desorption temperature is approximately 167 K. The absorption bands occur between 3200-3500 cm-1 for the OH stretching, suggesting hydrogen bonding. The OH stretching bands change their absorption signatures as a function of temperature. For 2 L exposure, one asymmetric broad band is observed at approximately 3350 cm-1 at 80 K , and becomes symmetric at 140K. At 150K, less water is adsorbed, exhibiting a sharper feature at 3250 cm-1 with both high and low frequency shoulders. Below 140K, the adsorbed water forms clusters, and above 150K, it forms clusters with more bulk-like character.

Thin Films

Room 329 - Session TF-FrM

Mechanical Properties of Thin Films

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

8:20am **TF-FrM1 Island Coalescence Stress Created During Thin Film Growth**, ***S.J. Hearne***, *J.A. Floro, C. Dyck, T. Christenson,* Sandia National Laboratories; *W. Fan, S.R.J. Brueck,* University of New Mexico

For over 30 years it has been generally accepted that island coalescence during thin film growth results in a tensile stress. However, prior to this work there had been no conclusive demonstration of the fundamental physical mechanism underlying this process. Using selective lateral film growth on patterned substrates during electrodeposition of Ni films, we have obtained the first unambiguous comparison of the experimentally-measured tensile stress due to island coalescence with theoretical predictions. This technique allows for the systematic variation of island size and geometry while maintaining temporally constrains of the coalescence of Ni islands during electroplating. This avoided the complications associated with stochastic island coalescence that have plagued previous measurements obtained over the last 30 years. We found that the functional dependence of the stress on island size and dimensionality is consistent with a Hertzian contact model recently proposed by Freund and Chason.@footnote 1@ However, the absolute magnitude of the measured stress is smaller by factors of 2-4x, and reasons for the discrepancy will be discussed. This work was partially supported by the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory of the United States Department of Energy operated by Sandia Corporation, a Lockheed Martin Company, under contract DE-AC04-94AL85000. @FootnoteText@ @footnote 1@L.B. Freund, E. Chason, JAP 89, 4866 (2001).

8:40am **TF-FrM2 Alloying Effects on Mechanical Behavior of Thin Metal Films**, ***R.P. Vinci,*** Lehigh University **INVITED**

Thin metal films such as Al, Pt and Au are often used in their pure state in microelectronics and MEMS applications. This is true despite the fact that their mechanical behavior is frequently critical for performance. When thin film alloys are employed, a specific alloy composition is often selected because it is a preexisting combination found in a particular fabrication facility, not because it is the optimum composition for the application at hand. In contrast, bulk metals are almost always alloyed for mechanical and microstructural stability, and the effects of various alloying elements are well characterized. Should a designer of microelectronics and MEMS applications need a particular set of mechanical properties (e.g., fatigue or creep resistance) there is no available equivalent understanding of alloy effects in thin film form. In this presentation, systematic experiments focused on elucidating the effects of alloying on thin film mechanical properties will be described. In particular, deviation from (or agreement with) bulk behavior will be discussed for several metal alloy systems.

9:20am **TF-FrM4 Mechanical Properties of Reacted Metal Multilayers**, ***D.P. Adams***, *M. Rodriguez, J.B. Kelley, T. Covert, T. Buchheit, M. Grubelich,* Sandia National Laboratories

Sputtered multilayer thin films composed of reactive material pairs are currently of interest for brazing, joining and other energetic applications. As shown extensively by Weihs et.al. several thin film material systems can be stimulated such that a rapid, self-propagating reaction occurs within a multilayer. This alloying reaction has great potential for joining, because it prevents global heating of parent materials. In this talk, we evaluate the resultant mechanical properties and microstructure of three different reacted multilayer systems. This includes Ni/Ti, Al/Pt and metal/B multilayers. Each material system was deposited by magnetron sputtering to thicknesses in excess of 1 ï�-m. First, we describe how the propagation velocity depends on multilayer design. Propagation velocities are measured by imaging the propagating reaction front using a high speed Cordin camera and strobe light assembly. Velocities in excess of 50 m/s are measured for some multilayer designs. We determine how changes in stoichiometry (specifically deviations from the targeted composition) affect velocity. Secondly, we discuss the stress in reacted films. Laser-based wafer curvature techniques are used to determine average in-plane stress in reacted films. Stresses in excess of 1 GPa have been measured for several reacted multilayers. To better understand the development of stress in these systems we have conducted x-ray diffraction to determine coefficients of thermal expansion. Films achieve extremely high temperatures during self-propagating reactions and extrinsic stress largely determines final stress state; this can greatly affect their usefulness in a braze process. Additional mechanical properties such as hardness are measured, and these are related to film microstructure probed by transmission electron microscopy.

9:40am **TF-FrM5 Intrinsic Stresses in CrN Films Deposited by Arc Ion Plating**, *T. Hanabusa,* ***K. Kusaka,*** Tokushima University, Japan; *T. Matsue,* Niihama National College of Technology, Japan

It is well known that large compressive residual stresses of the order of GPa develop in TiN and CrN films deposited by ion plating. The residual stress in the film is the sum of thermal stress and intrinsic stress. The former is the stress originated by the difference in the thermal contraction between the substrate material and the film, whereas the latter is originated by various factors during the depositing process. The residual stress in TiN or CrN film is predominantly the intrinsic stress. The object of this study is to investigate an essential meaning of the intrinsic stress in the films. In this experiment CrN film was deposited on a stainless steel substrate. Residual stress in the CrN film was measured by X-ray diffraction. The X-ray residual stress measurement revealed that macroscopic compressive stress and microscopic stress in the film are reduced by annealing the film/substrate system. The relation between the lattice strain and the applied stress is investigated for the specimen annealed at various temperature stage.

10:20am **TF-FrM7 Characterization of TiN Films Deposited on Electroformed Nickel Substrates**, ***M. Telgarsky***, *M.K. Ghantasala, E.C. Harvey, Y. Wang,* Swinburne University of Technology, Australia

The properties of thin films are mainly influenced by that of their substrates viz., the structure and microstructure. This paper describes the results of our investigations in understanding the effect of structure and microstructure of the electroformed Nickel substrate on the growth and properties of deposited TiN films. Nickel substrates were electroformed using two different Nickel sulfamate baths to thicknesses of between 100 and 200 µm. The grain size of these films was estimated to be around 15 to 50 nm. The grain size of the films formed in bath 1 was much larger than grains formed in bath 2. Interestingly, the films plated in bath 1 showed (200) orientation compared to those deposited in bath 2, which exhibited (111) orientation. Further, Nickel plated in bath 1 showed much better crystallinity compared to that deposited in bath 2. After releasing from their substrates, the electroformed Nickel foils were used in turn as substrates for the deposition of TiN thin films using filtered arc deposition (FAD). All films were deposited on the Nickel substrates under the same conditions. The electroformed Nickel and the TiN films were analyzed using Rutherford Backscattering Spectroscopy (RBS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Confocal Microscopy for analysis of composition, structure, microstructure and surface profile respectively. The presence of small quantities of oxygen was detected in the electroformed Nickel from both baths. RBS analysis of the TiN films indicated that they were stoichiometric. TiN films deposited at room temperature were nano-crystalline, while those deposited at higher substrate temperatures showed the formation of improved crystalline structures having a (111) or (200) orientation. The grain size of the TiN films varied between 35 to 70 nm and showed a strong dependence on the grain size of Nickel and substrate temperature during deposition. The dependence of the TiN film properties on the Nickel substrate characteristics will be discussed in detail in this paper.

10:40am **TF-FrM8 Novel Mechanical, Electrical and Optical Properties of Al and Mg Doped Boron Thin Films**, ***Y. Tian,*** Iowa State University

A new superhard and conductive (Al, Mg)-doped boron thin film with AlMgB@sub 14@ stoichiometry has been developed in this work for potential application as a hard coating on MEMS components and conductive atomic force microscope cantilevers. AlMgB@sub 14@ films were prepared on Si (100) using pulsed laser deposition at room temperature and 573 K. Transmission electron microscopy analysis reveals that the film structures are amorphous irrespective of substrate temperature during deposition. Nanoindentation tests show that hardnesses of 45 GPa and 51 GPa have been achieved in AlMgB@sub 14@ films deposited at room temperature and 573 K respectively. Except for their superhardness, AlMgB@sub 14@ films also display very low electrical resistivity and high optical absorption in a broad spectrum range, all these phenomena can be accounted for based on an electron transfer mechanism enhanced in amorphous structures.

11:00am **TF-FrM9 Synthesis of Super-Elastic Fullerene-Like Carbon Nitride Coatings by Unbalanced Reactive Magnetron Sputtering***, **J. Neidhardt,*** Linköping University, Sweden*; Zs. Czigány,* Hungarian Academy of Sciences*; L. Hultman,* Linköping University, Sweden

Carbon nitride (CN@sub x@) is an emerging material for wear-resistant coatings. Out of several characteristic structures, the so-called fullerene-like (FL) compounds are the most promising. The FL structure leads to extraordinary mechanical properties such as an extreme elasticity combined with high fracture toughness as assessed by nano indentation. Yet, FL-CN@sub x@ shows a low-to-moderate resistance to penetration. Hence, deformation energy is predominantly stored elastically and released after unload giving it the resilient character. The key for understanding its resilient character lies in a unique microstructure of bent, cross-linked and frequently intersecting nitrogen-containing graphite sheets, denoted "fullerene-like". This presentation elaborates on the growth mechanisms of FL CN@sub x@ synthesised by unbalanced reactive magnetron sputtering of graphite in a nitrogen-containing atmosphere. Preformed C@sub x@N@sub y@ (x, y < 2) species originating from the target were assigned a crucial role for the fullerene-like structure evolution. In fact, the conducted plasma analysis revealed that the majority of the film forming flux comprises multi atomic nitrogen-containing species, which are partly sputtered and also thermally emitted from the self-modified target surface. The arrival of C@sub x@N@sub y@ molecules besides carbon atoms at the substrate surface adds much complexity to the growth mechanisms. C@sub x@N@sub y@ species may act as growth templates whereas an oriented incorporation along the edges makes them more stable towards preferential chemical desorption and therefore the formation of extended and curved sheet-like structures is promoted. Also the role and extent of temperature dependent chemical desorption (sputtering) process for the FL structure evolution was investigated in order to identify the type of species incorporated.

11:20am **TF-FrM10 Hydrogenated Carbon Films and Sulfur Stabilization: Synthesis and Tribiological Characterization***, **C.A. Freyman**, Y.H. Yu, Y.W. Chung,* Northwestern University

Hydrogenated carbon films have been deposited on Si substrates and stainless steel ball bearings by magnetron sputtering. Hydrogen concentration was controlled by the percentage of hydrogen in the Ar/H@sub 2@ mixture. The friction coefficient showed a strong dependence on both the hydrogen content of the precursor gas and the relative humidity during testing. Twenty-five percent of hydrogen in the precursor gas produced the lowest frictional coefficient (0.01) at the lowest relative humidity measured (5%). Sulfur was incorporated into the film via the introduction of hydrogen sulphide in the precursor gas. Here, we attempted to use sulphur to make the surface hydrophobic and hence minimize the relative humidity effect. Hardness, friction and sensitivity towards the environment will be investigated as a function of deposition parameters.

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