Sunday Afternoon, November 3, 2002

Biomaterials Plenary Session
Room: C-201 - Session BP-SuA

Biomaterials Plenary Session
Moderator: K. Healy, University of California, Berkeley

3:00pm **BP-SuA1 Visions of Science at BESSY SASE FEL in Berlin Aldershof**, ***W. Eberhardt***, BESSY GmbH, Germany **INVITED**

BESSY is planning to build a SASE FEL facility covering the photon energy range from 20 eV to 1 keV at the site next to the existing BESSY II storage ring. This new facility will offer laser like photon beams with fully coherent, high power (mJ) pulses of ≤20 fs duration, enabling a whole set of novel experiments dedicated to understand dynamical processes in matter or for the investigations of very dilute systems. This SASE FEL covers the traditional BESSY II photon energy range, which is especially suited for electronic structure investigations of atoms, molecules, clusters, and solids. With the anticipated temporal resolution of ≤20 fs charge transfer processes and time resolved 'femtochemistry' studies as well as magnetization dynamics in magnetic materials establish some of the major areas of scientific interest in this new facility. Furthermore in microscopy on soft-matter and biological samples it is possible to acquire an image using a single laser pulse. Thus stroboscopic time resolved images of dynamical processes in living cells become possible. In general, the science planned at this facility is complementary to the science envisioned for the planned TESLA X-FEL facility at DESY and Linac Coherent Light Source (LCLS) at Stanford. Following the presentation of the parameters and the layout of the proposed facility, the Scientific Case will be presented as it was developed by the prospective user community in the course of several scientific workshops and in discussions.

3:40pm **BP-SuA3 Large Scale Integration of Microfluidic Devices, and Applications to Biology**, ***S. Quake***, Caltech **INVITED**

4:20pm **BP-SuA5 Biochips Designs, Challenges, and Bioanalytical Applications**, ***L.J. Kricka***, University of Pennsylvania Medical Center **INVITED**

Biochips, in all of their guises are the most active area of research and development in the analytical sciences. These micro-miniature devices are produced using techniques originally developed in the microelectronics and in the printing industry. Although some microchip devices have been commercialized (e.g., capillary electrophoresis chips), many challenges and issues remain for the routine implementation of these micro-analytical devices. These include surface chemistry effects in the sub-microliter confines of a microchip chamber, the interface between the <1 cm2 microchip and the human operator, utilization of plastics for construction, and the development of low cost, mass production methods. Biochips design has usually been empirical, but new micro-fluidics modeling software offers a route to rational design of at least the fluidic components of biochips. The current scope of applications for biochips include protein and nucleic acid analysis, genetic tests, cell selection, immunoassay, and various molecular separation techniques. A goal in biochip research is integration of all steps in an analytical process on a single chip - the so-called "lab-on-a-chip", and there are a range of biochips that combine several sequential steps of an overall analytical procedure on a single disposable biochip device. The benefit of this approach is faster and simpler analysis. Further miniaturization of the biochip will lead to the nanochip, i.e., a device with dimensions less than 100 nanometers. Nanotechnology is at an early stage, but already significant progress has been achieved in directions that may lead to useful analytical devices (e.g., carbon nanotubes). The control of atomic and molecular composition of surfaces in a nanochip device may provide unexpected improvements in analytical performance over conventional devices in which surface composition is imperfectly controlled, and much remains to be done in this active and speculative area of research.

Applied Surface Science
Room: C-106 - Session AS-MoM

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

8:20am **AS-MoM1 Maximizing and Automating Information Extraction in Time-of-Flight Secondary Ion Mass Spectrometry**, ***S.J. Pachuta***, 3M Company

Numerical techniques have been found useful in extracting information from the large data sets produced by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Simple univariate approaches to quantitation in static SIMS, including spectral normalization, smoothing, curve fitting, and generation of spectral overlays, will be described. The complexity of TOF-SIMS data makes multivariate approaches particularly useful, and multivariate statistical techniques such as principal components analysis (PCA) will be described in detail. PCA, in simplest terms, reduces a data set to its essential elements. A significant advantage of PCA over univariate methods is that it greatly compresses the data by combining variables. This is particularly beneficial in TOF-SIMS, where a data set may consist of a 256x256 pixel matrix in which each pixel contains a complete mass spectrum consisting of upwards of 100,000 mass channels. Applications of PCA which will be described here include automating complex tasks previously performed manually by the analyst, finding non-obvious information in data sets, and distinguishing relevant from non-relevant information. Situations in which PCA is particularly applicable are those in which differences are sought. Typical examples might be a comparison of spectra from a series of materials with different performance characteristics, or chemical imaging of a surface. Automation of some common imaging tasks, such as choosing which peaks to map or extracting spectra from regions of interest, is one of the key concepts to be presented.

8:40am **AS-MoM2 G-SIMS - Molecular Structure**, ***I.S. Gilmore***, *M.P. Seah*, National Physical Laboratory, UK

G-SIMS or gentle SIMS has already been demonstrated to provide a straightforward way to simplify static SIMS spectra.[1,2] These spectra are composed of parent fragment ions amongst a large number of high intensity degradation products. The fragmentation is quantified in terms of the partition functions of the fragments emitted from a surface plasma with effective temperature, T_p. It is found that fragmentation is least for high mass incident ions at low energies. By extrapolation of the data to low T_p, a new spectroscopy, known as gentle-SIMS or G-SIMS is formed. The significant peaks in the G-SIMS spectra are those peaks which would be emitted as a result of an ion impact that generates a surface plasma of very low T_p and thus have little post-emission rearrangement or fragmentation. Those peaks are, thus, directly characteristic of the material without rearrangement and enable direct interpretation and identification. G-SIMS has been successfully tested on a range of polymers, molecules and complex organics.[3] G-SIMS not only provides the parent molecule mass, and hence composition in terms of numbers of C,H,O,N etc atoms, but is also allows the molecular structure to be evaluated. Current work explores the re-building of parent molecules using the fragmentation pathways which are mapped out as T_p is varied. This new dimension to the technique has significant potential information not previously obtainable in static SIMS. G-SIMS-MS has some of the attributes of MS-MS. These effects and the use of G-SIMS with mixtures will be discussed.

[1] I S Gilmore and M P Seah, Appl. Surf. Sci. 161 (2000) 465.
[2] I S Gilmore and M P Seah, SIMS XIII proc, Appl. Surf. Sci. in the press.
[3] I S Gilmore and M P Seah, Appl. Surf. Sci. 187 (2002) 89.

9:00am **AS-MoM3 Recent Advances in Time-of-Flight SIMS**, ***E. Niehuis***, ION-TOF GmbH, Germany **INVITED**

When TOF-SIMS was introduced in the early 80's, it appeared to be the ideal instrument for surface analysis in static SIMS mode. It's most striking features were a very high transmission close to 100 %, a parallel detection of all masses and an unlimited mass range. At that time, the current density of the pulsed primary ion beam was so low that the lifetime of the uppermost monolayer exceeded thousands of seconds. Early applications of TOF-SIMS focused on the analysis of involatile molecules, prepared as thin layers on metal substrates. Improvements in mass resolution to a level above 10,000 and the development of an efficient charge compensation opened many new fields in surface analysis, like the detection of trace elements and surface analysis of bulk organic materials such as polymers. The combination with liquid metal ion guns towards the end of the 80's added powerful imaging capabilities with a lateral resolution well in the sub-micron range. In the mid 90's, TOF-SIMS started to become a depth profiling technique using the so-called dual beam mode. A low energy sputter gun was applied for sample erosion with a reasonable speed while the center of the sputter crater was analyzed with the pulsed high energy beam. In the recent years, TOF-SIMS has become a very powerful depth profiling technique with applications ranging from the analysis of ultra-shallow implants to the profiling of thick films. The combination of a small spot analytical beam with a low energy sputter beam offers new capabilities in 3-dimensional micro analysis. In this paper recent developments in TOF-SIMS instrumentation will be discussed and analytical examples from a variety of different fields will be given to highlight the capabilities of the technique.

9:40am **AS-MoM5 Applications of Time-of-Flight Secondary Ion Mass Spectrometry in Materials Research**, ***B.W. Schueler***, Physical Electronics **INVITED**

TOF-SIMS has gained increasing acceptance as a surface analysis techniques in scientific research and industrial applications. The most important features of the technique are its ability to (parallel) detect and identify all secondary ion species (molecular and organic)over a virtually unlimited mass range with high sensitivity. These properties result in an extremely efficient utilization of information from the analytical area and high detection sensitivity for identifying organic molecular species as well as trace element contaminants. The use of micro-focused primary ion beams enables measurement of the lateral surface distribution of molecules and atomic ion mapping with ~100nm resolution. Ion bombardment of organic surfaces results in the emission of characteristic fragments of the molecule and often the complete ionized molecule, providing a "fingerprint" spectrum of the molecule. This fingerprint may serve as unambiguous identification of the molecular species and functional groups. Parallel detection and high sensitivity of TOF-SIMS are equally important in inorganic (surface) analysis. For example, trace silicon surface metal contamination levels in the 0.1-1ppm levels across the periodic table are readily achieved. TOF-SIMS surface metal detection limits in Si are typically 10-100 times lower than those achievable by standard TXRF (Total Reflection X-Ray Fluorescence). This paper is intended to illustrate some key analytical and problem solving capabilities of TOF-SIMS with a range of materials research applications. The emphasis will be on semiconductor-related applications such as surface metal contamination transfer in process equipment, organic/inorganic contamination and etch/rinse residues, and depth profiling. Applications from the disk drive, and polymer industry will also be included. The relative merits of TOF-SIMS and other surface analysis techniques (i.e., XPS, AES, TXRF, etc.) will be discussed.

10:20am **AS-MoM7 Method to Quantify the Comparison of Predicted vs. Experimental Isotopic Clusters in Time of Flight Secondary Ion Mass Spectrometry for High Mass Peak Identification**, ***R.W. Nowak***, *C.M. Mahoney*, State University of New York at Buffalo, *A. Hawkridge*, University of Arizona at Tucson, *J.A. Gardella*, State University of New York at Buffalo

Investigation of the high mass range of the ToF-SIMS spectrum (800-4000 Da.) will yield information on long range polymer interactions which affect ion formation and will provide information about the long range forces between polymer chains. Peak assignment in the high mass region is not as straight forward as in the low mass region. Isotopes of the atoms that make up the fragments combine to yield clusters of peaks, not just single peaks as seen in the low mass regions. We are able to assemble predicted isotopic clusters to compare with the collected experimental data for identification. In past reports visual comparisons of the predicted and experimental isotope cluster results were used to judge the goodness of fit between two data sets. We have developed an analytical method to construct correlation plots for comparison with these data sets and to quantify the goodness of fit between the predicted and experimental results. This paper will illustrate a method to create correlation plots of the predicted vs. experimental results. Clusters from atomic constituents in the low mass region are used as a simple model to demonstrate the application. High Mass clusters from several previously published ToF-SIMS of high mass polymers will be utilized to show the effectiveness of this method.

10:40am **AS-MoM8 TOF-SIMS Characterization of Mixed Decanethiol - Octadecanethiol Self-Assembled Monolayers**, ***D.J. Graham***, *D.G. Castner*, University of Washington

Previous work in our labs has demonstrated the utility of TOF-SIMS in determining detailed chemical and structural information from self-assembled monolayers (SAMs). Much of this work has been done with homogeneous SAM surfaces. This study presents an investigation of a more complex mixed monolayer system using methyl-terminated SAMs. Other studies using mixed SAMs have used thiols with unique head groups to exploit a surface property or chemical signature. Thus, using methyl terminated SAMs increases the difficulty of interpretation due to the fact that there are no unique atoms to exploit between the thiol molecules. For this study, mixed monolayers of decanethiol (C10) and octadecanethiol (C18) were prepared from 1mM solutions at various mixture ratios (v/v). Using TOF-SIMS multivariate and univariate analysis, we demonstrate that the molecular specific information generated by TOF-SIMS enables both a detailed characterization of the mixed monolayer films and insight into their structure and surface arrangement. XPS analysis showed only the presence of the expected elements with all sulfur bound to the gold surface. Surface concentrations estimated by TOF-SIMS and XPS showed a significant enrichment of the longer chain thiol. Monitoring the yield of specific molecular ions in the TOF-SIMS spectra gave insight into the arrangement of the thiols on the gold surface. In particular the yield of the cluster ion Au[MC10-H][MC18-H] suggested the samples were phase segregated at least at a nanometer scale. Multivariate analysis of the TOF-SIMS data captured the changing composition across the series, and also highlighted structurally specific information about each thiol.

11:00am **AS-MoM9 Secondary Ion Emission from Thick Organic Films: Influence of Primary Ion Bombardment Conditions**, *E. Tallarek*, Tascon GmbH, Germany, *F. Kollmer*, ION-TOF GmbH, Germany, *B. Hagenhoff*, ***R. Kersting***, Tascon GmbH, Germany

Our ongoing studies focus on the secondary ion emission from thick organic layers under different primary ion bombardment conditions. As model analyte system spin coated layers of the polymer additve Irganox 1010 on low density polyethylene (LDPE) was used because the collision cascade takes place completely in organic material (simulation of "real" polymer conditions), the analyte of interest is only present in the uppermost monolayer (no contribution from deeper layers) and shows characteristic secondary ions covering the complete mass range from 1-1000u whereas the aliphatic substrate polymer LDPE emits ions only in the low mass range. The secondary ion parameters yield Y, disappearance cross-section σ and secondary ion emission efficiency E (yield per damaged area) were determined for primary ion bombardment with several monoatomic as well as polyatomic primary ions including Ga^+, Cs^+, Au^+ as well as SF_5^+, Au_2^+ and Au_3^+. Additionally, the primary ion energies were varied between 4 and 25 keV. The results can be summarized as follows: For monoatomic primary ion bombardment the efficiency increases with the primary ion mass. Maximum enhancement factors compared to Ga^+ bombardment are about 5-10. Polyatomic primary ion bombardment leads to enhancement factors of at least 60. Optimum primary ion energies depend on the respective ion species. These results have consequences for the achievable lateral resolution in ion imaging as well as for the detection limits in surface spectrometry. Examples will be given.

11:20am **AS-MoM10 A New Approach to Measuring the TRUE Boron Profile Near the Si Surface using SIMS**, *T.H. Büyüklimanli*, ***J.W. Marino***, *C.W. Magee*, Evans East

To date, SIMS measurements of the B distribution in the near-surface region have been made using an oxidizing ambient formed by either O2 flooding or by using normal incidence O2 bombardment to avoid possible near surface artifacts. However, the shape of the B depth profile obtained under these conditions at or near the surface has always been questioned. Separate measurements by poly-Si-encapsulation SIMS, RBS, ERDA and TEM have shown an implant peak below the surface contrary to the peak at the surface as usually depicted by SIMS with oxidizing ambient. Our paper investigates whether or not the apparent problems of profiling ULE B in Si under fully oxidizing conditions can be obviated by sputtering with oxygen under conditions that are not fully oxidizing. Correct measurement of the B profile shape in the top 1-2 nm of the sample would be useful to the TCAD modeling community. Our tests show that the B+ relative sensitivity factors with respect to Si+ were identical for both Si and SiO2. This suggests that the matrix effect due to the presence of surface oxide can be avoided by simply point-by-point normalizing the B+ intensity to the interpolated Si+ intensity. However, proper characterization of the detector electronics is required to record intensities accurately. The profiles acquired using low energy O2 bombardment at 60° incidence and processed using interpolated normalization resulted in doses matching values measured by nuclear reaction analysis (NRA). The profiles also show that B implant peaks for the range of low energies measured are, indeed, below the surface as measured by ERDA, RBS, TEM and poly-encapsulation SIMS. Another benefit of depth profiling without full oxidation is the ability to detect the surface oxide and location of the B implant with respect to the oxide. Profiles acquired under oxidizing ambient require a separate measurement to determine the oxide thickness and to correct for sputter rate changes from the oxide into the Si.

11:40am **AS-MoM11 Study of Electron Beam Excited Plasma SNMS for High Detection Sensitivity**, ***T. Noguchi***, The Graduate University for Advanced Studies, Japan, *S. Kato*, KEK & The Graduate University for Advanced Studies, Japan

SNMS has been developed for years to obtain precise depth profiling and high quantificability conquering the problems of SIMS. SNMS based on electron beam excited plasma (so called SNART: Sputtered Neutral Analysis-Riken Type) has several advantages; the high detection sensitivity with a high post ionization efficiency, the high depth resolution with low energy sputtering less than 100eV keeping a high sputtering rate, the relatively simple structure of the apparatus, the small dispersion of relative elemental sensitivity factors and the capability of insulator analysis without a charge neutralizer. In this study we attempted to improve the apparatus so as to obtain a higher sensitivity with maintaining a high depth resolution of around 1 nm. For this purpose, we have adopted a ToF mass spectrometer and made the plasma source be able to work in UHV. Detection sensitivities for metal surfaces were estimated to be less than 1 at.ppm keeping the high depth resolution on the basis of our preliminary experimental results of a sputtering rate, a post-ionization efficiency, a transmission of the ion optics and a total gain of the detection system. We will report our hardware development and results of experimental data compared with the estimated numbers.

Biomaterials
Room: C-201 - Session BI-MoM

Theoretical Studies of Biosurfaces/Biotribology and Biorheology

Moderator: R.A. Latour, Clemson University

9:00am **BI-MoM3 Molecular Simulation Studies of Orientation of Antibodies Adsorbed on Charged Surfaces**, *J. Zhou*, *J. Zheng*, ***S. Jiang***, University of Washington

Antibodies have found many applications in biotechnology and clinical medicine, including diagnostic assays, environmental testing, and process monitoring. It is well-known that Fab fragment of an antibody can bind its antigen with a very high specificity. Therefore, it is desirable to control the antibody orientation for immunoassay applications. In this work, Monte Carlo simulations are performed to study and predict the adsorption and orientation of antibodies as a function of surface and solution properties using hierarchical models, a simplified Y-shape 12-bead model antibody, a united-residue model, and an all-atom model. For all these three models, simulation results show that higher surface charge density and lower solution ionic strength favor narrower orientation distribution of adsorbed antibodies. Simulation results further show preferred antibody orientation under controlled surface and solution conditions, which are verified by our SPR and ToF-SIMS experiments. For the 12-bead model, it allows us to quickly map out the general trends of the orientation behavior of antibodies on surfaces. For the residue model we developed, more detailed residue-distribution information of antibody near surfaces can be achieved. For the all-atom model, the conformation change of an adsorbed antibody was obtained with a proposed hybrid method. The fundamental understanding of antibodies on surfaces of this work will facilitate the effort to develop better biosensors.

9:20am **BI-MoM4 Mapping the Free Energy State of Water in Hydration Layers and Its Importance for Ligand-Receptor Binding**, ***G.W. Grahek***, *R.A. Latour*, *S.J. Stuart*, Clemson University

The thermodynamic contributions of solvent molecules during ligand-receptor binding are generally believed to be very important, but relatively little is actually understood regarding how the entropy, enthalpy, and free energy of hydration layers change as a ligand approaches and docks with its receptor. We assume that both ligands and receptors perturb the thermodynamic state of their localized hydration layers, and that these effects must be superimposed on the intervening water layers as a ligand approaches its receptor. It is hypothesized that this effect may have a significant influence on the height of the activation barrier for ligand-receptor binding, and thus may serve as an important medium-range modulator of ligand-receptor binding. Based on this underlying hypothesis, we are investigating the development of statistical mechanics based molecular modeling methods to calculate the entropy, enthalpy, and free energy values of water as a function of position surrounding a designated solute molecule. Simulations have been conducted using both molecular dynamics (AMBER 6.0) and Metropolis Monte Carlo (BOSS 4.2; OPLS) methods using TIP3P and TIP5P water, respectively, and periodic boundary conditions surrounding a centralized solute molecule. Entropy, enthalpy and free energy are then mapped on a 3-dimensional grid. The simulations indicate that distinct changes do occur in the calculated free energy state of water molecules in the first two hydration layers surrounding the solute compared to bulk water. Further studies are being planned to investigate the effect of solute-solute separation distance on the intervening water layers. Following final development, these methods will be applied to actual ligand-receptor systems for the purpose of predicting the influence of water structure on binding. It is believed that these simulations may provide new insights that will facilitate drug design for specific receptor targets.

9:40am **BI-MoM5 Growth of a Polymer Brush from Solution: Adsorption, Desorption, Conformational Conversion and Charging**, ***H.J. Kreuzer***, Dalhousie University, Canada **INVITED**

Going beyond mean field theory we develop a model of a polymer brush that allows for inhomogeneity, confinement and lateral interactions. The model is developed for freely rotating chains and a realistic Interacting Chain Model for poly(ethylene glycol). The parameters in the latter are obtained from a first principles theory based on (i) ab initio (density functional theory) calculations of the potential energy surfaces of the polymer conformers, and (2) the proper statistical mechanics for which we succeeded to formulate and solve a Green's function approach (transfer matrix method) in the presence of an external force field. We set up kinetic equations for the time evolution of the growth of a brush from solution. For PEG a detailed analysis and discussion of recent data is made that identifies two time regimes of pancake adsorption and collision-induced conformational conversion to stretched moeities, respectively. Lastly we discuss the possibility that auto-ionization of water in contact with the brush may lead to preferential adsorption of hydroxide and hydronium ions depending on the pH.

H.J. Kreuzer, R.L.C. Wang, and M. Grunze, New Journal of Physics 1, 21.1 (1999). R.L.C. Wang, H.J. Kreuzer, and M. Grunze, Phys. Chem. Chem. Phys. 2, 3613 (2000). L. Livadaru, H.J. Kreuzer, and R.R. Netz. Interacting Chain Model for Poly(ethylene glycol) from First Principles. Macromolecules (in press). Kreuzer, H.J.; Payne, S.H.; Livadaru, L. Biophysical Journal 2001, 80(6), 2505-2514. Kreuzer, H.J.; Grunze, M. Europhys. Lett. 2001, 55(5), 640-646. M. Himmelhaus, T. Bastuck, S. Tokuitsu, M. Grunze, L. Livadaru and H.J. Kreuzer. Growth of a polymer brush from solution, (preprint).

10:20am **BI-MoM7 Puzzles of Fluid Flow in the Biomaterials Environment**, ***S. Granick***, University of Illinois, Urbana-Champaign **INVITED**

In areas from blood flow to biosensor applications, it is essential to predict fluid flow. The standard model states that fluid velocity is zero at solid surfaces, but evidence is accumulating against this in many situations, especially regarding aqueous solutions and surfaces coated with polymer cilia. We have studied flow of aqueous solutions containing variable amounts of monovalent and divalent electrolyte past solid surfaces whose charge was varied and whose 'softness' was varied by polymer cilia. Deviations from the standard model are observed when the wall shear stress exceeds a critical level whose magnitude depends on the system studied. In some respects this is understood, in other respects it is not. The puzzles will be emphasized.

11:00am **BI-MoM9 Hydration Forces on a Switchable Bioactive Surface**, ***B.-I. Kim***, *M.A. Samara, D.L. Huber, J.E. Houston, B.C. Bunker*, Sandia National Laboratories

Poly(n-isopropyl acrylamide) (PNIPAM) monolayers can be thermally switched between hydrophobic and hydrophilic states at a phase transition temperature of 35°C. Protein adsorption studies indicate that the hydrophilic state represents an anti-fouling state, while biomolecules form adherent monolayers on the hydrophobic state. We have used a scanning probe system called the interfacial force microscope (IFM) to probe the mechanisms for protein adsorption on this switchable polymer surface. With the IFM, we have simultaneously measured both normal and friction forces between a silica tip and a surface functionalized with PNIPAM as a function of separation distance. The results show that at room temperature, there is a repulsive hydration force between the tip and the substrate. As the phase transition temperature is approached, the repulsive force collapses, allowing the tip and substrate to come into adhesive contact. The transition from repulsive to attractive adhesive forces is accompanied by a doubling in lateral friction forces. IFM results obtained at different tip speeds at different temperatures suggest that the repulsive hydration force observed at room temperature is associated with the presence of ordered water structures within the polymer that break down at higher temperatures. Experiments are in progress with chemically-functionalized tips to provide us with fundamental insights of the parameters controlling the stability of this ordered water and its role in protein adsorption.

11:20am **BI-MoM10 Structural Properties of Nucleosomal DNA Characterized by Atomic Force Microscopy**, ***M.E. Greene***, *M.A. Ratner, J. Widom, M.C. Hersam*, Northwestern University

One of the fundamental problems in contemporary molecular biology involves whether a sequence dependence exists in nucleosomal DNA which gives the molecule certain structural properties leading to the formation of nucleosome with histone octamer. A way to approach the solution is to look at the isolated DNA molecules to discern the native structural properties in the absence of histones. Interfacing biological molecules with inorganic substrates and probing them using atomic force microscopy (AFM) allows for such study. AFM has been used to image surfaces with adsorbed biological molecules for over a decade, and in particular DNA has been characterized to an extent that imaging artifacts interfering with proper analysis have been identified. Several technical difficulties have been resolved as well, including substrate selection and a reproducible surface binding protocol, opening the door for AFM to be used as a powerful tool to investigate problems of genuine biological importance. In this investigation, a 342-bp strand of synthetic dsDNA dubbed "601" shown by Lowary and Widom to have a high affinity for binding to histone octamer is examined. This sequence is thought to mimic the behavior of DNA sequences found in chromatin. Preliminary analysis of AFM data of a natual nucleosomal DNA sequence isolated from chicken erythrocyte suggests agreement with the worm-like chain (WLC) model. Attention is given to the quantities of end-to-end distance, contour length, and intrachain bend angles in order to assess the persistence length, bendedness, and bendability of the sequence. AFM data is currently being gathered using Si cantilevers tipped with multiwalled carbon nanotubes as well as high aspect ratio Si tips with a nominal radius of curvature of 2 nm to obtain better lateral resolution and detailed measurements of bends and curvature fluctuations in the chains. An automated analysis methodology to allow the handling of large data sets will be introduced as well.

Electrochemistry and Fluid-Solid Interfaces
Room: C-104 - Session EC+SS-MoM

Fuel Cells and Surface Electrochemical Reactions
Moderator: J.G. Chen, University of Delaware

8:20am **EC+SS-MoM1 Imaging of Water Ionization at Platinum Surfaces in High Electric Fields**, ***C. Rothfuss***, *V. Medvedev, E.M. Stuve*, University of Washington

The high electric field intrinsic to the electrode/electrolyte interface plays an important role in electrochemical surface chemistry. To study these fields, which are of the order of 1 V/?, we employ a field ionization system in which water and other electrolytic species are adsorbed and ionized on Pt field emitter tips. Ions produced by the applied field are imaged onto microchannel plates and mass resolved with time-of-flight or ExB (Wien filter) mass spectrometers. Water ionization produces hydrated protons with 1-10 water molecules per proton, that are ejected from the tip. Images of ramped field ionization experiments show dramatic differences in ionization of amorphous vs. crystalline water. Below 135 K, where water exists in amorphous form, ionization is random overall, increasing in intensity with increasing field. Above 135 K, where water is crystalline, ionization occurs in long-lived zones that, with increasing field, increase in intensity and number and redistribute themselves about the surface so as to be as far apart as possible. Temperature dependent studies over the range of 80-300 K follow the energetic details of water ionization. Below 170 K the field required for dissociative ionization decreases linearly with increasing temperature. In a ramped field desorption experiment, ionization produces hydrated proton clusters with 2-7 water molecules per cluster. Above 170 K protonated clusters desorb sequentially beginning with the 6-water cluster and followed by progressively smaller clusters as the field increases. The disappearance of an n-water ion cluster results from loss of a water molecule to form cluster n - 1. The respective energies for water removal from clusters of n = 5, 4, and 3 were found to be 0.55, 0.76, and 0.85 eV. These numbers are in excellent agreement with previous measurements of water attachment energies. This work is supported by the Office of Naval Research.

8:40am **EC+SS-MoM2 A Specular He Scattering Study of Water Adsorption, Desorption, and Clustering on Pt(111)**, ***J.L. Daschbach***, *B.M. Peden, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Specular He atom scattering is used to probe the adsorption, desorption, and clustering kinetics of sub-monolayer H_2O on Pt(111) over the temperature range 22 K to 185 K. Water deposited on clean Pt at low temperatures is shown to be arranged randomly on the Pt substrate. Over a narrow temperature range, as the clean substrate temperature is raised, the deposited water transforms to a 2-D condensed phase. Rearrangement of randomly adsorbed H_2O is studied as a function of coverage and temperature. At low initial H_2O coverage the specular He waveform is dominated by the clustering of the isolated H_2O molecules. At higher H_2O coverage and temperature a second feature is manifest, which we interpret as the Oswald ripening of the 2-D islands. Adsorption and desorption kinetics are examined isothermally. Water, when fully clustered in two dimensions, gives rise to a He specular intensity that decreases linearly with coverage. Over essentially the entire sub-monolayer coverage regime the sample coverage changes linearly in time during both adsorption and desorption of H_2O. This requires that the desorption rate be independent of coverage and thus the desorption kinetics are zero-order. The zero-order kinetics are a consequence of the coexistence of a 2-D H_2O gas with a 2-D condensed H_2O phase on the Pt surface. At higher temperatures, depending on flux, non-zero order kinetics are observed which are indicitive of a transition to a single H_2O 2-D phase. Details of the experimental techniques and results will be presented. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the Department of Energy by Battelle under Contract DE-AC067-76RLO 1830.

9:00am **EC+SS-MoM3 Surface Chemistry of Solid Oxide Fuel Cells**, ***R.J. Gorte***, University of Pennsylvania **INVITED**

Fuel cells are an attractive method for electrical power generation because they offer the possibility of very high efficiencies compared to normal heat engines. One of the major hurdles preventing their implementation for a wide variety of applications is the fact that, until recently, only H_2 could be used as the fuel. We have recently demonstrated that stable power generation, without either internal or external reforming, can be achieved through the direct oxidation of hydrocarbons, including liquids, using a solid-oxide fuel cell (SOFC).[1] The anodes in these direct-oxidation SOFC were composites made of Cu, ceria, and yttria-stabilized zirconia (YSZ). In this talk, the methods for preparing these anodes will be described. It will be demonstrated that surface chemistry and structure are crucial for improved performance of these fuel cells. Attempts to control the surface chemistry and structure will then be discussed.

[1] S. Park, J. M. Vohs, and R. J. Gorte, Nature, 404 (2000) 265.

9:40am **EC+SS-MoM5 Strategies for the Study of Methanol and CO Electrocatalysis on Solid Electrodes and Nanometer-Scale Supported Catalysts**, ***C. Korzeniewski***, *G. Vijayaraghavan*, *L. Gao*, Texas Tech University **INVITED**

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 °C on methanol, or H_2 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 H_2. 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, atomic force microscopy (AFM) and wet-analytical methods. This presentation will focus on the surface electrochemistry of methanol and carbon monoxide at supported Pt and Pt-Ru catalysts. In situ infrared measurements are being performed with Vulcan carbon supported fuel cell catalysts. The carbon supported materials are adsorbed onto a smooth gold electrode to enable infrared sampling in a standard reflectance geometry. A thermostatted cell allows in situ infrared measurements between ambient and 80 °C. Similar to the bulk metals, thermal effects on methanol oxidation at nanometer-scale catalysts are stronger for Pt-Ru (atomic percent Ru = 50%) than Pt. The influence that metal particle size distribution and spatial arrangement on carbon supports has on methanol oxidation pathways is being investigated by depositing metal particles on highly ordered pyrolytic graphite. The surface electrocatalytic properties of the supported particles are investigated with cyclic voltammetry. AFM is used to determine the catalyst size distribution and spatial arrangement at different stages of preparation and electrochemical characterization. Properties of nanometer-scale metal particles in relation to methanol oxidation pathways will be discussed.

10:20am **EC+SS-MoM7 Potential Application of Tungsten Carbides as Direct Methanol Fuel Cell (DMFC) Electrocatalysts**, ***H.H. Hwu***, *J.G. Chen*, University of Delaware

The Pt/Ru anode in direct methanol fuel cells (DMFC), though effective, is disadvantageous in terms of its prohibitively high costs and limited supplies. In this work, we are evaluating the effectiveness of tungsten and molybdenum carbides as alternatives to Pt/Ru electrocatalysts by studying their reactivities towards methanol, water, and carbon monoxide. Using Temperature Programmed Desorption (TPD) and High-Resolution Electron Energy Loss Spectroscopy (HREELS) the reaction pathways of these DMFC molecules on carbide-modified Mo(110), W(110), and W(111) can be understood. On both W(110) and W(111) carbide surfaces, methanol readily decomposes into gas-phase CO, methane, hydrogen, and surface carbon and oxygen. In addition, both tungsten carbide surfaces are active toward the dissociation of CO and water. Preliminary studies on the Mo(110) carbide surface also show strong decomposition activity toward methanol, but through a different pathway than either the W(110) or W(111) carbide surfaces. Results from parallel studies of DMFC molecules on thin film tungsten carbides will also be presented.

10:40am **EC+SS-MoM8 Ru Nanoparticles Prepared by Decomposition of $Ru_3(CO)_{12}$ on Au (111): Structural Characterization and Chemical Properties**, ***T. Cai***, *Z. Song*, *Z. Chang*, *G. Liu*, *J.A. Rodriguez*, *J. Hrbek*, Brookhaven National Laboratory

Supported ruthenium metal particles prepared from ruthenium carbonyl have been shown as a most active catalyst for ammonia synthesis. In the emerging field of nanoscience, a goal is to make nanostructures with interesting functional properties. We have started a research program using metal carbonyls as precursors in the synthesis of nanoparticles on well-defined templates. In this study, we prepared and characterized a Au-supported Ru model catalyst under UHV by depositing metallic Ru on a Au (111) surface using triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, as a molecular precursor. We used the reconstructed Au (111) surface as an inert template for metallic cluster growth. Carbonyl adsorbs molecularly on the surface at 90 K and starts to dissociate at 280 K by CO elimination, as shown in TPD studies. The complete decomposition of the carbonyl occurs above 500 K, leaving metallic Ru on the surface with no significant C or O as detected by XPS. Such an atomically clean Ru deposit is also obtained on Au (111) by MOCVD of $Ru_3(CO)_{12}$ at an elevated substrate temperature of 550 K. The morphology of the Ru nanoparticles investigated by STM and their chemical reactivity toward simple molecules (CO, N_2, NH_3, O_2, NO_2) studied by XPS and TPD will be discussed. The research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

11:00am **EC+SS-MoM9 Development of a Microreactor System for Electrocatalytic Studies of Methanol Oxidation**, ***N. Arvindan***, *E.M. Stuve*, University of Washington

We report on the development of a microreactor for studies of methanol electro-oxidation on platinum catalysts. One of the primary benefits of the microreactor is the ease of temperature control and low consumption of reactants. Temperature can be adjusted and controlled nearly instantaneously over the range of 20 to 100 C. Higher temperatures are possible depending on the pressure limitations of the fluidic connec-tions to the microreactor. The microreactor enables studies of methanol electro-oxidation at high temperatures to achieve accelerated kinetics and freedom from CO poisoning. 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. Initial results demonstrate clean voltammetry of polycrystalline platinum electrodes for all temperatures. Reaction studies over the range of 80 to 100 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 C. At 95 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 C and support the feasibility of high temperature direct methanol fuel cells. This work is supported by the National Science Foundation and the UW Center for Nanotechnology.

11:20am **EC+SS-MoM10 Combined Atomic Force Microscope and Acoustic Wave Devices: Application to Electrodeposition**, ***J.-M. Friedt***, *L. Francis*, *K.-H. Choi*, *A. Campitelli*, IMEC, Belgium

We here present the development of an instrument based on a new combination of techniques including scanning probe microscopy (atomic force microscopy, AFM, in our case) and acoustic wave devices (quartz crystal microbalance - QCM - and acoustic wave resonators). We display the ways these two measurement techniques interact and show that their performances are not degraded through interaction. Using finite element analysis, we explain observations compatible with the generation of longitudinal acoustic waves in the liquid, creating standing wave patterns between the QCM sensing electrode and the AFM cantilever holder leading to resonance frequency instabilities of the QCM. QCM electrode vibration in liquid is also shown not to degrade AFM lateral resolution. We then show measurement results from electrodeposition of copper and silver on gold electrode obtained using this instrument, and demonstrate how the data from both techniques (QCM-D and AFM) are complementary. Since QCM-D allows simultaneous measurement of the resonance frequency at several overtones of the quartz crystal resonator as well as the dissipation (quality factor) of each of these overtones, we show how the relative frequency shifts of the overtones informs on the kind of interactions between the oscillating acoustic wave device and the surrounding media (electrodeposited layer and solution used for electrochemistry). This combined measurement was performed on AT-cut quartz resonators (QCM), SH-SAW lithium tantalate and quartz acoustic wave devices and Love mode quartz acoustic wave devices. Finally, we show that after identifying the types of interactions we can efficiently use electrodeposition as a mean of calibrating the sensitivity of acoustic wave devices. Sensitivities close to the theoretical values and compatible with previous values given in the literature are presented.

11:40am **EC+SS-MoM11 Study of Bismuth Thin Film Electrodeposition and Oxide Formation on Au(111)**, *C.A. Jeffrey, D.A. Harrington*, University of Victoria, Canada, ***S. Morin***, York University, Canada

Bismuth and bismuth oxide films have been well studied due to their magnetoresistive and semiconducting properties. In this work, the formation of electrodeposited bismuth thin films is studied using in-situ scanning tunneling microscopy (STM). Their growth mode and morphology provide useful information for the production of well-defined bismuth thin films. Electrodeposition of bismuth is performed on Au(111) in acidic solution and the bismuth film transformation to bismuth oxide in alkaline solution is studied using in-situ atomic force microscopy (AFM). Our study of the underpotential deposition process indicate that the reconstruction of Au(111) is lifted by the adsorbed bismuth, resulting in the formation of gold islands at potentials negative of 0.170 V_{SCE}. Scans taken during the overpotential deposition process at potentials negative of -0.070 V_{SCE} reveal 'needle' growth starting at step edges. These needles propagate over the surface and eventually form relatively uniform films. Atomic resolution images of the needle structures show the nearly rectangular unit cell 3.9 Å x 4.3 Å that contains one bismuth atom. The shorter side of the unit cell lies in the direction of the growth axis of the needle. This reduced spacing results in preferential incorporation of surface diffusing atoms at the needle tip, as opposed to along the edge, and accounts for the anisotropic growth. Bismuth oxide was formed by first forming the bismuth layer in acidic solution followed by a gradual shifting of the solution pH to a value of 10. Under these conditions, the transformation to the oxide film is monitored as the potential is made more positive. Close to the potential where the formation of bismuth oxide is expected, the morphology changes abruptly; small isolated protrusions form on the needle structures and cover the entire surface. The surface oxide formed can be reduced back to bismuth and this results in a disordered Bi film.

Electronic Materials and Devices
Room: C-107 - Session EL+SC+MI-MoM

Semiconductors
Moderator: A. Rockett, University of Illinois

9:00am **EL+SC+MI-MoM3 Low-temperature Epitaxial Growth of the Wide Bandgap Semiconductor SiCAlN**, ***I.S.T. Tsong***, Arizona State University **INVITED**

Two compounds, SiC and AlN, normally insoluble in each other below 2000C, are synthesized as a single-phase solid solution thin film by molecular beam epitaxy (MBE) at 750C using a unimolecular precursor H3SiCN and Al atoms. The growth of epitaxial SiCAlN films with hexagonal structure takes place on 6H-SiC(0001) and Si(111) substrates. The surface morphology, microstructure, and composition of the films are analyzed by atomic force microscopy (AFM), cross-sectional transmission electron microscopy (XTEM), Rutherford backscattering spectrometry (RBS) and high-resolution electron energy loss spectroscopy (EELS). Two structural models for the hexagonal SiCAlN films are constructed based on first-principles total-energy density functional theory calculations, each showing agreement with experimental XTEM observations. The predicted fundamental bandgap is 3.2 eV for the stoichiometric SiCAlN, in good agreement with photoluminescence (PL) measurements. Bandgap engineering is a distinct possibility by varying the composition of the pseudo-binary (SiC)-(AlN) film.

9:40am **EL+SC+MI-MoM5 Evolution of Structure and Optical Properties of GaAsN Films Grown by Reactive Molecular Beam Epitaxy**, ***M.J. Reason***, *W. Ye, X. Weng, V. Rotberg, R.S. Goldman*, University of Michigan

Narrow gap nitride semiconductor alloys have shown significant promise for a wide range of electronic, optoelectronic and photovoltaic applications. At present, the ultimate limit of nitrogen solubility in GaAs, as well as the effects of growth conditions on stress relaxation and optical properties of narrow gap nitride films are not well understood. In this work, we have examined the evolution of nitrogen incorporation, strain relaxation, and optical properties of GaAsN films grown by solid-source molecular beam epitaxy using an N2-rf plasma source. The samples consisted of 500 nm buffer layers of GaAs grown at 580C and 20 nm layers of GaAs grown at 500C, both using a high arsenic flux; followed by 100-500 nm thick layers of GaAsN grown at 400C using a 10% N2/Ar gas mixture at a 0.15 sccm flow rate, with a variety of arsenic beam equivalent pressures (BEP). The structure and properties of the samples were investigated by reflection high energy electron diffraction (RHEED), multi-beam optical stress sensing (MOSS), high resolution x-ray rocking curves (XRC), nuclear reaction analysis (NRA), atomic force microscopy, and photoluminescence. For all of the arsenic fluxes studied, in-situ RHEED during the GaAsN layer growth reveals a pattern similar to that observed during the growth of the GaAs layers. As the arsenic BEP is increased, MOSS shows that the film stress decreases, indicating a lowering of the apparent nitrogen incorporation into GaAsN. Interestingly, variations in the absolute nitrogen concentrations determined from NRA analysis and a Vegard's law interpretation of XRC suggest significant nitrogen incorporation into interstitial sites. We will discuss the effects of arsenic flux on the stress relaxation and optical properties of a variety of GaAsN and InGaAsN films and heterostructures.

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.

10:00am **EL+SC+MI-MoM6 Effects of LED Processing Steps on the Surface of Doped GaN Epilayers**, ***K.H.A. Bogart***, *D.D. Koleske, A.A. Allerman, A.J. Fischer, K.W. Fullmer, K.C. Cross, C.C. Mitchell*, Sandia National Laboratories

Gallium nitride (GaN)-based materials are critical for the creation of UV optoelectronic devices such as light-emitting diodes (LEDs). Ohmic contacts with low contact resistivities to p-type (<$1x10^{-3}\Omega cm^2$) and n-type (<$1x10^{-5}\Omega cm^2$) GaN are essential for improving optical device performance. Understanding the characteristics of p- and n-type GaN epitaxial layer surfaces and the interfaces formed with the contact metals is vital for optimization. Fabrication of an LED requires several processing steps including dicing, annealing, surface cleans (to remove native oxides), lithography, metal deposition, and plasma etching. The effects of processing steps on the surface morphology and electrical characteristics of the epitaxial materials and metal contacts have been investigated using scanning probe microscopies and the circular transmission line method (CTLM). One of the first LED processing steps is dicing a 50 mm wafer using photoresist for surface protection, which is later removed with solvents. For p-type GaN ($5x10^{17}cm^{3}$), AFM analysis showed that the surface roughness nearly doubled after photoresist exposure from an average of 0.24±0.05 nm to 0.50±0.10 nm. The source of the roughness increase was the formation of pits into the surface, ~1 nm in depth. In another LED processing step, n-type GaN is exposed by plasma etching a mesa structure into the p-type GaN overlayer. One half of a wafer with a 1.2µm n-type GaN ($1.7x10^{18}cm^{3}$) epitaxial film was plasma etched with chlorine-based chemistry. AFM analysis showed that the etched n-type GaN film (RMS=1.11±0.23nm) was not significantly more rough than non-etched n-type GaN film (RMS=1.70±0.59nm). However, after annealing (500°C/N^{2}), the plasma etched film had more Ohmic behavior by (CTLM) than did the non-etched film. More extensive experiments following the GaN epitaxial layers in processing will be presented and effects on contacts discussed.

10:20am **EL+SC+MI-MoM7 Hydrogen Removal Mechanisms from Gallium Nitride**, ***B.D. Thoms***, *Y. Yang, J. Lee*, Georgia State University **INVITED**

The reaction between hydrogen and GaN is important since hydrogen is often present (sometimes in abundance) during growth and processing and since it produces significant effects. For instance, the effect of hydrogen on the efficacy of Mg dopants has been widely reported and both annealing and electron exposures have been used to remove hydrogen. In addition, recombinative desorption of hydrogen is an important part of many dry etching processes. Removal of hydrogen requires both the transport of hydrogen to the surface and desorption from the surface. In this talk, the authors will discuss characterization of surface and subsurface hydrogen on GaN(0001) and its removal by annealing and by electron exposure.

11:00am **EL+SC+MI-MoM9 N-type Diamond Electronics With Nitrogen Doped Ultrananocrystalline Diamond**, ***J.E. Gerbi***, Argonne National Laboratory, *B.W. Alphenaar,* University of Louisville, *O. Auciello,* Argonne National Laboratory, *J. Birrell,* University of Illinois at Urbana-Champaign, *J.A. Carlisle, D.M. Gruen*, Argonne National Laboratory

Thin diamond films have extremely attractive properties for electronic device applications: high thermal conductivity, carrier mobility, and breakdown fields. However, efforts to create diamond based electronic devices have been hampered by the difficulty in incorporating dopants. Attempts to dope diamond films have resulted in low p-type carrier concentrations or unstable p-type surface layers. N-type doping has been even less successful, and it has not yet been possible to synthesize n-type diamond films with sufficiently high room-temperature conductivities. Ultra-nanocrystalline diamond (UNCD) is a fine-grained (3-5nm), phase-pure diamond material with atomically abrupt grain boundaries. Synthesized by microwave CVD using Ar-rich Ar/CH$_4$ plasmas, both the structure and electronic properties of UNCD can be tailored by doping with a controlled amount of N$_2$ in the plasma. As the N$_2$ content in the plasma increases to 20% , the grain size and grain boundary width of the UNCD films increase. This microstructural change correlates with a striking increase in room-temperature conductivity . Most importantly, nitrogen doped UNCD films are n-type with activation energies as low as 0.05 eV. This is striking, as traditional nitrogen substitutional doping of diamond produces a very deep state of 1.7eV, rendering the material useless for room-temperature applications. We use this material to demonstrate the first n-type diamond MESFET that can be operated at room temperature. We have characterized the films using Raman spectroscopy, NEXAFS, SIMS, Hall mobility measurements, and HRTEM, and measure device properties such as I-V curves and transconductance. The ohmic vs. Schottky behavior of various contacts to nitrogen doped UNCD as a function of growth chemistry has also been studied. A discussion of the microstructure-property relationship of nitrogen-doped UNCD films will be presented in the context of the UNCD-based MESFET performance.

11:20am **EL+SC+MI-MoM10 Electronic Structure and Spin-Polarization of Mn-containing Dilute Magnetic III-V Semiconductors**, ***L. Kronik***, *M. Jain, J.R. Chelikowsky*, University of Minnesota **INVITED**

The systematic use of electron spin, in addition to its charge, holds great promise for a new class of semiconductor devices with unprecedented functionality. Recently, Mn-containing, "dilute magnetic", III-V semiconductors have emerged as candidate materials for such a technology. They can potentially produce charge carriers with well-defined spin, yet are compatible with already existing semiconductor technologies. In order to assess the performance limits of such materials theoretically, we present first principles pseudopotential - density functional calculations for the electronic structure of the dilute magnetic semiconductors Mn$_x$Ga$_{1-x}$As and and Mn$_x$Ga$_{1-x}$N, with an experimentally relevant realistic x=0.063, in their ordered ferromagnetic phase. We predict that both materials allow, in principle, for a theoretical limit of 100% spin-injection, and that spin-polarized transport can be attained in both materials in the context of a simple band picture. This is because in MnGaAs, hybridization of As 4p and Mn 3d orbitals splits the valence band, resulting in a ~0.5 eV energy range where holes have a well-defined spin and an effective mass comparable to that of GaAs. In MnGaN, the situation is even more favorable: hybridization of Mn 3d and N 2p orbitals results in the formation of a ~1.5 eV wide impurity band, which supports effective mass transport. We will discuss the technological impact of these findings and compare our results to pertinent experimental data.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+EL-MoM

Spintronic Materials and Hybrid Devices
Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI+EL-MoM1 Spin-transport in Ferromagnet/Semiconductor Structures**, ***R. Jansen***, University of Twente, The Netherlands **INVITED**

Taking full advantage of electron spin in spin-electronics will eventually require an intimate integration of ferromagnetic and semiconductor materials. While device concepts are emerging, the understanding of spin transport in such hybrid ferromagnet/semiconductor structures is still at its infancy. We have focused on transport of non-equilibrium, hot-electron spins, for which spin currents can be controlled and manipulated via the electron energy and momentum. A particularly useful device for that purpose is the spin-valve transistor[1], consisting of a metallic spin-valve base, sandwiched between a semiconductor emitter and collector. Using the spin-valve transistor, we address the relative importance of interface, volume and thermal scattering of hot electron spins, and present new insight into the sources of spin-asymmetry in hot-electron transport.[2,3] From an application point of view, enhancing the output current of the transistor is desired. We demonstrate several routes to enhance the transfer ratio, culminating in an overall improvement by two orders of magnitude while preserving the low-field magnetic response above 200% at room temperature.[4] We also present transport in novel structures such as the magnetic tunnel transistor and the hot-electron spin-filter, and demonstrate that the latter allows room temperature injection of almost fully spin-polarized electrons into semiconductors.

[1] R. Jansen et al., J. Appl. Phys. 89, 7431 (2001).

[2] R. Jansen et al., Phys. Rev. Lett. 85, 3277 (2000).

[3] R. Vlutters et al., Phys. Rev. Lett. 88, 027202 (2002).

[4] O.M.J. van 't Erve et al., Appl. Phys. Lett. 80, to appear 20 may 2002.

9:00am **MI+EL-MoM3 Spin Dependent Electron Transport in Hybrid Ferromagnet/GaAs Structures at Room Temperature**, *S.J. Steinmuller, W.S. Cho, A. Hirohata, C.M. Guertler, G. Wastlbauer, T. Taniyama,* ***J.A.C. Bland***, University of Cambridge, UK

We report on the investigation of room temperature (RT) spin dependent electron transport in ferromagnet(FM)/GaAs hybrid Schottky barrier structures by photoexcitation. Spin accumulation in the GaAs was achieved by optical pumping with circularly polarised light. The photon helicity and the applied magnetic field were both introduced perpendicular to the plane of the film. Various FM materials were used (NiFe, Fe and Co) and investigated at different thicknesses (t=2.5nm, 5.0nm and 7.5nm). Furthermore an antiferromagnetic Cr sample was prepared as a reference. We measured the helicity-dependent photocurrent (PC), that is the difference in PC for illumination with right (i^+) and left circularly polarised light (i^-), for applied magnetic fields in the range from -2 T to 2 T as well as the spin polarisation $P=(i^+ - i^-)/(i^+ + i^-)$ of PC. NiFe and Fe showed a rather strong effect (P in the range 0.2-2%) increasing with film thickness, whereas almost no effect was observed in the Co. The magnetic field dependence of the helicity-dependent PC was in good agreement with polar MOKE measurements, proving that magnetic effects in the GaAs are negligible at RT. No field dependent effect was seen for the Cr as expected. Moreover we carried out measurements at different doping densities of the GaAs substrate (n- and p-type), showing the importance of the Schottky barrier in our experiment, and different photon energies. We also discuss the results of similar measurements on NiFe/Cu/Co spin valve structures. We show that our combined data provides strong support for our model of electron spin filtering at RT based on tunnelling of spin polarised electrons across the Schottky barrier followed by ballistic transport in the FM.

9:20am **MI+EL-MoM4 Tunneling Transport Across Reverse Biased Ag/Fe/Ag/GaAs Schottky Barriers**, ***D.A. Hite***, *S.E. Russek, D. P. Pappas*, National Institute of Standards and Technology

Electrical transport characteristics for the epitaxial Ag/Fe/Ag/GaAs(100) system have been studied under various growth conditions. The surfaces and structure of the multilayer were characterized by low energy electron diffraction and angle-resolved Auger electron diffraction at all steps of the fabrication. We have been able to prepare clean, well-ordered, epitaxial multilayers. The ultra-thin Ag buffer layer (~7 atomic layers) was prepared in a manner to create an ultra-thin layer to mediate the growth morphology of the Fe layer, to prevent the undesired intermixing associated with the Fe/GaAs system, and to create a tunneling barrier in reverse bias. In-situ conductance spectroscopy measurements were performed in order to characterize the rate of electron injection into the semiconductor as a function of bias voltage. We find that these multilayer diodes exhibit a reverse bias tunneling effect above 0.6 V. This is significant because it shows that we have been able to overcome the conductivity mismatch problem between the Fe and GaAs using an ultra-smooth, ultra-thin Ag buffer layer. The possibility of using these structures for direct spin injection from the Fe across the Ag/GaAs Schottky barrier will be discussed.

9:40am **MI+EL-MoM5 Modeling of Spin Injection into Disordered Semiconductors**, ***E.Y. Tsymbal***, University of Nebraska-Lincoln, *V.M. Burlakov,* University of Oxford, UK, *I.I. Oleinik*, University of South Florida **INVITED**

Spin injection into semiconductors is a topic of growing interest within the field of spin electronics. Developing a realistic model for spin injection is important both for the understanding of basic mechanisms that govern this phenomenon and for the application of spin injection in semiconductor devices. All the existing models so far either take into account a realistic band structure but neglect disorder within the semiconductor or consider phenomenologically defect scattering within a free-electron-type model. This talk will address the approach which combines an accurate description of the atomic structure, the electronic structure, and the conductance within a unique microscopic model. Within this approach the atomic structure is simulated using Metropolis MonteCarlo technique, the electronic structure is modeled using a multiband tight-binding approximation, and the conductance is calculated using the Landauer-Buttiker formalism including inelastic scattering. We will demonstrate results of the application of this model to amorphous silicon - a representative semiconducting material suitable for spin injection. We will discus decisive factors that control the efficiency of spin injection into disordered semiconductors.

10:20am **MI+EL-MoM7 Surface and Interface Properties of a Half-Metallic Alloy**, ***S.J. Jenkins***, *D.A. King*, University of Cambridge, UK **INVITED**

The ferrimagnetic semi-Heusler alloys have received considerable experimental and theoretical attention since the prediction in 1983 that they may show half-metallic behaviour (i.e. complete spin polarization at the Fermi level). Bulk properties of these alloys are now well understood. Nevertheless, application of these materials in practical situations is likely to be contingent upon the influence of their surface and interface properties, which have thus far been less thoroughly studied. This presentation will focus on recent calculations of the electronic structure of the NiMnSb(001) surface, with and without an Sb overlayer, carried out within the framework of density functional theory. Particular emphasis will be placed on the role of surface- and interface- localised electronic states in modulating the Fermi-level polarization.

11:00am **MI+EL-MoM9 Electrical Spin Injection from NiMnSb into GaAs**, ***W. Van Roy***, *P. Van Dorpe, V.F. Motsnyi, G. Borghs, J. De Boeck*, Imec, Belgium

We demonstrate electrical spin injection from NiMnSb into a GaAs light-emitting diode (LED). We compare single crystalline films grown epitaxially on GaAs(111)B with and without an additional AlAs tunnel barrier, and polycrystalline films grown on top of an AlO$_x$ tunnel barrier on GaAs(001). The LEDs and NiMnSb films were grown by MBE in two chambers connected under vacuum. For the deposition of AlO$_x$ tunnel barriers the samples were transported through air to a sputter system for the deposition of Al and oxidation in a controlled O$_2$ atmosphere. Spin injection was measured optically at T = 80 K. Electrons were injected with an in-plane spin-component. We used the oblique Hanle effect to transform this spin ensemble into an out-of-plane ensemble and used the circular polarization of the light emitted in the surface-normal direction as a measure of the electrical spin injection. The results were corrected for the out-of-plane tilting of the NiMnSb magnetization in the small oblique magnetic field, and for the MCD effect. We find electrical spin injection of up to 5% for polycrystalline NiMnSb films on top of an AlO$_x$ barrier. The spin injection drops with increasing bias voltage. The low values indicate a strongly reduced spin polarization for the polycrystalline NiMnSb films. Epitaxial NiMnSb films, especially on (111)B interfaces, are expected to show a much larger spin polarization for the conduction carriers. However, we did not yet observe spin injection from these films. This is attributed to the low interface resistance of this configuration in combination with a NiMnSb surface polarization that, although larger than for the polycrystalline films, is still short of 100%.

11:20am **MI+EL-MoM10 Epitaxial Growth and Annealing Studies of Single Crystal, Ferromagnetic Co$_2$MnGa of GaAs (100)**, ***D.M. Carr****, *S. McKernan, F.M. Abdulle, J.W. Dong, C.J. Palmstrom*, University of Minnesota

Spintronic devices that use electron spin in semiconductor devices are promising candidates for the next generation of electronic devices. Ferromagnetic metals with high spin polarization may be required for successful implementation of these devices. The Heusler alloys are a promising family of metals because the material properties such as lattice parameter, saturation magnetization, Curie temperature, and spin polarization can be altered by changing the elemental composition. In addition, their lattice parameters span most of the lattice parameters of the compound semiconductors. Films of the Heusler alloy Co$_2$MnGa have been epitaxially grown on GaAs (100) using molecular beam epitaxy. In situ reflection high-energy electron diffraction patterns and ex situ x-ray diffraction patterns of 300 Å thick films indicate single crystal growth with an out-of-plane lattice constant of 5.94 Å, which suggests tetragonally distorted growth since the bulk lattice parameter is 5.77 Å. Variable temperature vibrating sample magnetometry measurements show the Co$_2$MnGa films to be ferromagnetic with in-plane magnetization and a Curie temperature close to the bulk value of approximately 690 K. Ex situ annealing at different temperatures from 300 to 450 degrees C reveals an increase in the saturation magnetization and reduced coercivity for anneal times as short as 5 minutes at 425 degrees C. Annealed films exhibit a smaller out-of-plane lattice constant suggesting relaxation of the strained films. Cross sectional transmission electron microscopy studies will be used to characterize the level of interfacial reaction before and after annealing.

11:40am **MI+EL-MoM11 Growth Temperature Controlled Magnetism in Molecular Beam Epitaxially Grown Ni$_2$MnAl Heusler Alloys**, ***X.Y. Dong***, *J.Q. Xie, J.W. Dong**, T.C. Shih, S. McKernan, C. Leighton, C.J. Palmstrom*, University of Minnesota

The Heusler alloy Ni$_2$MnAl is thought to be either antiferromagnetic or ferromagnetic depending on its crystal structure, B2 (disordered Mn-Al sublattice) or L2$_1$.[1] This suggests that a ferromagnet/antiferromagnet interface should be possible to be formed with Ni$_2$MnAl by controlling its crystal structure. Single crystal Ni$_2$MnAl thin films have been grown by MBE on GaAs (001) using Sc$_{0.3}$Er$_{0.7}$As interlayers. The effects of growth temperature on its structural and magnetic properties were studied. For all the films grown at different temperatures, streaky RHEED patterns were observed during the growth. The Ni$_2$MnAl / Sc$_{0.3}$Er$_{0.7}$As / GaAs (001) films were single crystals with cube on cube epitaxial relationship. The Rutherford backscattering spectrometry channeling minimum yield, χ_{min}, of ~ 5 %, confirms a relatively good quality crystal. XRD and TEM show that the Ni$_2$MnAl films have a tetragonally distorted structure with its c axis oriented along the growth direction. Higher growth temperature tends to result in ferromagnetic films suggesting a more L2$_1$-like structure, while lower temperature growth gives rise to non-ferromagnetic behavior, suggesting a more B2-like structure. For the ferromagnetic Ni$_2$MnAl film, the Curie temperature was determined to be approximately 220K. The exchange bias effect was observed for Co (70Å) / Ni$_2$MnAl (360Å, B2-like structure) bilayers, suggesting that the low temperature grown Ni$_2$MnAl is antiferromagnetically ordered. Therefore the self exchange biased Ni$_2$MnAl bilayers can be expected to be grown by varying the temperature during the growth. In this presentation, the effect of growth temperature on the structural and magnetic properties will be emphasized as well as the approaches of making self exchange biased structures will be reported.

[1] F. Gejima, Y. Sutou, R. Kainuma, and K. Ishida, Metal. Mater. Trans. A 30A, 2721 (1999).

Manufacturing Science and Technology
Room: C-109 - Session MS+SE-MoM

In-Situ Monitoring and Metrology for Coating Growth and Manufacturing
Moderator: A. Diebold, International Sematech

8:20am **MS+SE-MoM1 Product Development and Yield Enhancement through Failure Analysis of Integrated Circuits with Scanning Capacitance Microscopy**, ***P. Tangyunyong***, *C.Y. Nakakura*, Sandia National Laboratories

Scanning capacitance microscopy (SCM) has become a widely used metrology tool in the microelectronics industry due to its ability to measure two-dimensional free carrier profiles with nanometer-scale resolution. To date, SCM has been used primarily to characterize source/drain formation by imaging cross-sectioned, metal-oxide-semiconductor field effect transistors (MOSFETs). We have extended the role of SCM in our Fab from an off-line research instrument to a routinely-used failure analysis tool, active in providing feedback in new product development, process validation, and yield enhancement. The SCM measurement can be performed on any two-dimensions of the sample, thus providing unique information that cannot be obtained with other analysis techniques. This information has been instrumental in helping to identify several yield-limiting defects in our CMOS device product line. In addition, SCM measurements are performed in-house with quick turnaround, yielding a considerable advantage over off-site analysis techniques, such as secondary ion mass spectroscopy. The methodology for performing both top-down (parallel to the wafer surface) and cross-sectional SCM measurements will be presented. We will show, in detail, several examples of how SCM information has been used to identify the root causes of device failures and discuss some of the corrective actions taken to reduce defects and improve yield.

This work was performed at and supported by Sandia National Laboratories under DOE contract DE-AC04-94AL85000. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation for the United States Department of Energy.

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* Falicov Student Award Finalist

8:40am **MS+SE-MoM2 Integrated CD Metrology for Poly Si Etching**, ***G.P. Kota***, *C. Lee*, Lam Research Corporation, *T. Dziura, A. Levy*, KLA-Tencor Corporation

Advanced process control (APC) is gaining widespread use because of the costs associated with 300mm wafer processing and because of the stringent control required for CD and profile due to the shrinkage of critical feature dimension. APC can be used in Feed forward, Feed back and Fault detection control modes. The KT metrology module called iSpectra is integrated on to the Lam 2300 Versys etch platform. This modular design allows for real time APC. Integrated metrology also enhances the overall equipment efficiency. A comparison of iSpectra, CD-SEM, and x-SEM results will be presented. iSpectra shows good correlation to the CDSEM measurements as well as x-SEM profiles. In addition, iSpectra repeatability is superior to conventional methods such as CD-SEM. It is common knowledge that 193nm PR shrinks during CDSEM measurements due to exposure of the PR to e-beam. This shrinkage has been measured to be up to 17nm after about 30 repeated measurements on the CDSEM. In comparison, the iSpectra measurement technique results in minimal CD shrinkage.

9:00am **MS+SE-MoM3 Metrology for Manufacturing**, ***U. Whitney***, KLA-Tencor **INVITED**

9:40am **MS+SE-MoM5 Measurements of Shallow Trench Isolation by Normal Incidence Optical Critical Dimension Technique**, ***J. Hu***, *D. Shivaprasad, F. Yang, R. Korlahalli*, Nanometrics, Inc.

Shallow Trench Isolation (STI) has emerged as one of the primary techniques for device isolation in complementary metal-oxide semiconductor (CMOS) technologies. This device isolation technology has become extremely important to satisfy the high density requirements of modern integrated circuits, It is of paramount importance to measure the critical dimensions of the STI structure. Currently used CD-SEMs cannot identify the rounding typically present at the bottom or top of the profile, and it is difficult to differentiate between the top and bottom line-width values. X-SEMs which can give the profile information require the destruction of the wafer. In this paper we present the work done on STI using the Optical Critical Dimension (OCD) technique. This technique measures line or trench profiles using Normal Incidence Polarized Reflectometry with a sensitivity to sub-50nm grating lines. In the OCD technique, a broadband polarized light beam is focused onto the grating surface, and the reflected 0th order is measured as a function of wavelength. The data obtained by measuring the grating structure gives a signature of the profile structure which is analyzed in real time using Rigorous Coupled Wave Analysis (RCWA). Since the data is fitted in real time, there is no requirement for library generation, which makes the analysis simpler and easier to extend to other structures without the need of lengthy re-generation of a new library of profile data. Data from STI wafers before and after ashing (removal of the developed resist) will be presented. Sensitivity to the oxide notching and repeatability data will also be presented.

10:00am **MS+SE-MoM6 The Evolution of Single Atomic Steps on vicinal Si(111) in NH$_4$F**, ***J. Fu***, National Institute of Standards and Technology, *H. Zhou*, University of Maryland, *J.A. Kramar, R. Silver*, National Institute of Standards and Technology

Determining the width of a feature or the scale in a pitch measurement with appropriate accuracy is fundamental for process control in state-of-the-art semiconductor manufacturing. To meet these needs as well as the future measurement and calibration needs of the emerging nanomanufacturing industry, the National Institute of Standards and Technology (NIST) has been pursuing research and development on techniques for the fabrication and measurement of atom-based dimensional standards. The key elements in the development of atom-based standards are the ability to prepare atomically ordered surfaces,and the ability to count the atoms making up the features of interest. One of the most difficult challenges in atom-based metrology has been the fabrication of an appropriate atomic template. Atomically ordered surfaces provide an intrinsic template which have both scale and orthogonality. Using Scanning Probe Microscopy(SPM), We have examined the surface produced by etching several different vicinal Si(111) sample in 40% NH$_4$F. In agreement with others, we find that deoxygenation of the etchant generally reduces the number of triangular etch pits. The formation of single atomic steps is evolved from these etch pits. These etch pits undergo nucleation, growth, merging, and corner rounding which can lead to single atomic steps. We also find that for maximum uniformity and minimum root mean square roughness, a certain minimum miscut angle is required. This angle is related to the maximum clear terrace width, which in turn is related to the relative etching rate of the step-edge sites and the terrace sites. The time evolution of the surface-smoothing etching process was also examined.

10:20am **MS+SE-MoM7 Real Time in situ Spectroellipsometry**, ***J.A. Woollam***, *B. Johs, J. Hale*, J. A. Woollam Co., Inc. **INVITED**

This talk reviews applications of spectroscopic ellipsometry for in situ monitoring and control during deposition, thermal processing, and etching of surfaces and thin-films. In situ spectroscopic ellipsometry is valuable for calibrating film growth and etch rates, controlling the thickness of each layer in multi-layer structures, and investigating nucleation phenomenon. It is also useful for measuring surface and interfacial roughness, substrate and film optical constants (with and without surface oxides), alloy composition, and substrate temperature. There have been numerous challenges to implementing in situ spectroscopic ellipsometry, including how to deal with substrate wobble and the effects of windows, and how to accurately measure thickness and material properties during growth of large numbers of layers in multi-layer stacks. Solutions to these practical problems will be discussed, and example applications described.

11:00am **MS+SE-MoM9 Real Time Process Control by Spectroellipsometry**, ***D. Daineka***, *P. Bulkin, T. Novikova, B. Drévillon*, CNRS, Ecole Polytechnique, France

In situ ellipsometry is well known to be the most sensitive, non-invasive tool for monitoring and control of thin film growth. In the fabrication of optical coatings and thin films in general the refractive index of the material is usually assumed to remain constant within a single layer. With such assumption only optical thickness of the layer can be controlled. For modern complex structures, however, even insignificant variation in the refractive index can be very detrimental to the final performance of the coating. Simultaneous real-time determination of refractive index and growth rate is required in order to comply with strict specifications. If the index departs from the pre-calculated target value, one has to adjust process parameters. In PECVD such control variables are gas flows of the precursors. We report on the closed-loop control of the silicon oxynitrides deposition by in situ phase modulated kinetic spectroellipsometry using a direct numerical inversion algorithm for the real-time reconstruction of refractive index and layer thickness. This technique is tested on constant index layers as well as on graded refractive index profiles and shown to be efficient and reliable.

11:20am **MS+SE-MoM10 In-Situ Studies of the Amorphous to Microcrystalline Transition of Hot-Wire CVD Si:H Films Using Real-Time Spectroscopic Ellipsometry**, ***D.H. Levi***, *B.P. Nelson, J.D. Perkins*, National Renewable Energy Laboratory

In-situ real-time spectroscopic ellipsometry (RTSE) provides detailed information on the evolution of the structural and optical properties of Si:H films during growth.[1] We have used in-situ RTSE to characterize the morphology and crystallinity of hot-wire CVD (HWCVD) Si:H films as a function of substrate temperature T$_s$, hydrogen dilution R=[H]/[H+SiH$_4$], and film thickness d$_b$. Transitions from one mode of film growth to another are indicated by abrupt changes in the magnitude of the surface roughness during film growth. The degree of crystallinity of the film can be determined from the bulk dielectric function. We have studied the growth parameter space consisting of R from 0 to 14, T$_s$ from 250°C to 550°C, and d$_b$ from 0 to 1 µm. For each set of R and T$_s$ values, the structural evolution of the film can be characterized by the shape of the surface roughness thickness d$_s$ versus bulk thickness d$_b$ curve. In contrast to studies done by Collins et al on PECVD growth of Si:H films, our studies of HWCVD growth find no conditions where d$_s$ remains constant after coalescence of the initial nucleation centers. Most of the films grown within the range of parameters studied exhibit a secondary nucleation and coalescence signature. The transition between a-Si:H and uc-Si:H growth is near the R=3 to R=4 dividing line. Initial coalescence of purely uc-Si:H material does not occur until R>8. We have verified the RTSE crystallinity classification using ex-situ Raman scattering.

[1] R.W. Collins, Joohyun Koh, H. Fujiwara, P.I. Rovira, A.S. Ferlauto, J.A. Zapien, C.R. Wronski, R. Messier, Appl. Surf. Sci., 154-155, 217-228 (2000).

11:40am **MS+SE-MoM11 Post-Deposition Control of Resistivity and Anisotropy in ZnO Thin Films**, ***J.S. Lewis***, *B. Stoner, C. Pace*, MCNC

A method for post-deposition control of the resistivity of ZnO thin films has been developed, and a method for providing anisotropic sheet resistance in the plane of the film has been demonstrated. Military needs for real-time image processing can be met using thin film analog image processor (TAIP) devices. TAIP chips provide compact and power-efficient analog processing, including high- or low-pass spatial frequency filtering. The analog spatial filters are based on the RC time constant of the circuit, and therefore require thin films with controlled, repeatable sheet resistance in the range of MΩ/sq. This range of sheet resistance can be difficult to achieve with good repeatability for inorganic films. ZnO thin films were sputtered from an undoped ZnO target by RF magnetron sputtering. The as-deposited sheet resistance of the films was in the range 5-50 kΩ/sq. Post deposition processing yielded films with sheet resistance in the range from the as deposited value to > 100 MΩ/sq. Target values of sheet resistance were obtained routinely. Using an in-situ monitor of sheet resistance during processing resulted in much better repeatability than that possible for as-deposited films. For TAIP chips, anisotropic sheet resistance in the plane of the film can allow more sophisticated algorithms for image processing. Post processing techniques were used to fabricate ZnO thin films with sheet resistance anisotropy ratios in the range of 2:1 to 25:1, and larger anisotropies should be possible. This work was sponsored by DARPA (contract no. DAAD19-00-1-0002).

Nanometer Structures
Room: C-207 - Session NS-MoM

Nanomechanics
Moderator: N.A. Burnham, Worcester Polytechnic Institute

9:00am **NS-MoM3 Structural Properties of Polymeric Nanostructures**, ***J.J. de Pablo***, University of Wisconsin-Madison **INVITED**

9:40am **NS-MoM5 Dynamics and Mechanics of Nanoscale Adhesive Contacts**, ***K.J. Wahl***, U.S. Naval Research Laboratory, *S.A.S. Asif*, Hysitron, Inc. **INVITED**

Recent advances in atomic force microscopy (AFM) and nanoindentation enable examination of surface mechanical properties of ultrathin films and compliant materials with far greater resolution and accuracy than ever before. In our laboratory, we have implemented dynamic mechanical analyses of nanoscale adhesive contacts using a 'hybrid' nanoindenter, coupling depth-sensing nanoindentation with AFM positioning capabilities. This combination allows surface sensitive, quantitative mechanical properties measurements of nanostructures and thin films, at a single point as well as while scanning. We illustrate these expanded capabilities with several examples: 1) a dynamic nanoscale Johnson-Kendall-Roberts (nano-JKR) adhesion test, and 2) scanning nanomechanics. The nano-JKR test allows study of processes that occur during the formation and breaking of adhesive contacts with diameters smaller than the optical limit, and can be used to measure dynamic visco-elastic properties including loss and storage moduli, adhesion energy, and strain energy release rate. Scanning nanomechanics provides a means of directly imaging mechanical response and properties with sub-micron spatial resolution. We will discuss how these new capabilities can be used to test the models and limits of continuum contact mechanics.

10:20am **NS-MoM7 Creep Compliance and Stress Intensity in Small Viscoelastic Contacts**, ***W.N. Unertl***, University of Maine, *M. Giri*, Hewlett-Packard - Corvallis

Adhesive contacts to viscoelastic materials with dimensions smaller than a few microns are difficult to analyze. This is due, in part, to the inability to measure the contact size directly. One consequence is the lack of a quantitative method to measure time-dependent mechanical properties. We demonstrate a method to overcome these difficulties. First, we extend a theory of viscoelastic contact[1] to show how the contact radius, the stress intensity at the contact edge, and the creep compliance function can be extracted directly from load vs. deformation data. Then, we apply this analysis to load controlled indentation data for a paraboloidal diamond probe on a styrene-butyl acrylate substrate with 27 C glass transition temperature. The probe is brought into contact, the load is increased linearly to a predetermined maximum, and then decreased until the contact ruptures. Loads up to 3 mN result in deformations up to 2 mm in depth depending on the loading rate and contact time. Viscoelastic effects, indicated by the occurrence of maximum penetration after maximum load, were largest for contact times near 20 s. Calculated contact radii are up to 6 mm. The creep compliance for this material is described by a power law in time with exponent near 0.8. In contrast to predictions of simple fracture mechanics models, the stress intensity is not a unique function of the speed of the contact edge. This suggests either an interaction potential between the probe and polymer that is rate dependent or a polymer response that is non-linear under the conditions that occur at the contact periphery in these experiments. These results bring into question all previously reported nanoscale measurements of the mechanical properties of viscoelastic materials.

[1] C.Y Hui, J.M. Baney, and E.J. Kramer, Langmuir 14, 6570 (1998).

10:40am **NS-MoM8 Mechanical and Electrical Properties of Mo_3Se_3-Nanowires and Nanowire-networks**, ***A. Heidelberg***, *G. Staikov*, *J.W. Schultze*, Heinrich-Heine-Universität Düsseldorf, Germany, *J.J. Boland*, University of North Carolina at Chapel Hill

Nanowires and nanotubes have attracted enormous interest as potential building blocks for nanotechnology.[1] This interest can be traced to the novel structural, mechanical and electronic properties of these nanomaterials. Here we describe a study that measures these properties in the case of the $(Mo_3Se_3)^-$-nanowire system.[2] The mechanical properties of single nanowires or bundles were studied using an SPM-nanomanipulator. This instrument allows us to controllably apply forces (µN-nN range) to supported Mo_3Se_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 nanowires can be calculated. The electrical properties of bare $LiMo_3Se_3$-nanowires have previously been shown to have metallic behaviour.[3] Exchanging the Li-counterion to alkylammonium, alkylpyridinium or alkylpiperazinium counterions produces network structures of the nanowires with a defined interwire spacing. Conductivity measurements at different temperature and oxidation times show that these networks act as percolation networks and have semiconducting behaviour. In addition the corrosion rate of the Mo_3Se_3-nanowires is slowed down in the wire networks, demonstrating that the organic coating forms partially insulating layers.

[1] J. Hu, T. W. Odom, C. M. Lieber; Acc. Chem. Res. 32 (1999) 435

[2] J. M. Tarascon, F. J. DiSalvo, Solid State Commun. 52 (1984) 227

[3] J. H. Golden, F. J. DiSalvo, J. M. J. Fréchet, Chem. Mater. 7 (1995) 232.

11:00am **NS-MoM9 Towards the Sensing of Atomic Interactions by Nanoindentation with Extremely Sharp Tips**, ***J. Fraxedas***, ICMAB-CSIC, Spain, *S. Garcia-Manyes*, CBEN and University of Barcelona, Spain, *P. Gorostiza*, University of California, Berkeley, *F. Sanz*, CBEN and University of Barcelona, Spain

A force F applied to a surface acts directly on the surface atoms and is transmitted to the bulk atoms via the crystal lattice. The bonds play thus a crucial role in the mechanical response because of their strength and spatial distribution. For a point force only few atoms are involved. In this case the elastic deformation of the surface critically depends on in-plane interactions. In order to demonstrate the relevance of such interactions we have done nanoindentation experiments on 2D materials and ionic single crystals with an AFM. The stiffness k of the crystal and an estimated radius d_s of the elastically perturbed surface can be evaluated from expression $F(\delta)=k\delta(1-d_s/\sqrt{(\delta^2+d_s^2)})$,[1] where δ stands for the surface deformation. k is related to the Debye frequency ω_D ($k_D=m\omega_D^2$), where m represents the mean atomic mass. The calculated values of k_D are very close to the experimentally derived values of k (i. e., $k=84\pm13$ Nm^{-1} and $k_D=86$ Nm^{-1} for NaCl). Nanoindentation thus reveals the collective behavior of nanoscale volumes since many atoms are involved in the process (ca. 140 ion pairs for the alkali halides). We observe that $k/d_s=c_{11}$, where c_{11} represents the (1,1) component of the elastic tensor. Feynman developed a simple model relating the anion-cation interatomic interaction k_{ac} to elastic constants for small strains for NaCl-type crystals assuming central forces.[2] Within this approximation we obtain $k_{ac}<13$ Nm^{-1}, in good agreement with $k_{ac}=10\text{-}12$ Nm^{-1}, obtained in the harmonic limit from long wavelength TO phonon frequencies.

[1] J. Fraxedas, S. Garcia-Manyes, P. Gorostiza, F. Sanz, Proc. Natl. Acad. Sci. USA 99, 5228 (2002)

[2] R. P. Feynman, R. B. Leighton, M. Sands in The Feynman Lectures on Physics (Addison-Wesley, 1964), pp. 10.

11:20am **NS-MoM10 Playing Nano-squeeze with Fluids**, ***M. Heuberger***, ETH Zuerich, Switzerland **INVITED**

It was found, over two decades ago, that some fluids exhibit a remarkable spectrum of new properties when confined between two atomically smooth and nearly parallel mica sheets in the surface forces apparatus. Oscillatory or structural forces, as well as a dynamic solidification of such thin fluid films were reported. What do these fluids have in common and what can we learn from their behavior? Well-established thermodynamic measurements of fluids adsorbed into porous materials suggest a shift of critical points, transition temperatures and enthalpies, which are more pronounced the smaller the pore radius. Recently, unexpected density and film-thickness fluctuations were discovered in these confined fluid films. Can a shift of thermodynamic quantities in small volumes account for the observed fluctuations? Recent results reveal a relationship between the thickness of the mica sheets and the amplitude of the fluctuations in the eSFA. I will present new details of the contact mechanics at sub-Angstrom resolution and discuss the role of nano-particles in SFA measurements. A comparison of measurements obtained with conventionally prepared and particle-free surfaces is shown. A mechanical model involving nano-particles is invoked to explain the observed effects.

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-MoM

Nanotubes: Growth and Characterization
Moderator: S.B. Sinnott, University of Florida

8:20am **NT-MoM1 Synthesis and Applications of Vertically Aligned Carbon Nanofibers**, ***V.I. Merkulov***, *A.V. Melechko, M.A. Guillorn, D.K. Hensley, D.H. Lowndes, M.L. Simpson*, Oak Ridge National Laboratory **INVITED**

Vertically aligned carbon nanofibers (VACNFs) prepared by direct-current (dc) plasma enhanced chemical vapor deposition (PECVD) are important for various applications including electron field emitters, tips for scanning microscopy, and biological probes, among others. To date, the crucial advantage of using VACNFs is the ability to grow them deterministically, i.e. their location, height, tip and base diameters, and, to some extent, shape, orientation, and chemical composition can all be controlled, and mechanically and electrically reliable contact to the substrate can be established. We will discuss various aspects of the VACNF growth by dc PECVD including the effects of the growth parameters on the properties of resultant VACNFs, the VACNF alignment, etc. We will demonstrate significant progress toward the ability to deterministically synthesize VACNF-based carbon nanostructures in a large-scale synthesis process. In addition, phenomenological models that explain important aspects of VACNF growth will be presented. Finally, various potential applications of VACNFs will be discussed, and the possibility of large-scale fabrication of several types of devices based on individual VACNFs will be demonstrated.

9:00am **NT-MoM3 Facilitating Single-wall Nanotube Formation by Plasma Excitation**, *B. Simard,* ***C.T. Kingston****, S. Denommee, D. Ruth*, National Research Council Canada

We have investigated the effects of laser excitation of the ablation plasma on single-wall nanotube (SWNT) formation using the laser-oven method. In the first study a high-power kilohertz YAG laser was used to thermally excite the target and ablation plasma. A sustainable production rate of 125 mg/hr of very pure SWNT material has been achieved. A second study involved the use of an argon-ion laser to electronically excite the C_2 molecule via the swan-band transition. The results with respect to nanotube yield, purity and characteristics for both studies will be presented.

9:20am **NT-MoM4 Directed Growth of Carbon Nanotubes on Anodized Aluminum Surfaces**, ***J.D. Whittaker****, M. Housley, W. Wilson, R.C. Davis*, Brigham Young University

Aluminum oxide surfaces were prepared from 20 nm aluminum films by anodic oxidation. The anodization was performed in a solution of tartaric acid and propylene glycol yielding smooth alumina surfaces. Iron was then deposited by thermal evaporation, in varying thicknesses, to act as a catalyst. Carbon nanotubes were grown on the surface by chemical vapor deposition, and characterized using scanning electron microscopy and atomic force microscopy. We will also discuss NT growth from ordered porus alumina films. These growth methods are being developed to control the location and orientation of tubes grown on solid surfaces.

9:40am **NT-MoM5 A Novel CVD Method for Large-scale Synthesis of Carbon Nanotubes**, ***B. Simard****, S. Denommee, Z. Yang, D. Ruth, C.T. Kingston,* National Research Council of Canada, *N. Braidy, G. Botton*, McMaster University, Canada

A novel CVD method for large scale synthesis of carbon nanotubes is demonstrated. It relies on the "in-situ" formation of metal nanoparticles into the feedstock solution, which is then vaporized from an aerosol nozzle into a furnace maintained between 800-1000 C. The nanoparticles are formed from laser vaporization of the bulk materials, either Ni/Co 50/50 or Co/Mo 50/50 directly in the feedstock. The nanoparticles are produced with a very narrow distribution of less than 1 nanometer with average size smaller than 3 nm. The technique is fully scalable. TEM of the synthesized nanotubes and the nanoparticles has been performed and the results will be shown at the meeting as well as more detailed description of the apparatus.

10:00am **NT-MoM6 Preparation, Chemical and Physical Properties of Large Area Free-Standing Carbon Nanofilms**, ***M.M. Kappes***, Universität Karlsruhe, Germany

Thin free standing films of single-walled carbon nanotubes (SWNT) were prepared by a novel ultrafiltration process. 1 cm x 1 cm films of less than 200 nm thickness can be routinely prepared for a variety of SWNT materials ranging from as-prepared to chemical derivatized (via amide coupling). Such films are particularly useful for transmission spectroscopic probes. We present results on gas-adsorption leading to changes in electronic structure. Furthermore we have investigated changes to optical properties associated with thermally induced deintercalation of SWNT bundles. Such processes may also be induced via visible laser irradiation thus allowing for spatial resolution.

10:20am **NT-MoM7 Growth of Aligned Arrays of Carbon Nanotubes from Patterned Catalyst Particles**, ***M.J. Bronikowski****, D.S. Choi, M.E. Hoenk, R.S. Kowalczyk, F. Noca, M.E. Taylor, R.M. Williams, E.W. Wong, B.D. Hunt*, Jet Propulsion Laboratory

Carbon nanotubes (CNT) are expected to have a wide variety of uses due to their many exceptional properties. In particular, regular arrays of CNT are expected to have applications ranging from biomolecular filters to nano-scale electronics, oscillators, and signal processors. Of central importance in such applications is the ability to grow arrays of CNT with identical dimensions and tube-tube spacings. This talk will discuss our recent efforts in JPL's Microdevices Laboratory toward this goal. CNT are grown from gaseous carbon-containing precursors (hydrocarbons, CO) on substrate surfaces such as Si or SiO2 by chemical vapor deposition (CVD): CNT nucleate and grow from nanometer-size particles of catalytic metals (Fe, Ni, Mo) that have been pre-deposited on the substrate. CNT dimensions and arrangement are determined by the size and arrangement of the catalyst dots, and by the CVD growth parameters. Various methods for controllably placing catalyst particles on surfaces will be demonstrated and discussed. In particular, methods for patterning catalytic metals with nanometer precision using self-assembling thin films of block copolymers will be presented.

10:40am **NT-MoM8 Carbon Nanotube Growth for Nanomechanical Devices**, ***M.E. Hoenk****, R.S. Kowalczyk, M.J. Bronikowski, E.W. Wong, D.S. Choi, F. Noca, R.M. Williams, M.E. Taylor, B.D. Hunt*, Jet Propulsion Laboratory, California Institute of Technology

Mechanical resonators with nanometer dimensions offer the capability for sensors and actuators to interact with materials at the molecular scale. We are developing device structures based on carbon nanotube mechanical resonators. While the unique mechanical and electronic properties of carbon nanotubes are promising for this application, the relationship between growth conditions and nanotube properties plays a major role in nanotube device development. In this paper, we will present our most recent results on the growth, processing, and characterization of carbon nanotube arrays. We have grown aligned carbon nanotube arrays over a wide range of pressures and temperatures using thermal and plasma-enhanced chemical vapor deposition. We have experimented with a variety of catalyst materials, growth conditions, and patterning techniques, and we have characterized the catalysts and nanotubes using scanning and transmission electron microscopy, Raman spectroscopy, and atomic force microscopy. We have demonstrated growth of aligned arrays of carbon nanotubes at temperatures as low as 411 C. The research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, and was jointly sponsored by the National Aeronautics and Space Administration, Office of Aerospace Technology, and the Defense Advanced Research Projects Agency, Microsystems Technology Office.

11:00am **NT-MoM9 High-resolution Transmission Electron Microscopy Study of Catalyst Metal Particle at the Tip of Carbon Nanotube**, ***T. Ikuno****, S. Takahashi, K. Kamada, S. Ohkura, M. Katayama, T. Hirao, K. Oura*, Osaka University, Japan

Carbon nanotubes (CNTs) have been attracted much attention due to their fundamental research interest and potential applications. Control of alignement of CNT is essential for applications such as field emission display (FED), quantum wire, and field effect transistor. For FED application, to concentrate electric field at the CNT tip, vertically aligned CNT is desirable. On the other hand, lateral alignment is necessary for nanodevice application. In this study, we have performed high-resolution transmission electron microscopy (TEM) analysis focused on the metal particle at the tip of CNT to clarify correlation between growth mechanism of CNT and crystallography of metal catalyst. Specimens are randomly and vertically aligned CNTs which are synthesized on Ni (50 Å)/ Si (100) substrates by thermal chemical vapor deposition and RF-plasma CVD, respectively. From TEM observation of Ni particle at the tip, it was found that randomly CNT (bamboo-like CNT) has spherical Ni particle at the tip, and vertically CNT (multi-wall CNT) has a wedge shape with flat facets. Both particles were found to be monocrystalline. The crystalline orientations of the particles were also investigated. The axial directions of the vertically CNT are mainly parallel to the <111> and <311> direction of Ni. From high-resolution TEM image of Ni / CNT interface, graphite layers were formed along the ridge line of Ni particle for randomly CNTs, whereas they were formed along specific planes parallel to the growth direction for vertically CNTs. On the basis of these results, we will discuss the mechanism of alignment process associated with growth front of graphite layers precipitated from the Ni particle. This work was performed with

Japan Fine Ceramic Center under the Frontier Carbon Technology Project of the New Energy and Industrial Technology Development Organization.

11:20am **NT-MoM10 Nitrogenated Carbon Nanostructures Grown by Microwave Induced Hot-filament CVD Techniques**, ***D. Sarangi***, *A. Karimi*, FSB-IPMC, EPFL, Switzerland

Nitrogenated carbon nanotubes and nanostructures were grown by microwave induced hot-filament chemical vapor deposition (CVD) technique. The mixture of methane or acetylene gas with ammonia or nitrogen gas was used as feed gas. The nanostructures were grown on silicon substrates using iron (Fe) and nickel (Ni) as catalysts. The morphological properties of the nanotubes and nanostructures were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effect of microwave power and the influences of precursor gases on the structures of nanotubes were discussed. About 5 atomic percentage of nitrogen was observed as measured by electron energy loss spectroscopy (EELS). High-resolution TEM observation revealed that, with the increase of nitrogen concentration the outer graphane shell of the nanotube becomes more rough, retaining the crystallinity. In general, this paper will discuss the morphological properties of the carbon nanostructures with respect to the mechanical properties.

Plasma Science
Room: C-105 - Session PS-MoM

Conductor Etch I
Moderator: S. Han, University of New Mexico

8:20am **PS-MoM1 The Evolution of Plasma Etching in Integrated Circuit Manufacturing**, ***J.W. Coburn***, University of California, Berkeley **INVITED**

Anisotropic plasma etching methods were introduced into semiconductor manufacturing in the late 1970s. The notion of using reactive gas glow discharges to etch solid materials had been described much earlier but it was not until the mid 1970s that the anisotropic etching capabilities of plasma etching were recognized. At this time, it was understood that the requirements for anisotropic etching were both energetic ion bombardment of the surface being etched and an exothermic chemical reaction between the gas phase reactants and the surface that form a volatile reaction product. Early plasma etching systems were primarily capacitively coupled, single frequency diodes with either planar or cylindrical geometry. In order to achieve the desired etch rates, relatively high energy (0.5 to 1 keV) ion bombardment of the surface being etched was required. However this bombardment tended to reduce etch selectivities and increase wafer damage. Furthermore, the plasma potential in capacitively coupled systems can exceed 100 volts, resulting in high energy ion bombardment and sputtering of grounded surfaces; a possible source of wafer contamination. These issues were addressed by separating the plasma generation from the wafer bias. During the early 1980s, single frequency and dual frequency triodes were popular. Later in the 1980s, inductively coupled and wave-generated plasma sources were introduced. These sources allowed the generation of high density plasmas (10^{11} to 10^{13} electrons/cm^3) which, when combined with a relatively low power capacitively coupled chuck, allowed high etch rates to be achieved with relatively low ion energies (50 - 200 eV). Today, each wafer is exposed to a plasma etching environment between 10 and 20 times during its manufacture and without the highly anisotropic etching provided by this critical process, high density IC manufacturing would not be possible.

9:00am **PS-MoM3 Resist Transformation under High Density Plasma Exposure**, ***E. Pargon***, *J. Foucher, J. Detter, L. Vallier, G. Cunge, O. Joubert*, CNRS/LTM, France, *Th. Lill*, Applied Materials

We are now entering in the development of sub 0.1 µm Integrated Circuits device fabrication where a very accurate control and understanding of plasma processes is essential to address the road map requirements. In particular, plasma processes involved in gate stack processes need special attention since several steps such as resist trimming, hard mask opening and silicon etching impact the final gate dimension. In any of these processes, the etching behaviour of photoresist exposed to the plasma plays a key role. In this study, we have performed chemical topography analyses using XPS to explore the chemical nature and thickness of the reactive layers formed on the resist patterns. XPS analyses show that the resist transformation during the resist trimming process is well correlated with the trim rate measured in HBr/O$_2$ and HBr/Cl$_2$/O$_2$ /CF$_4$ chemistry. In particular, a decrease in trim rate obtained when increasing the bias power is well correlated with a thicker perturbed layer formed on the resist sidewalls. A good correlation between reactive layer thickness on the sidewalls and decrease in trim rate is also observed with CF$_4$ addition. CF$_4$ based plasmas used for hard mask opening generate reactive layers as thick as 10 nm on the resist sidewalls (through the formation of a CFx-based layer). This layer is suspected to generate a loss of CD control during hard mask patterning. Deep transformations of the resist during silicon gate etching are also observed. XPS studies show that the resist mask strongly loads chlorine species as compared to an oxide hard mask and that thick passivation layers are formed on the resist sidewalls using HBr/Cl$_2$/O$_2$ and HBr/Cl$_2$/O$_2$/CF$_4$ chemistries. Correlations between resist behaviour and process control (mainly CD control) can be established

9:20am **PS-MoM4 A Novel Gate-Electrode Fabricating Technique using a Sequential UHF-ECR Plasma Process**, ***M. Mori***, Hitachi, Ltd.,Japan, *T. Tsutsumi*, Hitachi High-Technologies Corp.,Japan, *N. Itabashi, M. Izawa*, Hitachi, Ltd.,Japan

For fabricating beyond 90 nm-node devices, ArF lithography will be increasingly used. This process demands that the gate electrode must be trimmed more than 50 nm after lithography and critical dimension (CD) shift variation must be suppressed within 3-5 nm across the wafer. However, gate-electrode trimming of more than 50 nm using only ArF trimming is difficult, because the resist is too thin or bent in followed hard-mask etching. Therefore, we have developed a sequential gate process consisting ArF/polySi trimming that uses a UHF-ECR plasma. This plasma has capability to precisely CD-shift control, because of its moderate ion-current flux (ICF) at low pressure and its by-product uniformity control.[1] In polySi trimming, we evaluated the vertical undercut process. By using this process, we can measure gate-length with a CD SEM after wet etching. For vertical undercut process, we used multi-step etching, consisting a polySi main etching step with a thin side-wall protection film, followed by a highly selective trimming step. The amount of trimming could be controlled by the time of trimming step, and 86.5±1.5 nm trimming was obtained without punching through in a 2.5-nm gate-oxide layer. Regarding ArF trimming, it was confirmed that O$_2$ containing gas chemistry provided good hard-mask selectivity and good linearity of time control. Trimming - rate variation across the wafer was within 2.7 nm/min. To suppress resist bending in hard-mask etching, the vertical/horizontal etching rate ratio was controlled in ArF trimming, and CHF$_3$ based gas chemistry was used for the hard-mask etching. This good linearity of CD control with time in ArF/polySi trimming will be caused by UHF-ECR plasma that has more moderate ICF and less interaction with the reactor wall.

[1] M. Mori, et al., (2000), Proceeding of Solid State Devices and Materials, p. 192.

9:40am **PS-MoM5 Impact of Chemistry and Mask Nature on Critical Dimension Control of Gate Etch Processes**, ***X. Detter***, STMicroelectronics, France, *G. Cunge, E. Pargon, L. Vallier, O. Joubert*, CNRS/LTM, France, *R. Palla, I. Thomas-Boutherin*, STMicroelectronics, France

During a CMOS gate etch process, requirements in terms of Critical Dimension (CD) bias and microloading are more and more severe. Since gate etch processes are composed of several steps (resist trimming, BARC and probably hard mask opening, poly-silicon main etch step, soft landing step (to preserve the gate oxide) and over-etch step), a good understanding of the mechanisms influencing the CD deviation is necessary for each of them. During a classical poly-silicon gate etch process, passivation layer deposition on the gate sidewalls is known to be one source of CD microloading and the main source of CD bias for isolated patterns. However, as the aspect ratio is increasing, the profile evolution is more complicated and may be influenced by loading and shadowing effects as well as charging effects. Indeed, the passivation layer formation results from deposition of inhibitors and etching by radicals which are both strongly influenced by the nature of the mask and total aspect ratio of the structure. In this talk, we present a study of profile evolution during the poly-silicon etch steps with a resist and an oxide hard mask. Aspect ratio dependent etching and passivation layer deposition mechanisms are investigated for chemistries used in today's gate etch processes : HBr/Cl$_2$/O$_2$ and HBr/Cl$_2$/O$_2$/CF$_4$. Loading and shadowing effects induced by the mask are more precisely investigated (in a range of aspect ratio varying from less than 0.1 to more than 3 and a minimal space between lines of 60 nm). A correlation with X-ray Photoelectron Spectroscopy analysis of passivation layers composition and emission spectroscopy of by-products present in the gas phase is also performed. Finally, the limits of the current processes and potential strategies for future gate etch processes are discussed.

10:00am **PS-MoM6 Deposition of Silicon Oxychloride Films on Chamber Walls during Cl_2/O_2 Plasma Etching of Si**, ***S.J. Ullal***, *H. Singh, V. Vahedi*, Lam Research Corporation, *E.S. Aydil*, University of California, Santa Barbara

Chlorine plasma etching of silicon is widely used in gate etching and shallow trench isolation. During etching, the silicon chloride etch products react with oxygen present in the plasma to deposit a glassy silicon oxychloride film on the chamber walls. The chemical nature and deposition rate of the silicon oxychloride films deposited on the chamber walls during Cl_2/O_2 plasma etching of Si were investigated using multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy. The differences in the infrared spectra of films deposited under different etching conditions were quantified through the Si-O and OSi-Cl absorption band intensities and positions to determine the growth rate and composition of these films. The changes in the film's deposition rate and composition with rf bias power and O_2 flow rate gave insight into the deposition mechanism. Based on our experimental observations, we propose that the silicon oxychloride film is deposited through oxidation of $SiCl_x$ $(0 \le x \le 4)$ molecules adsorbed on the reactor walls and suggest a kinetic expression for the film deposition rate. This kinetic expression may also be used judiciously for describing the silicon oxychloride deposition on the sidewalls of etched features in gate etching and shallow trench isolation.

10:20am **PS-MoM7 HBr Outgassing and Condensation from Silicon and Polysilicon Wafers after Plasma Etching**, ***H. Singh***, *D. Outka, J.D. Daugherty*, Lam Research Corporation

HBr gas is commonly used in dry etching of poly-silicon gate structures and in shallow trench etching since HBr-rich etch chemistry provides good profile control and high selectivity to gate oxide. As a result, the surface of wafers in many silicon etch processes are bromine terminated at the end of plasma etching. Subsequently, HBr outgasses from etched wafers upon exposure to atmosphere. HBr also condenses on the etched wafer and neighboring wafers in the form of HBr-hydrate and bromine-hydrate. HBr and bromine hydrates crystals are stable at ambient conditions. The timescale for HBr outgassing and condensation varies from few seconds to days, depending on the etch and ambient conditions (e.g. humidity). HBr outgassing and condensation also occurs on bare silicon wafers commonly used to condition plasma etchers before etching production wafers. The re-use of these bare silicon wafers results in micro-masking of the wafer by the HBr-hydrate crystals, resulting in formation of silicon pillars on the wafer. The micro-masking of the wafer results in formation of so-called "black silicon" rendering the wafer unusable. Various methods investigated to minimize the outgassing and condensation of HBr on wafers, including the heating of the wafer in vacuum, heating the wafer after exposure to atmosphere, and treating the wafer with oxygen plasmas, show limited success in removing bromine from the wafer surface. Separation of unetched and etched wafers on the etcher is the most effective method of eliminating micro-masking of unetched wafers. For bare silicon wafers, post treatment of the wafer with fluorine plasma is an effective way to remove the bromine from the wafer. A phenomenological model explaining the processes involved is presented, elucidating the role of chemisorbed and physisorbed bromine on the wafer.

10:40am **PS-MoM8 Energetic Neutral Fluxes Towards Surfaces in a MERIE Like Reactor**, ***W. Sabisch***, *M. Kratzer*, Infineon Technologies AG, Germany, *R.P. Brinkmann*, Ruhr University Bochum, Germany

In VLSI microelectronics fabrication Magnetically Enhanced Reactive Ion Etch (MERIE) reactors are established for many dry etch processes. One example is the etch of high aspect ratio capacitor trenches.[1] For feature scale profile evolution the angularly and energetically resolved distributions of the surfaces incident particles (ions and neutrals) as well as the fluxes of ions and neutrals play an essential role. Butterbaugh et al.[2] showed that the etch yield for the selective SiO_2 / Si etch is strongly influenced by the ratio of neutral to ion fluxes. The focus of this work is set on the calculation of the neutral to ion fluxes ratio. Therefore the MERIE reactor's boundary sheath is simulated by the TCAD simulation tool Hybrid Plasma Sheath Model (HPSM).[3,4] HPSM consists of a self-consistent coupling of a fluid dynamical part to a Monte-Carlo part. Sheath and presheath region are described in one unified model. Energetic neutrals impinging the surface can be monitored in addition to the positive ion species. Presented are simulations with parameters typical for a trench etch with pressures in the range of about 100 mTorr, rf voltages of a few 100 Vs, magnetic fields of about 100 Gauss and plasma powers of about 1000 W. The simulations show that the flux of the energetic neutrals compared to the flux of the ions is not neglectable and that the neutral flux gives an important contribution to the energy budget of the surface impinging particles.

11:00am **PS-MoM9 ICP Etching of Poly-crystalline Si-Ge as a Gate Material**, *K.M. Tan*, ***W.J. Yoo***, *W.K. Choi, Y.H. Wu, J.H. Chen, D. Chan*, National University of Singapore

In recently years, silicon germanium ($Si_{1-x}Ge_x$) is receiving significant attention as a candidate gate material to replace polycrystalline silicon, since Si-Ge can have advantages over poly-Si in achieving small threshold voltage and high trans-conductance required in sub 100 nm CMOS devices. In this work, we wish to demonstrate etching properties of the $Si_{1-x}Ge_x$ films using an inductively coupled plasma. The polycrystalline $Si_{1-x}Ge_x$ films were deposited by sputtering at 250°C and annealed at 900°C subsequently. The amount of Ge in the $Si_{1-x}Ge_x$ films varied from 10% to 60% by changing the sputtering target. According to preliminary results obtained using ICP of CF_4+H_2, the etching rates were strongly dependent on the amount of Ge in the $Si_{1-x}Ge_x$ films. The maximum etching rate was obtained at the chamber pressure of 20mTorr: 2.2 µ/min at 60% Ge and of 0.9 µ/min at 10% Ge when an inductive RF power of 1000W was applied. The etching rates were increased almost linearly as a function of %Ge. We were able to obtain anisotropic etching profiles over the entire experimental range of %Ge, despite that photoresist profiles prior to the ICP etching were not anisotropic. To control critical dimension of gate structures precisely and to obtain high selectivity with respect to thin oxide under-layer, we propose etching mechanisms of $Si_{1-x}Ge_x$ gates in ICP using Cl_2, HBr, and O_2, and also reveal their sidewall passivation properties.

11:20am **PS-MoM10 Endpoint Strategies for Recess Etch Processes in DRAM and eDRAM Applications**, *J.P. Merceron*, Ecole Polytechnique, France, ***V.C. Venugopal***, *A.J. Perry, A.J. Miller*, Lam Research Corporation

Developing a robust and reliable strategy to determine the end point of recess etch processes for DRAM and eDRAM applications presents some unique challenges. These processes involve etching the poly-Si back-filled into trenches in a Si substrate. The tight depth control required necessitates accounting for incoming material variations, mask erosion, and variations in the densities of incoming patterns. In addition, if an optical diagnostic tool such as an interferometer is used, the high aspect ratio structures and low open area lead to low signal levels, low fringe contrast and signal noise. Incoming nitride mask thickness could vary depending on the planarization process used (either CMP or etch) and the device being fabricated. Target depths are usually specified with respect to the bottom of the nitride layer. The starting recess depth (after planarization) is usually not known either. These uncertainties necessitate measurement of the starting nitride thickness as well as the initial recess depth to achieve the required accuracy. We have developed a robust endpoint strategy based on a broadband (UV-VIS-NIR) reflectometer, adapted to provide a high signal-to-noise ratio (SNR), to achieve the desired degree of control for recess etch processes. The broadband reflectance spectrum carries sufficient information to be able to determine the starting parameters of interest. The evolving recess structure causes a discernible modulation of the reflected light from the wafer, especially at short wavelengths (typically <300nm). A robust fringe counting method which accounts for mask erosion and etch rate variations but is insensitive to signal noise is then used to determine the change in depth of the recess relative to its initial value.

11:40am **PS-MoM11 Numerical Model of a Cl_2-BCl_3 Metal Etch Reactor**, ***G.I. Font***, *W.L. Morgan*, Kinema Research

Plasmas containing Chlorine (Cl2) and Boron trichloride (BCl3) are used in the patterning of interconnects during integrated circuit manufacturing. Optimization of the plasma uniformity in the reactor is important for the purpose of accurate pattern transfer across the entire wafer. Optimization, however, requires understanding of the influence of the reactor variables (power, pressure, and geometry) on the plasma chemistry. Simulation can aid in providing understanding of metal etch reactors by providing insight into the relative importance of chemical path ways and their dependence on reactor external variables. We have developed a chemical model for an Ar, BCL3, Cl2 discharge. Comparisons with experimental measurements inside a commercial reactor demonstrate good agreement with plasma density and electron temperature. The model also captures the plasma density distribution across the reactor and the dissociation characteristics with respect to pressure. Results below 10 mTorr suggest that parent negative ions may play an important role in the discharge.

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[1] J. Bondur, R. Bucknall, F. Redeker, and J. Su: Proc. of the SPIE 1992, vol. 1803, pp. 45ff

[2] J.W. Butterbaugh, D.C. Gray, and H.H. Sawin: JVST B, vol. 34, 1991, pp. 1461ff

[3] M. Kratzer and R.P. Brinkmann: The IEEE Int. Conf. on Plasma Science 2000, 3D03

[4] M. Kratzer, R.P. Brinkmann, W. Sabisch, and H. Schmidt: JAP, vol. 90 (5), 2001, pp. 2169 ff.

Surface Science
Room: C-108 - Session SS1-MoM

Adsorption and Chirality
Moderator: B.E. Koel, University of Southern California

8:20am **SS1-MoM1 STM Studies of the Role of Copper in Chlorosilane Desorption Mechanisms from Cl-exposed Cu/Si(111) Surfaces**, ***D.V. Potapenko***, *S.E. Sysoev, A.V. Ermakov, D. Maithil, B.J. Hinch*, Rutgers University

TPD experiments show that the presence of copper on a Si(111) surface significantly influences the desorption kinetics of chlorosilanes from chlorine-exposed Si(111) surfaces. The major desorption peak (of SiCl$_2$) occurs at ~600°C from Cl-covered Cu/Si(111) surfaces, and complex desorption kinetics are exhibited that indicate an active role of chlorine-free sites in the SiCl$_2$ desorption process. In contrast, SiCl$_2$ desorption from Si(111) 7x7 surfaces is observed at ~650°C and this follows comparatively simple second-order kinetics. Here we report on STM studies of the Cl-covered Cu/Si(111) surfaces, following low temperature (~450°C) restructuring and at the onset of chlorosilane desorption at 600°C. We will display evidence for the direct role of copper in the aggregation of Cl in compact Cl-containing regions during the high temperature chlorosilane desorption process. We will also discuss possible mechanisms of Cu-catalyzed desorption of chlorosilanes from the Si(111) surface.

8:40am **SS1-MoM2 Dynamics of Oligomer Desorption from Surfaces**, *A.J. Gellman,* ***K.R. Paserba***, *N. Vaidyanathan*, Carnegie Mellon University

A study of the desorption of long chain oligomers from surfaces has revealed that the measured desorption energies are non-linear in the oligomer chain length. This work has used alkanes, polyetheyleneglycols, and polyethyleneglycol dimethylethers with chain lengths in the range 5 to 60 atoms. These have been adsorbed on the surface of graphite at low temperature and the kinetics of desorption have been measured using temperature programmed desorption. Empirically we find that the desorption energies scale as the square root of the chain length. A model has been proposed for oligomer desorption that accurately accounts for the observed dependence of the desorption energy on chain length. The adsorbed oligomers can be considered to consist of segments that are attaching to and detachng from the surface independently. Within the context of transition state theory these partially detached oligomers are in equilibrium with a transition state to desorption which is fully detached from the surface. The energy of each of the detached states is simply proportional to the number of detached segments. The entropy is given by the number of ways of detaching segments and by the partition function for trans-gauche conformations about each detached bond. These energies and entropies determine the equilibrium constants for each of the partially detached species. These considerations can be formulated into an analytical expression for the measured desorption energy that accurately reproduces the experimental results. One of the interesting insights that our model provides is that the analytical expression for oligomer desorption energies exactly matches the predictions of Tolman's theorem. Because the oligomers on the surface can adopt a huge number of conformations this leads to a substantial non-linearity in the desorption energy as a function of chain length.

9:00am **SS1-MoM3 D Abstraction by H on Si(111) Surfaces: Temperature and Coverage Dependence**, ***F. Khanom***, *F. Rahman, A. Aoki, A. Namiki*, Kyushu Institute of Technology, Japan

Influences of surface temperature T_s and D adatom coverage on direct abstraction (ABS) as well as collision-induced-desorption (CID) of surface D adatoms by H atoms have been studied on Si(111). We found that D_2 CID as a result of reaction H + D/Si --> D_2 , obeys a third-order kinetics with respect to θ_D, ruling out the so-called hot atom mechanism. D_2 CID rate versus T_s curves were found to exhibit a close similarity in spectral line shape with a β_2 temperature-programmed-desorption (TPD) spectrum arising from a dideuteride phase. The spectral similarity between CID and TPD suggests that D_2 CID obey the same mechanism as for the β_2 TPD. In order to understand the underling mechanism we measured reaction order of the β_2 TPD. As a consequence, 1.5th-reaction order was obtained with respect to dideuteride coverage. The 1.5th reaction order suggests that three D atoms are involved in a single D_2 desorption, which rationalizes the third-order reaction observed in D_2 CID. Regarding ABS to form HD molecules, HD rates were determined for various θ_D. As a result, we found that a first-order kinetics prevails the HD ABS for low D coverage regime below 0.5ML, but strangely enough, a second-order kinetics becomes dominant for high coverage regime around 1.0 ML. The second-order kinetics suggests that a direct Eley-Rideal reaction mechanism as well as hot atom mechanism are ruled out. We propose a new mechanism of hot complex mediated ABS and CID: the incident H atoms form a complex with D-Si system in the very early stages of sticking. ABS and dihydride formation occur competitively during the relaxation process of the hot complex.

9:20am **SS1-MoM4 Adsorption and Abstraction of H Atoms on the Graphite (0001) Surface**, ***T. Zecho***, Max-Planck-Institut für Plasmaphysik (EURATOM Association), Germany, *A. Güttler, C. Drummer*, Universität Bayreuth, Germany, *X. Sha, B. Jackson*, University of Massachusetts, *J. Küppers*, Max-Planck-Institut für Plasmaphysik (EURATOM Association), Germany

The interactions of hydrogen atoms with graphite surfaces are of interest for many areas like astrophysics, plasma surface interactions in controlled fusion devices and diamond synthesises. Nevertheless most of the knowledge up to now is deduced from theoretical work and without experimental evidence. The present study has been performed in order to verify recent theoretical results on the interactions of hydrogen atoms with the graphite basal plane. Highly oriented pyrolytic graphite (HOPG-ZYH) was used and characterised by scanning electron microscopy (SEM) prior to the experiments. Hydrogen atoms were generated by thermal dissociation of hydrogen molecules in a tungsten capillary heated to 2000 K. Adsorption and abstraction were investigated by thermal desorption spectroscopy (TDS), electronic and vibrational energy loss spectroscopy (EELS, HREELS) and in situ measurment of the abstraction products. Admission of hydrogen atoms at low temperatures (100 K-300 K) leads to adsorption of hydrogen on graphite up to coverages of about 0.5 monolayer. In EEL spectra the intensity of the π-plasmon of graphite decreases upon hydrogen adsorption indicating a decreasing sp^2 character of surface carbon 2sp electrons. HREEL spectra allowed to determine the C-H normal and parallel vibrational frequencies which are close to theoretical predictions. Heating of H(D) covered graphite surfaces leads to desorption of hydrogen (deuterium) molecules with peaks between 300 K and 600 K. The thermal desorption peak maxima show a large isotope effect of about 50 K. The admission of deuterium atoms to H covered graphite surfaces leads to the release of HD and a very small amount of H_2. The abstraction reaction shows a coverage dependent cross section which decreases from about 16 Å^2 at low coverages to about 4 Å^2 close to saturation.

9:40am **SS1-MoM5 Experimental and Theoretical Characterization of the Vibrational Properties of Aminocarbyne Surface Intermediates**, *B. Chatterjee, D.H. Kang*, University of Illinois at Chicago, *P. Mills*, North Central College, ***M. Trenary***, University of Illinois at Chicago

Density functional theory (DFT) calculations and measurements using reflection absorption infrared spectroscopy have been used to characterize aminocarbynes on a Pt(111) surface. The three aminocarbynes considered are CNH_2, $CNHCH_3$ and $CN(CH_3)_2$. The CNH_2 species, known simply as aminocarbyne or as aminomethylidyne, is formed from HCN, methyl amine, or the hydrogenation of surface CN. Methylaminocarbyne, $CNHCH_3$, can be formed from the N-protonation of methyl isocyanide ($CNCH_3$) or from the partial dehydrogenation of dimethyl amine, $HN(CH_3)_2$. Dimethylaminocarbyne, $CN(CH_3)_2$, is formed from the decomposition of trimethylamine, $N(CH_3)_3$. The DFT calculations were based on a model consisting of only two Pt atoms, as would be appropriate for bonding at a two-fold bridge site. Gaussian 98 with the B3LYP functional and a 6-311G** basis set along with effective core potentials for the Pt atoms was used. The calculations converged and optimized to reasonable geometries. For example, Pt_2CNH_2 converged to a C_{2v} symmetry structure with a CN bond length of 1.32 Å with calculated frequencies (using the appropriate scale factor of 0.9613) for the ν(CN), $\delta(NH_2)$, and ν_s(NH) fundamentals of 1393, 1564, and 3407 cm^{-1}, respectively, compared to experimental values for CNH_2 on Pt(111) of 1323, 1567, and 3363 cm^{-1}. The calculations successfully reproduce not only the measured vibrational frequencies, but also the relative intensities and the measured shifts that occur with various isotopic substitutions. Calculations using larger Pt clusters, which are much more time consuming, lead to only modest improvements. The results suggest that the internal vibrations of polyatomic adsorbates can be successfully calculated using models of the surface that are surprisingly simple.

10:00am **SS1-MoM6 Adsorption and Adhesion Energies of Pb on (1x1)-MoC/Mo(001) by Single-crystal Adsorption Calorimetry**, ***M.H. Smedh***, *S.F. Diaz, C.T. Campbell*, University of Washington

The heat of adsorption, sticking probability and film growth mode of Pb adsorption was studied on a thin, ordered MoC film at 300 K. A several layers thick film of MoC displaying a (1x1) LEED pattern was grown by dissociating ethylene on hot Mo(100), following Frühberger.[1] The Pb atoms were deposited in a chopped molecular beam, with 0.1 s pulses containing 0.015 ML Pb every 2 s. The Pb beam flux was determined using a quartz crystal microbalance. The heat of Pb adsorption was measured by single-crystal adsorption microcalorimetry, based on King's approach,[2] with a different heat detection scheme. The adsorption of a Pb pulse causes a transient heat input and temperature rise, detected by a pyroelectric polymer ribbon in contact with the backside of the sample.[3] An initial heat of adsorption of 245 ± 5 kJ/mol was found. It stayed constant up to ~0.5 ML, then dropped smoothly up to 1 ML to ~195 kJ/mol, within a few percent of the heat of sublimation for Pb, where it remained constant up to ~ 8 ML. The implications of these results with respect to Pb-Pb repulsions and Pb mobility in the adlayer will be discussed. From the integral heat of adsorption at 8 ML, a Pb/MoC adhesion energy of ~180 $\mu J/cm^2$ was obtained. This will be compared to results obtained from the contact angle of molten Pb drops. The sticking probability was found to be 0.96 initially, increasing linearly up to ~1 ML to 0.994 ± 0.003, where it remained for higher coverages. The growth mode of Pb on (1x1)-MoC/Mo(100) was further investigated by comparing the behavior of the Pb and Mo AES intensities as a function of the Pb coverage to different growth models.

[1] B. Frühberger and J.G. Chen, Surf. Sci. 342 (1995) 38.

[2] C.E. Borroni-Bird and D.A. King, Rev. Sci. Instrum. 62 (1991) 2177

[3] J.T. Stuckless, N.A. Frei, and C.T. Campbell, Rev. Sci. Instrum. 69 (1998) 2427.

10:20am **SS1-MoM7 Enantioselectivity on Naturally Chiral Surfaces**, ***A.J. Gellman***, *J. Horvath*, Carnegie Mellon University **INVITED**

Chirality is an omnipresent feature of the biochemical and biophysical world. The handedness of the molecules that form the basis of life creates the need for enantiomeric purity in the chemicals used for pharmaceutical and other bio-active purposes. Many of the processes used for synthesis and preparation of enantiomerically pure compounds rely on the use of chiral surfaces. The high Miller index surfaces of metals have chiral structures and can, in principle, be used for to control enantioselectivity in chemical processes. The kinked step structures of such surface are chiral and thus serve as chiral binding sites for a number of enantiospecific adsorption, desorption and surface reactions. As an example, the orientation of chiral molecules on chiral surfaces can be shown to depend on the relative handedness of adsorbate and substrate. This has been shown by study of the infrared reflection absorption spectra of 2-butanoxy groups on the Ag(643) surface. The intensities of the absorptions by R- and S-2-butanoxy groups are dependent on the handedness of the Ag(643) substrate. Similarly, the heats of adsorption of small chiral molecules such as R- and S-propylene oxide (CH3CH(O)CH2) and R-3-methylcyclohexanone are sensitive to the handedness of surfaces such as Cu(643). This has been observed using thermally programmed desorption measurements which reveal that the desorption kinetics of these chiral molecules are enantiospecific on chiral surfaces. They do not exhibit enantiospecificity on achiral surfaces such as Cu(111). In the course of this work we have been able to identify chiral adsorption sites on high Miller index metal surfaces. Most recently we have been able to demonstrate an enantioselective separation using such surfaces to purify a racemic mixture of 3-methylcyclohexanone. Understanding and controlling these enantiospecific properties poses some extremely interesting challenges for surface chemistry and surface physics.

11:00am **SS1-MoM9 Self-assembly of Chiral Nanoclusters of Cysteine on Au(110)-(1x2)**, ***A. Kühnle***, *T.R. Linderoth, L. Molina, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark

We have performed a comprehensive STM-based study of the adsorption of the chiral amino acid cysteine, $HS\text{-}CH_2CH(NH_2)\text{-}COOH$, onto the missing-row reconstructed Au(110)-(1x2) surface under UHV conditions. In experiments where we deposit cysteine either as the pure enantiomeric forms or as the racemic mixture, we have identified a rich variety of chiral adsorption phenomena. The results are interpreted with the aid of density functional theory calculations. Previously, we have reported on the enantioselective dimerization of cysteine into homochiral molecular pairs and identified the atomic-scale interactions responsible for this intermolecular chiral recognition.[1] Here, we focus first on supramolecular chain-like assemblies of cysteine molecules that coexist with the molecular pairs. The chiral chains extend over several hundred Ångström and consist of two adjacent rows of cysteine molecules. Formation of these chains is accompanied by a pronounced surface reconstruction, involving the removal of two close-packed rows of gold atoms underneath each molecular double row, and is driven by the formation of hydrogen bonds between the carboxylic groups of the cysteine molecules in the rows. Secondly, we discuss the self-assembly of molecular nanoclusters of cysteine. When cysteine is deposited at a substrate temperature of 120 K, small, irregular agglomerates of molecules are formed. A remarkable transition is seen upon annealing to 270 K, where the molecules self-assemble into completely identical clusters with a size of 18 by 24 Å. The molecules appear to segregate into homochiral clusters when the racemic mixture is deposited.

[1] A. Kühnle, T.R. Linderoth, B. Hammer and F. Besenbacher, Nature 415, 891 (2002).

11:20am **SS1-MoM10 Towards Epitaxial Growth of Chiral Metal Films on Metal Oxide Substrates**, ***D.S. Sholl***, *A. Asthagiri, A.J. Francis, C. Niederberger, L.M. Porter, P. Salvador*, Carnegie Mellon University

Although intrinsically chiral metal surfaces have been demonstrated to have intriguing enantiospecific adsorption and electrochemical properties, current studies of these materials are performed using small single-crystal samples. To move towards practical applications of these surfaces, techniques for substantially increasing the surface area of these chiral films need to be developed. One avenue towards this goal is the controlled growth of thin metal films on suitable chiral metal oxide substrates. We will report theoretical and experimental results for the growth of Pt films on $SrTiO_3$ substrates. This metal/metal-oxide pair was chosen because of the catalytic properties of Pt, the close lattice match between Pt and $SrTiO_3$, and the availability of $SrTiO_3$ as single crystal substrates. To control metal film growth on stepped metal oxide substrates it is necessary to understand the growth modes on the relevant atomically flat surfaces. We have studied Pt deposition on the non-polar $SrTiO_3(100)$ surface and the polar $SrTiO_3(111)$ surfaces using various experimental probes and ab initio Density Functional Theory. Our results identify the preferred binding geometries and film orientations of Pt films on these substrates. X-ray diffraction and low energy electron diffraction confirmed epitaxial growth of the Pt films, with the number of in-plane orientations dependent on both the substrate temperature and the nature of the substrate surface. We are currently extending our studies to the deposition of Pt on intrinsically chiral $SrTiO_3$ substrates and will discuss the prospects for creating robust chiral metal films with this process.

11:40am **SS1-MoM11 Novel Low-Temperature Reactivity of Model Bimetallic Surfaces with Monolayer Coverages**, ***N.A. Khan***, *J.G. Chen*, University of Delaware

Bimetallic surfaces have gained considerable interest in fundamental surface science research because of their unique catalytic activity and electronic properties. By studying these surfaces at an atomic level, we can gain more insight into the origin of these novel properties. In this study, we have used various surface science techniques (TPD, HREELS, NEXAFS, and XPS) to investigate the properties of model bimetallic surfaces. We have shown that the one monolayer Ni/Pt(111) surface exhibits novel chemical reactivity, unlike the pure Ni(111) or Pt(111) surfaces. Temperature-programmed desorption (TPD) results indicate that hydrogen has a lower binding energy to the 1 ML Ni/Pt(111) surface than on the other two surfaces.[1,2] In principle, a weak metal - hydrogen interaction should lead to an increase in the hydrogenation activity of other species on the surface. We have used other catalytically important probe molecules, such as cyclohexene and thiophene to further investigate this hydrogenation activity. XPS and NEXAFS also showed that the oxidation state and density of unoccupied states of one monolayer Ni/Pt(111) are similar to that of bulk Ni(111). In addition to studying the Ni/Pt(111) surface, we have also investigated the Ni/W(110) surface for comparison. On the Ni/W(110) surface, the probe molecules also undergo hydrogenation at a low temperature. However, the maximum activity occurs at about 0.4 ML Ni. At this coverage of Ni, Schmidthals, et. al. have found a large amount of surface strain.[3] We will attempt to correlate this lattice mismatch to a novel chemical reactivity seen on the 0.4 ML Ni/W(110) surface.

[1] H.H. Hwu, J. Eng Jr., J.G. Chen, J. Am. Chem. Soc. 124 (2002) 702.

[2] N.A. Khan, H.H. Hwu, J.G. Chen, J. Catal. 205 (2002) 259.

[3] C. Schmidthals, et. al. Surf. Sci. 402-404 (1998) 636.

Surface Science
Room: C-112 - Session SS2-MoM

Oxide Structure and Surface Chemistry

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

8:20am **SS2-MoM1 TPD Studies of the Chemistry of CCl_4 on Fe_3O_4 (2x2)-(111) Surfaces in the Presence of Adsorbed D_2O**, ***K. Adib***, *G. Totir, J.P. Fitts, K.T. Rim, G.W. Flynn, R.M. Osgood, Jr.*, Columbia University

Due to their abundance in the crust of the Earth and their high reactivity, the oxides of iron serve as ideal model mineralogical surfaces in environmental catalysis studies. The relevance of the environmental studies is enhanced by considering the effect of water on the reactivity of iron oxide surfaces. Natural single crystals of $\alpha\text{-}Fe_2O_3$ were cut and polished in the (0001) orientation. They were processed in ultrahigh vacuum to produce a surface selvedge of Fe_3O_4 (111)- 2x2 and exposed at ~100 K to D_2O and CCl_4. The TPD studies of adsorbed D_2O indicate a rich surface chemistry with multiple desorption events extending to as high as ~ 800 K consistent with dissociative adsorption of D_2O on the Fe_3O_4 (111) surface. Previous TPD and XPS results indicate that in the absence of D_2O, CCl_4 dissociatively adsorbs on Fe_3O_4 (111) producing chemisorbed Cl and CCl_2 which upon subsequent heating of the surface, abstract lattice iron and oxygen atoms to desorb as $FeCl_2$ and $OCCl_2$, respectively. In the presence of adsorbed D_2O, it is observed that the production of $FeCl_2$ and $OCCl_2$ are substantially suppressed indicating that the D_2O fragments block the surface reactive sites. The evolution of the reaction products of CCl_4 with the Fe_3O_4 surface as a function of pre-adsorbed D_2O coverage will be presented.

8:40am **SS2-MoM2 Variable Temperature Scanning Tunneling Microscopy Studies of a Natural Single Crystal a-Fe_2O_3(0001) Sample: Termination and Surface Chemistry with CCl_4 and Cl_2**, ***K.T. Rim***, *T. Müller, J.P. Fitts, K. Adib,* Columbia University, *N. Camillone III, R.M. Osgood, Jr.,* Brookhaven National Laboratory, *S.A. Joyce,* Los Alamos National Laboratory, *G.W. Flynn*, Columbia University

Variable Temperature Scanning Tunneling Microscopy (VT STM) has been used to study the reactivity of the reduced surface of a natural single crystal α-Fe_2O_3(0001) sample. STM and LEED measurements reveal that the surface cleaned in ultrahigh vacuum is reduced and composed of a Fe-terminated Fe_3O_4 (111) region and an O-terminated Fe_3O_4(111) or biphase region. The Fe-terminated Fe_3O_4(111) region exhibits reaction with CCl_4 and Cl_2, but the O-terminated Fe_3O_4(111) (biphase) region does not undergo reaction. Reaction products (Cl) on the Fe- terminated Fe_3O_4(111) region were observed with STM at room temperature after the reduced surface was exposed to CCl_4 and Cl_2. Chlorines are found to occupy two distinct sites, Fe top sites and O vacancy sites when the surface is exposed to CCl_4 vapor. However Cl occupies only the top sites when Cl_2 is dosed on the surface. The O vacancy sites are created only after surface oxygen atoms are abstracted via reaction with CCl_4 to produce phosgene. The reduced surface was exposed to CCl_4 at 238K and the surface temperature changed from 238K to 600K in order to identify reaction products and intermediates (chlorine and dichloro-carbene) and to observe oxygen vacancies following oxygen abstraction from the surface. Related TPD, AES, and XPS results will also be presented to support the VT STM observations.

9:00am **SS2-MoM3 Influence of Surface Composition on the Pyrite Mediated Dechlorination Kinetics of Alachlor**, ***H. Fairbrother***, *D.L. Carlson, M.M. McGuire, A.L. Roberts,* Johns Hopkins University

The effects of different pyrite surface compositions on the dechlorination kinetics of the herbicide alachlor were investigated. Chloroacetamides, including alachlor, are an important class of herbicides, which are encountered as ubiquitous contaminants in surface and groundwater. Currently, the understanding of the processes controlling the environmental fate and transformations of alachlor is somewhat fragmented. Alachlor can be dechlorinated by Fe(0). Because several iron sulfide minerals have been shown to dechlorinate low molecular weight alkyl and vinyl halides, we investigated the reactivity of alachlor with pyrite (FeS_2), a common minor constituent of sediments and aquifers. We found that the primary product is deschloroalachlor, the result of reductive dechlorination. This process may be important in natural systems, as previous work has identified deschloroalachlor in groundwater. In this study, we have employed a liquid cell directly coupled to a surface analysis chamber to examine the effect of surface defect sites on the pyrite mediated dechlorination kinetics of alachlor. The influence of surface chemical composition on the dechlorination of the organohalide alachlor (a herbicide) by pyrite was studied by XPS in conjunction with GC-MS. On natural pyrite surfaces, the dechlorination process exhibited first-order kinetics, indicative of a limited number of surface sites that were consumed during reaction. In contrast, pyrite surfaces modified by ion bombardment, which are dominated by sulfur vacancies, exhibited markedly different reaction kinetics characterized by an initial induction period of low reactivity during which time the surface is oxidized by water. These results indicate that monosulfide species are not responsible for alachlor reduction on pyrite. In a broader sense this study illustrates the intimate relationship that exists between surface chemical composition and reactivity at the liquid-solid interface.

9:20am **SS2-MoM4 Adsorption and Desorption of Methanol on WO_3 (100) Surfaces**, ***S. Ma***, *F.G. Amar, B.G. Frederick*, University of Maine

We have investigated the role of intermolecular interactions, surface site heterogeneity, and surface diffusion during the desorption of methanol from the oxidized and reduced surfaces of (100) oriented, epitaxially grown WO_3 films on Al_2O_3(1-102) substrates. Ultra-violet photoelectron spectroscopy (UPS) showed that methanol adsorbed molecularly on the oxidized WO_3 surface but dissociatively on the reduced surface. On both surfaces, calibrated thermal desorption spectroscopy (CTDS) showed desorption of methanol in an asymmetric peak which shifts to lower temperature with increasing coverage, typical of water and alcohols on other oxide surfaces. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface by monitoring the W4f and valence band region, while separate STM studies indicate that the surface is heavily stepped. Monte Carlo simulations indicate that surface heterogeneity and rapid diffusion are consistent with the observed desorption spectra. By contrast, simulations on a homogeneous surface require repulsive intermolecular interactions, which is inconsistent with hydrogen bonding.

9:40am **SS2-MoM5 Interaction of Co_3O_4 Single-Crystal Surfaces with Water**, ***M.A. Langell***, *D.A. Pugmire,* University of Nebraska-Lincoln, *W.H. McCarroll,* Rider University

Vacuum-annealed and vacuum-cleaved Co_3O_4 single-crystal substrates have been characterized using the UHV surface analytical techniques of Auger electron spectroscopy, x-ray photoelectron spectroscopy, low energy electron diffraction and high resolution electron energy loss spectroscopy. Particular emphasis in this study has been placed on the characterization of surface oxygen, which often shows complex photoemission structure from core oxygen states, and of the tetrahedral/octahedral site occupancy of cobalt surface cations as it relates to the defect character of the spinel surface. These well-defined surfaces are subsequently probed by adsorption of H_2O, both at low ($\leq 10^{-6}$ Torr) and high (1-10 Torr) water vapor pressures. Dissociative adsorption to produce surface hydroxyls is an important process for air-exposed oxides and this mechanism was found to occur upon water exposure for the Co_3O_4 surface under UHV conditions. However, hydroxylation was most readily observed for stoichiometric surfaces upon electron or thermal activation of the water adsorbate. These surface species will be compared to hydroxyls generated under high vacuum and atmospheric conditions.

10:00am **SS2-MoM6 Surface Chemistry of Calcined UO_2 Powders**, ***A.J. Nelson***, *T.C. Meier, C.K. Saw, L.V. Griffith*, Lawrence Livermore National Laboratory

High resolution X-ray photoemission spectroscopy (XPS) was used to examine the surface composition and chemical bonding of calcined UO_2 powders as a function of process parameters. It is believed that the surface composition of the powder grains ultimately affects packing density. XPS quantitative analysis revealed O/U ratios indicative of mixed uranium valences. In addition, high resolution U $4f_{7/2,5/2}$ core-level spectra revealed reoxidation of U^{4+} to U^{6+} for the lower temperatures, and a reduction of U^{6+} to U^{4+} for the higher temperatures using 4% H_2/Ar. Reoxidation can also be affected by the presence of water or OH, and the powder samples calcined at the lower temperatures have the highest $OH^?/O^{2?}$ peak area ratio. Also, electrons in the 6d, 5f, and 7s orbitals near the valence band maximum can participate in bond formation so long as adjacent atoms are capable of donating their electrons to these unfilled orbitals. The valence band electronic structure for the higher temperature calcinations clearly shows a stronger 5f emission peak near the Fermi edge, a feature that is indicative of a highly localized state. Results were correlated with bulk structural analysis using x-ray diffraction. 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.

10:20am **SS2-MoM7 Examination of the Redox Chemistry of Water with the Oxidized and Reduced Surfaces of CeO_2(111)**, ***M.A. Henderson***, *M.H. Engelhard, C.H.F. Peden, C.L. Perkins, S. Thevuthasan*, Pacific Northwest National Laboratory

Ceria is important in automotive three-way catalysts because of its ability to store and release oxygen as reaction conditions oscillate between oxidizing and reducing conditions. The effect of such redox oscillations on adsorbate chemistry is not well understood, although the chemistry of water on oxide surfaces is known to depend on the surface's redox state.[1] Two groups have recently reported conflicting results for the interaction of water with reduced CeO_2(111) films, with one group reporting Ce^{3+} oxidation[2] and the other reporting Ce^{4+} reduction.[3] In both cases, the CeO_2(111) films were thin (≤ 50 Å) and were grown on metal substrates (Ru(0001)[2] and Pt(111)[3]). We have studied the interaction of water with a 500 Å CeO_2(111) film grown on Y-stabilized ZrO_2(111). TPD measurements for varying coverages of water on either oxidized (800 K in O_2) or vacuum reduced (at 850 K) CeO_2(111) are suggestive of predominately molecularly adsorbed water, and show no evidence for irreversible decomposition either in terms of water consumption or H_2/O_2 desorption. Complimentary core and valence band photoemission results show that adsorbed water does not increase or decrease the level of Ce^{3+} in the reduced CeO_2(111) surface, although water exposure at 600 K shows a slight increase in Ce^{3+} over that seen from annealing in UHV at the same temperature. Comparison of our results for the CeO_2/ZrO_2(111) system with those from thin CeO_2 films grown on metal substrates suggests that metal substrates may participate in water redox chemistry on ceria.

[1] M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1.

[2] Lj. Kundakovic et al., Surf. Sci. 457 (2000) 51.

[3] U. Berner et al., Surf. Sci. 467 (2000) 201.

10:40am **SS2-MoM8 Interface Mediated Defect Formation in Ultrathin Cerium Oxide Films**, ***C. Castellarin-Cudia***, *S. Surnev, S. Eck, M.G. Ramsey, F.P. Netzer*, Karl-Franzens-Universität Graz, Austria

The oxygen storage and release capabilities of cerium oxide are important factors for its use as an additive in the three-way catalyst for automotive emission control. The ceria can act as an oxygen pump, which under fuel-rich conditions gives up oxygen, whereas under fuel-lean conditions it can take in oxygen. A key step in this process is the formation and destruction of oxygen vacancy defects at the ceria surface. Here we report the observation of defect formation, at the atomic level using STM, in ultrathin cerium oxide layers on a Rh(111) substrate surface. The ceria overlayers have been fabricated in situ by reactive evaporation of Ce metal onto the heated substrate (250°C) in an oxygen atmosphere, and reducing ambient conditions have been simulated by annealing in vacuum. Ceria overlayers on Rh(111) grow in a CeO$_2$(111)-type structure and annealing of submonolayer coverages to ~500°C produces thin, well-ordered Ce-oxide island nanostructures. The island surfaces display atomic resolution in the STM and reveal a Moiré superstructure, as a result of the lattice mismatch between the oxide overlayer and the Rh substrate. Further annealing to ~600°C leads to partial reduction and an ordered array of oxygen vacancies, which form a defect superlattice of the same dimensions as the Moiré structure. Several defect signatures can be distinguished in the atomically resolved STM images. We propose that the defect superlattice is mediated by the metal-oxide interface, via a lattice-mismatch induced strain effect.This creates catalytically active sites for the preferential reduction of the ceria, i.e. the formation of oxygen vacancy defects, and constitutes a novel mechanism for the formation of interface-stimulated active centers.

*Supported by the Austrian Science Foundation.

11:00am **SS2-MoM9 Identification of Defect Sites on Oxide Surfaces**, ***Y.D. Kim***, *J. Stultz, T. Wei, A.K. Santra, D.W. Goodman*, Texas A&M University

Defect sites on oxide surfaces play an important role in various catalytic reactions, as well as in adhesion and in nucleation of metal clusters. Thus, identification and quantification of defect sites on oxide surfaces are important steps in the understanding of many catalytic reactions. Recently we have used several techniques to identify various defect sites on oxide surfaces including metastable impact electron spectroscopy (MIES), water and CO-temperature programmed desorption (TPD), MIES of adsorbed Xe (MAX), and electron energy loss spectroscopy (EELS). MIES data for MgO(100) and SiO2 thin films are very sensitive to extended defect sites as well as point defect. Point defects result in the appearance of band gap states, whereas extended defects cause broadening of the O(2P) band. MAX data change significantly with increasing defect densities for various oxide surfaces. The adsorption of D2O and CO also has been used to identify various defect sites since their TPD spectra change significantly in the presence of defect sites. Recent EELS data acquired for low and highly defective oxide surfaces will also be discussed.

11:20am **SS2-MoM10 Polar ZnO(0001)-Zn and ZnO(000-1)-O Surfaces: Geometric and Electronic Structure, Stabilization Mechanisms**, ***O. Dulub****, *U. Diebold*, Tulane University

The geometric and electronic structure of the (0001)-Zn and (000-1)-O polar surfaces of ZnO were studied with Scanning Tunneling Microscopy (STM) and Spectroscopy (STS), as well as Low Energy Electron Diffraction (LEED). Sharp (1x1) LEED patterns were recorded for both surfaces. The STM images of the ZnO(0001)-Zn surface reveal flat triangular terraces of single step height (~2.6 Å), exhibiting two domains rotated by 180 degrees with respect to each other. STM shows a high density of triangular pits of various sizes and slightly rounded small holes. Triangular islands of different sizes were also observed on the terraces, and the smaller ones exhibit size-dependent special shapes. STM images from the O-terminated (000-1) surface reveal a quite different morphology. The surface is composed of flat, well ordered terraces without pits or added small islands. The terraces are separated mainly by double-layer high step edges (~5.2 Å) that include an angle of 120 degrees. STS indicates a slightly (but reproducibly) different electronic structure of the two polar surfaces. The filled states on the O-terminated face are shifted toward the Fermi level. Based upon the STM and STS results, two stabilization mechanisms are proposed for (0001)-Zn and (000-1)-O surfaces. A charge transfer from the O- to the Zn-terminated surface makes the latter more metallic. Since metallic Zn is known to have an extremely high vapor pressure even at low temperatures, it possibly evaporates off the surface. Depleting the Zn-terminated surface of 1/4 of zinc atoms removes the infinite dipole moment and therefore stabilizes the crystal. The special shapes of the smallest ('magic') islands observed in STM images of the (0001)-Zn surface are consistent with the proposed model.

11:40am **SS2-MoM11 The Polar O-ZnO(000-1) Surface: Stability and Interaction with Hydrogen**, ***M. Kunat***, *St. Gil Girol, U. Burghaus, Ch. Wöll*, Ruhr-University Bochum, Germany

The question about the stability of the polar surfaces of zinc oxide has been the topic of many experimental and theoretical investigations. Here we report on an investigation using the highly surface sensitive method of He-atom scattering (HAS). The clean, H-free surface shows (1x3) superlattice spots in He-atom diffraction scans. This finding is in contrast to previous work[1] where the presence of a (1x1) overlayer was found, but is in agreement with Taskers rule,[2] which predicts instabilities for polar oxide surfaces. After optimizing the preparation conditions for the O-ZnO(000-1) surface, in particular by employing annealing in an oxygen atmosphere, we were able to observe weak (1x3) spots not only with HAS but also in low energy electron diffraction (LEED). Exposure to hydrogen atoms leads to the disappearance of the (1x3) overlayer spots and the formation of a well-defined (1x1) diffraction pattern in both HAS and LEED, similar to the case of the Zn-ZnO(0001) surface previously studied in our laboratory.[3] The formation of the H-atom overlayer is accompanied by a shoulder in the O1s XPS data, indicating the formation of OH-species. In addition first results of sticking coefficients of carbon monoxide as a function of hydrogen preexposure will be discussed.

[1] A. Wander, F. Schedin, P. Steadman, A. Norris, R. MCGrath, T.S. Turner, G. Thornton, and N.M. Harrison, Phys. Rev. Lett. 86 (2001) 3811.

[2] P.W. Tasker, J. Phys. C: Solid State Phys. 12 (1979) 4977.

[3] Th. Becker, St. Hövel, M. Kunat, Ch. Boas, U. Burghaus, and Ch. Wöll, Surf. Sci. 486 (2001) L502.

Thin Films
Room: C-101 - Session TF-MoM

Optical Thin Films
Moderator: S. McEldowney, JDSUniphase

8:20am **TF-MoM1 Progress in Optical Thin-Films: A Telecommunications Perspective**, ***G. Ockenfuss***, JDSU/OCLI **INVITED**

Thin-Film filters are widely used in fiber-optic telecommunication networks. Important applications include channel and band selection, gain-flattening, and pump isolation/combining. As telecommunications networks evolve toward more spectral efficiency and higher data rates, filter manufacturers will be challenged to produce thin-film filters with better performance at a lower cost. This talk will detail the evolution of filter performance and complexity, and report on recent progress toward the development of extremely thick filters with very low stress. Such filters enable very good performance at a low cost. Some of the most significant results of this research will be presented, including the characteristics and resulting optical performance of a 94+ micrometer thick "8-skip-0 100GHz" filter for DWDM bandsplitting applications.

9:00am **TF-MoM3 Hybrid Deposition of Sputtered and Evaporated Multilayer Thin Films**, ***P.M. Martin***, *L. Olsen, J.W. Johnston*, Pacific Northwest National Laboratory, *D.M. DePoy*, Knolls Atomic Power Laboratory

Si:H/CaF$_2$ high reflectors with as many as 27 layers were deposited by a hybrid process that combined reactive magnetron sputtering and electron beam evaporation. The ultimate goal of this work was to deposit interference filters with low NIR and LWIR absorption for use in thermophotovoltaic systems. The high index Si:H layers were deposited by reactive magnetron sputtering in mixtures of Ar + H$_2$. Electron beam evaporation was the preferred deposition method for the CaF$_2$ layers.[1] The multilayer hybrid coatings were deposited in the same chamber by sequentially rotating the substrate over the Si sputtering target and the CaF$_2$ evaporation source. The deposition rate of the evaporated CaF$_2$ was 600 Å/min, compared to 25 Å/min for sputtered CaF$_2$. The deposition rate of the Si:H layers was 56 Å /min. The optical performance of the hybrid deposited and fully sputter-deposited coatings will be compared. The refractive index of the SiH at NIR wavelengths was 3.25, with extinction coefficient < 0.001. The refractive index of the CaF$_2$ in the same wavelength range was 1.34, with an extinction coefficient < 0.0001. The resulting multilayer coatings had lower physisorbed water, lower optical absorption and lower mechanical stress than those with sputtered CaF$_2$ layers. Advantages of this hybrid deposition method were reduced deposition times, optimum deposition process for each layer material, and improved optical and mechanical properties. This deposition method could be used for any type

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* Morton S. Traum Award Finalist

of multilayer optical or non-optical coating design, including but not limited to high reflectors, notch filters, beam splitters, antireflection, edge filters, polarizers, Fabrey-Perot filters, tuned absorbers, heterojunction semiconductor devices, thin film photovoltaic devices, superlattice devices, and thermoelectric devices.

[1] J. D. Traylor Kruschwitz and W. T. Pawlewicz, Appl. Opt. (1997), 36(10), 2157-2159.

9:20am **TF-MoM4 Electron Cyclotron Resonance Sputtering Apparatus for Optical Band-pass Filters for Wavelength Division Multiplexing**, ***Y. Jin***, *M. Shimada*, NTT Telecommunications Energy Laboratories, Japan

We have developed a new apparatus for fabricating narrow band-pass multilayer filters for dense wavelength division multiplexing (DWDM) that uses electron cyclotron resonance (ECR) sputtering with two plasma sources. ECR sputtering with Ar/O_2 gas and a metallic target has a stable metal-mode deposition. The target is sputtered in a metallic state, and this is followed by oxide film formation, which is enhanced by ECR plasma irradiation on the substrate.[1] The ECR sputtering of metal-mode SiO_2 and Ta_2O_5 films is suitable for the fabrication of optical multilayer filters because it provides surface smoothness, low optical loss, and stability of the refractive index. These depositions were carried out at room temperature. The sputtering system consists of two ECR plasma sources, which are coupled with divided microwaves (2.45 GHz), and cylindrical sputtering targets (Si: 99.999%, Ta: 99.99%) biased by using rf-power (13.56 MHz). The deposition-thickness uniformities are ±0.65% for SiO_2 and ±0.44% for Ta_2O_5 over a 200-mm diameter. The refractive indices of the SiO_2 and Ta_2O_5 films are 1.47 and 2.10 at a wavelength of 1550 nm. This technique produces a typical surface roughness of 0.12-nm rms. To achieve precise deposition of these films, a new optical thickness monitoring system was developed. This system directly measures spectral transmission curves during film deposition using incandescent light and an infrared spectrometer, and detects the endpoint of the demanded thickness. Using this method, we fabricated a narrow band-pass filter with 43 layers on a 100-mm quartz substrate, and obtained a half bandwidth with 0.27-nm ±0.0253-nm band-pass filtering characteristics with low optical loss over the whole 100-mm diameter. ECR sputtering deposition in the metal mode is thus effective for DWDM optical band-pass filter fabrication.

[1] M. Shimada et al., Vacuum 59, 727 (2000).

9:40am **TF-MoM5 A New Dual Ion Beam Sputter Deposition System for the Production of Complex Optical Telecommunication Filters**, ***D. Siegfried***, *C. Montcalm, R. Blacker, D. Burtner, J.D. Deakins, A. Dummer, T.A. Erguder, J. George, C. Heizer, I. Kameyama, S.M. Lee, D. Walters*, Veeco Instruments, Inc.

Dual-ion-beam sputter deposition (DIBSD) is a technique used to produce various coatings for telecommunication applications in the near-infrared wavelength region (1300-1600 nm) such as anti-reflection coatings, low loss laser mirrors, dense wavelength division multiplexing filters, and gain flattening filters. This deposition technology benefits from inherently stable deposition rates and produces dense, bulk-like films that are stable in a wide range of environmental conditions. However, compared to competing technologies such as ion-assisted electron-beam evaporation or magnetron sputtering, this technology typically has lower deposition rates and limited deposition uniformity over large coating areas. These two main limitations have been addressed by developing an entirely new DIBSD system. The deposition rates in this new system are >0.5 nm/s for Ta_2O_5 and >1.0 nm/s for SiO_2 over a 300 mm diameter substrate, which are now comparable to those obtained in electron beam evaporation systems used for similar applications. The increased rates have been achieved with several process and hardware changes, while preserving the favorable optical and physical properties of the films generally produced by DIBSD. Specific examples include the use of reactive deposition processes and the development of a new high current ion source. Simultaneously, the chamber geometry was optimized to achieve uniform films, both in terms of thickness and index, while the overall stability and robustness of the process was increased by judicious placement of all critical components. Finally, improvements in the vacuum pumping system have reduced the pumpdown time by a factor of 2 and have eliminated the need for lengthy cryopump regenerations. We describe these major improvements that have led to large yields and reduced production cost for optical filters.

10:00am **TF-MoM6 Optical Thin Film Formation by Oxygen Gas Cluster Ion Beam Assisted Depositions**, ***N. Toyoda***, *I. Yamada*, Himeji Institute of Technology, Japan

High-quality Ta_2O_5/SiO_2 and Nb_2O_5/SiO_2 were deposited with oxygen gas cluster ion assisted deposition at low-temperature for optical filters. As one cluster ion has thousands of O_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_2-GCIB was applied to form high quality optical films. With gas cluster ion assisted deposition, high refractive index and very smooth surface of Ta_2O_5 films were deposited. The optimum cluster ion energy and cluster ion current density for Ta_2O_5 films were found to be 7keV and 0.5uA/cm^2, respectively. The structure of film was very uniform and no porous or columnar structures were observed. The surface or interfaces of Ta_2O_5/SiO_2 films were also very flat by surface smoothing effect of cluster ion beams. Very smooth surface can be realized even though the bottom surface was rough. There was no wavelength shift of filters after environmental tests, which indicates that dense oxide films were formed at low-temperature with O_2 cluster ion assisted deposition.

10:20am **TF-MoM7 Plasma Deposited Inhomogeneous Optical Filters**, ***S. Larouche***, *A. Amassian, H. Szymanowski, J.E. Klemberg-Sapieha, L. Martinu*, Ecole Polytechnique, Canada

Plasma enhanced chemical vapor deposition (PECVD) of inhomogeneous optical filters with a continuously varying refractive index profile (for example, rugate filters) offers a unique opportunity to combine the advantageous optical (elimination of harmonics, suppression of sidelobes), mechanical (compensation of stress, scratch- and wear resistance), and technological (high deposition rate) characteristics. In the present work, we study the optical and structural properties of mixed TiO2/SiO2 materials obtained by PECVD from TiCl4 and SiCl4 precursors. We evaluate the effect of the fabrication conditions on the refractive index, deposition rate, chemical structure and morphology at every moment of the film growth using numerous complementary techniques; this includes in-situ and ex-situ wide-range spectroscopic ellipsometry (UV-VIS-NIR-IR), spectrophotometry, FTIR, XPS, XRD, AFM, and other methods. Detailed knowledge of the microstructural evolution, combined with real-time in-situ spectroellipsometric process monitoring, is then used to fabricate model single-band and multiband optical filters in the visible and NIR regions. Optical and mechanical performance, environmental stability, and advanced applications of such filters are evaluated and discussed.

10:40am **TF-MoM8 Scandium and Vanadium Multilayer Mirrors: Working towards High Reflectivity in the Extreme Ultraviolet**, ***G.A. Acosta***, *D.D. Allred, N.D. Webb*, 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 (Optics Letters, Vol. 23, No.10) 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 reflectivities. To characterize our thin film samples, they were studied using X-ray diffraction, atomic force microscopy, ellipsometry, X-ray photoelectron spectroscopy, and an EUV scanning monochromator. Optical constants were found experimentally over the 800-200nm range, as well as in the EUV.

11:00am **TF-MoM9 Measuring Optical Losses in Thin Films with Ringdown Cavity**, ***G. Vaschenko***, *Y. Godwal, C.S. Menoni*, Colorado State University , *C. Montcalm, R. Blacker, D. Siegfried*, Veeco Instruments Inc.

Optimization of multilayer optical components (such as wavelength division multiplexing (WDM) filters for fiber optics communications) often requires measuring the losses in the individual films composing these optical elements. Ion beam sputtering yields films with optical losses on the scale of parts per million (ppm), which is significantly smaller than the sensitivity threshold of conventional analytical techniques such as ellipsometry or spectrophotometry. In this contribution we demonstrate a new, highly sensitive experimental configuration for the characterization of losses in thin films on optically transparent substrates. Our method is based on synchronous pumping of the ringdown cavity by the pulses of a mode-locked Ti:Sapphire laser. The length of the ringdown cavity is selected to match that of the laser, therefore the pulse inside the ringdown cavity is significantly boosted on every roundtrip. The thin film sample grown on a transparent substrate is introduced in the cavity and aligned exactly perpendicular to the axis of the cavity, so that the light reflected from the sample interfaces is recycled and the reflection loss does not contribute to the total measured loss of the film. The losses are determined by measuring the time dependent decay of the ringdown signal. This method allows us to obtain high signal-to-noise ratio decay signals with small pulse energy and without signal integration over large number of shots. Using this technique we have detected record low single pass loss of only 64 ppm in a 2 mm fused silica substrate and 79 ppm loss in a 4 µm tantalum pentoxide film fabricated with a SPECTOR ion beam sputter system.

11:20am **TF-MoM10 Efficient Infrared Emission for Zinc Sulphide: Rare Earth Doped Thin Films**, ***A.S. Kale***, *W. Glass, M. Davidson, P.H. Holloway*, University of Florida

Infrared emitters (IR) are widely being used for a variety of applications ranging from commercial based fiber optic communication devices and industrial gas sensors to remote controls for televisions. ZnS doped rare earth fluoride thin films typically 1 micron thick have been fabricated by RF sputter deposition in the conventional metal-insulator-semiconductor-insulator-metal configuration as novel structures for emission of IR radiation. The current study investigates three different kinds of phosphors, namely, ZnS:TmF$_3$, ZnS:NdF$_3$ and ZnS:ErF$_3$ for their IR versus visible emission. Electroluminescence has been studied before and after annealing at temperatures up to 510°C to determine the effects on the emission properties. As annealing improves the crystallinity of the film, the emission improves. Emission spectra of the devices have been measured at wavelengths ranging from 0.35 to 1.5 microns, and the films studied for their emission efficiency and luminescent decay times. Methods of enhancing the IR with respect to the visible emission will be reported, including codoping with two or more rare earth elements, interfacial modifications and conditions of annealing.

11:40am **TF-MoM11 Polycrystalline Thin Film Photovoltaics**, ***H.S. Ullal***, National Renewable Energy Laboratory

Significant technological advances have occurred in the area of polycrystalline thin film photovoltaic technologies based on cadmium telluride (CdTe) and copper indium diselenide (CuInSe$_2$, CIS). In the past few years, the many advances made in materials research, device development, manufacturing technology, reliability testing of modules and systems, technical R&D issues relating to CdTe & CIS, and early commercialization efforts underway in the United States and worldwide are reported in this paper. A typical thin-film CdTe solar cell structure is glass/SnO$_2$/CdS/CdTe/contacts. A world-record, total-area efficiency of 16.5% has been achieved by scientists at NREL. One of the most active areas of research is the study of the interdiffusion at the CdS/CdTe interface, where diffusion of S in the range of 4%-12% into the CdTe absorber has been observed by SIMS technique. Other areas of research include developing new transparent conductors such as Cd$_2$SnO$_4$ to replace SnO$_2$2, and the study of back contact stability to develop stable thin film CdTe solar cells. A number of vacuum based thin film growth techniques will also be reported. For thin-film CIS-based solar cells, the typical cell structure is ZnO/CdS/CIS/Mo/glass. Low-cost sodalime glass is normally used for device fabrication. In addition, polymer, metal foils, and stainless substrates are being investigated as alternate substrates. The highest world-record, total-area efficiency achieved thus far by NREL scientists for thin-film CIGS solar cell is 21.5% using a concentration of ~14X by the physical vapor deposition method. The CdS is deposited by the chemical bath deposition (CBD) technique. The process is reproducible and quite robust. The Ga:In ratio is typically 30:70. Areas of research worldwide include the role of Na that diffuses from the glass into the CIGS absorber, the optimum amount of Ga which help increase the bandgap from 0.95 eV to 1.2 eV, such that, there is better match with the solar spectrum, and developing alternate buffer layers to replace CBD CdS. The major players developing thin-film CdTe module fabrication are ANTEC Solar, Germany; BP Solar (BPS), USA, First Solar, USA, and Matsushita Battery, Japan. For thin-film CIS technology, the major players are Energy Photovoltaics, USA, Global Solar Energy (GSE), USA, Honda Engineering, Japan, International Solar Electric Technology, USA, Matsushita Industry, Japan, Showa Shell, Japan, Shell Solar Industries (SSI), USA, and Wurth Solar, Germany. Multi-megawatt manufacturing facilities for module fabrication are currently underway in Germany, Japan, and USA. Early commercial products (5-40 W) of CIS are available from SSI, and GSE for military applications. Prototype thin-film CdTe Apollo module with aperture-area efficiency of 11.0% and power output of 92.5 W has been developed by BPS for commercialization in 2003. This work was supported by NREL under Contract no. DE-AC36-99G010337

Applied Surface Science
Room: C-106 - Session AS-MoA

Quantification & Accuracy in Surface Analysis
Moderator: C.R. Brundle, Applied Materials

2:00pm **AS-MoA1 Toward a Comprehensive Quantitative Workbench for Surface Analysis**, ***R.A. Weller***, Vanderbilt University **INVITED**

I will address issues in the application of symbolic computation to surface analysis. Until quite recently, the most important factors affecting the style of technical software have been the limitations imposed by the speed and storage capacity of contemporary computing hardware. In retrospect, while understandable in the context of the times, this linkage has produced computational tools that lack generality, are inflexible, or that must be frequently updated because of evolving computer hardware or operating system software. The seeds of an alternative approach have been sown by the authors of modern tools for general-purpose symbolic mathematical computation, where fundamental considerations argue for hardware independence and the generality of algorithms. Symbolic computation is a revolutionary computing technology. Mathematics is an exercise in discovering patterns and manipulating symbols according to complex and exceedingly numerous, but well defined and self-consistent rules. When advances in computer speed and memory capacity made it possible to store and implement these rules automatically, the stage was set for a revolution on a scale comparable to the revolution produced by automatic numerical computation five decades ago. Some implications of this revolution for the field of surface analysis will be presented, through examples drawn from medium energy backscattering spectrometry, four-point probe measurements, and radiation effects in semiconductors. The distinctive properties of an extensible surface analyst's quantitative workbench will be discussed. An important conclusion is that most technical software now being written should be based on robust algorithms and fidelity to correct physics without (much) regard for the characteristics of the hardware on which it will initially be implemented.

This work has been supported in part by the U.S. Army Research Office through grant DAAD 19-99-1-0283.

2:40pm **AS-MoA3 Quantitative XPS and the Morphology Problem : Simple Algorithm for the Amount of Substance at the Surface**, ***S. Tougaard***, University of Southern Denmark

It is well known that due to electron attenuation, the measured XPS-peak intensity depends strongly on the in-depth atom distribution. Quantification based only on the peak intensity leads therefore to huge uncertainties. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in.[1] These algorithms have been extensively tested experimentally and found to be able to determine the morphology of surfaces with quite high accuracy.[2] Practical application of these algorithms has increased after ready to use software packages were made available[3] and they are now being used in labs worldwide. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is an additional need for simplified strategies that can be automated. In this paper we report on a very simple algorithm that takes the morphology effect into account. It is a slightly more accurate version of the algorithm previously proposed by Tougaard (eq.(8) in[4]). Although it was proposed more than a decade ago, the practical applications of this simple formula has not previously been studied in any great detail. The algorithm gives the amount of atoms within the outermost 3 IMFPs with a good accuracy and it also gives a rough estimate for the in-depth morphology. The validity of the simple algorithm is tested on several experimental systems and the results are compared to analysis of the same samples quantified by more accurate methods.

[1] S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996)

[2] S. Tougaard, Surf. Interf. Anal. 26, 249 (1998)

[3] S. Tougaard: QUASES-Tougaard, Software package for Quantitative Analysis of Surfaces by Electron Spectroscopy, Ver 5.0 (see: www.quases.com).

[4] S. Tougaard, J. Vac. Sci. Technol. A8, 2197 (1990).

3:00pm **AS-MoA4 The Information Depth and the Mean Escape Depth in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy**, ***A. Jablonski***, Polish Academy of Sciences, Poland, *C.J. Powell*, National Institute of Standards and Technology

The information depth (ID) is a measure of the sampling depth for the detected signal in Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) while the mean escape depth (MED) is a measure of surface sensitivity. We report ID and MED calculations for Si 2s, Si $2p_{3/2}$, Cu 2s, Cu $2p_{3/2}$, Au 4s, and Au $4f_{7/2}$ photoelectrons excited by Mg Kα x rays. Similar calculations were made for Si L_3VV, Si $KL_{23}L_{23}$, Cu M_3VV, Cu L_3VV, Au N_7VV, and Au $M_5N_{67}N_{67}$ Auger transitions. The ID and MEDs were derived from an analytical expression for the electron depth distribution function obtained from a solution of the kinetic Boltzmann equation within the transport approximation. The ratios of the IDs and the MEDs to the corresponding values found if elastic-electron scattering effects were negligible, R_{ID} and R_{MED}, were less than unity and varied slowly with electron emission angle α for emission angles less than 50°. For larger emission angles, these ratios increased rapidly with α. For $\alpha \leq 50^o$, average values of R_{ID} and R_{MED} varied linearly with the single-scattering albedo, ω, a simple measure of the strength of elastic scattering effects. For $\alpha = 70^o$ and $\alpha = 80^o$, R_{ID} also varied linearly with ω but R_{MED} showed a quadratic variation. As a result of elastic scattering of the signal electrons, AES and XPS measurements at $\alpha = 80^o$ are less surface-sensitive than would be expected if elastic scattering had been neglected. Conversely, AES and XPS measurements made for $\alpha \leq 50^o$ are more surface sensitive as a result of elastic-scattering effects.

3:20pm **AS-MoA5 Wavelets: A New Technique for Spectral Processing in Surface Science - Applications to Filtering and Deconvoluting HREELS and XPS Data**, *C. Charles, J.P. Rasson, G. Leclerc, P. Louette,* ***J.J. Pireaux***, Facultés Universitaires Notre-Dame de la Paix, Belgium

Last decade has witnessed the emergence of new powerful signal analysis tools: the wavelet transform is one of them.[1] By simultaneously taking into account both the time and frequency domains, a wavelet analysis is a priori more efficient and covers a larger spectrum of applications than the Fourier Transform. The wavelet theory will be briefly presented, with comparison to Fourier analysis. Three applications for HREELS (High Resolution Electron Energy Loss Spectroscopy) and XPS (X-Ray Photoelectron Spectroscopy) will follow: noise filtering, peak detection and deconvolution. We first use synthetic data, a quite common practice in statistics: the correct answer is indeed known; it is thus possible to assess the validity and robustness of the algorithms, under clear hypotheses; errors can be calculated. The filtering algorithm proceeds with an original 'Local in Time and Frequency Translation Invariant Poisson Smoothing' code, that adapts itself to a spectrum containing peaks of very different amplitudes. Regions with a local maximum is then automatically detected with wavelets, allowing a Localized Least Squares method to precisely locate and determine the intensity of a peak. Different applications on real HREELS and XPS data are illustrated; they are particularly encouraging.

[1] I. Daubechies, Ten lectures on wavelets. Philadelphia, PA, SIAM, 1992

3:40pm **AS-MoA6 Ultra Thin SiO_2 on Si: Quantification of the Oxide Thickness and Carbonaceous Contamination**, ***M.P. Seah***, *S.J. Spencer*, National Physical Laboratory, UK

An analysis is made of the quantification issues in the measurement of ultra-thin layers of SiO_2 and of carbonaceous contamination on (100) and (111) polished Si surfaces. For the analysis of the oxide thickness, a simple equation is generally used involving two parameters; the attenuation length of photoelectrons in the oxide, L, and the ratio, R_o, of the intensities of the Si 2p peak from bulk thermal SiO_2 and from pure Si. An analysis of previously reported measurements of L gives an average value of only 6% less than the theoretical value. However, careful measurements of R_o, via two routes, indicate consistently that a value of 0.88 ± 0.05 should be used rather than the calculated value of 0.53 ± 0.05. This difference may arise through systematic errors in the values for the relevant inelastic mean free paths, the silicon dioxide density and the shake-up intensity contributions. Previously reported experimental values of R_o range from 0.67 to 0.87. Sources of uncertainty in these parameters and in the thickness will be addressed. Measurements of a basis set of materials for an international study, started in March 2002 under the auspices of the Consultative Committee for Amount of Substance (CCQM), show average correlations with ellipsometry better than 0.13 nm over the thickness range 2 nm to 8 nm. Measurements of the carbonaceous contamination show how to clean and store the samples effectively and the relevant parameters for a consistent carbon quantification.

4:00pm **AS-MoA7 Correcting for Detector-Induced Non Linearity in Photoelectron Spectroscopy Counting Systems**, ***C.S. Fadley***, *N. Mannella, S. Marchesini,* University of California at Davis, *A. Kay,* Intel Corporation, *S.-H. Yang,* IBM Almaden Research Center, *S. Mun,* Intel Corporation, *M.A. van Hove*, Lawrence Berkeley National Laboratory

The photoelectron intensity levels reached in exciting surfaces with both laboratory sources and third-generation synchrotron radiation can in many cases exceed the linear response range of the final detection system involved.[1] For example, the quantitative analysis of complex oxides via core-level intensities has been found to be strongly influenced by this non-linearity,[2] as have angle-resolved valence spectra[3] and magnetic dichroism measurements on magnetic systems.[2] Experiments involving resonant photoemission, in which the photon energy is scanned through an absorption edge, are also strongly affected.[4] In this paper, we demonstrate two quantitatively accurate procedures to correct for such non-linearity effects. The first method directly yields the detector efficiency by measuring a flat-background reference intensity as a function of incident x-ray flux, while the second method determines the detector response from an analysis of broad-scan survey spectra at different incident x-ray fluxes. Although we will use one spectrometer system (the Scienta ES200) as an example, the methodologies discussed here should be useful for many other cases. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098.

[1] M.P. Seah, M. Tosa, Surf. Interface. Anal. 18 (1992) 240; (b) M.P. Seah, I.S. Gilmore, S.J. Spencer, J. Electron Spectrosc. 104 (1999) 73-89.

[2] P. Wernet, N. Mannella et al., to be published.

[3] D. Dessau and Y. Chuang, private communication.

[4] A. Kay, Ph.D. Thesis, University of California Davis, 1998; A.W. Kay et al., Physical Review B 63, 115119,U214-U222 (2001) and references therein.

4:20pm **AS-MoA8 Theoretical Foundations of Surface Stress Measurements using Atomic Force Microscope Cantilevers**, ***J.E. Sader***, The University of Melbourne, Australia

Due to its extreme sensitivity and speed, the atomic force microscope (AFM) has recently emerged as an important tool in the measurement of surface stress. Fundamental to this application is theoretical knowledge of the effects of surface stress on the deflections of AFM cantilever plates. This is normally obtained by use of Stoney's equation, which is derived for a completely unrestrained plate. In this talk, the validity of Stoney's equation to rectangular and V-shaped AFM cantilever plates is investigated. It is found that use of Stoney's equation can lead to significant errors in measurements made using AFM cantilevers. Detailed finite element results and new analytical formulae, which replace Stoney's equation and greatly improve on its accuracy, shall be presented.

4:40pm **AS-MoA9 Elementary and Structure Analysis of Si Wafers and Thin Films by Using an X-ray Waveguide-Resonator**, ***V.K. Egorov***, *E.V. Egorov*, Russian Academy of Science (IPMT RAS), Russia

Analysis of composition and structure for Si wafers surface and thin films is carried out at X-ray beam grazing incidence (TXRF, GIRD). The methods fulfillment requires creation of an X-ray line beam with small width, low divergence and high radiation density. Monochromatization of the beam is nonobligatory demand. Such X-ray beam is formed indeed by planar X-ray waveguide-resonator (PXWR).[1] PXWR is the narrow extensive slit formed by two planes polished dielectric reflectors. The slit size must fall into the certain size interval. At quartz reflectors intervals for MoKα and CuKα are limited by sizes: 15-45 nm and 15-95 nm. Waveguides capture radiation in the angle aperture $\Delta\theta<2\theta_c$, where θ_c is the total reflection critical angle. Realistic emergent beams have width 50-100 nm, hight 1-10 mm, divergence $\Delta\theta<2\theta_c$ and radiation density exceeded one in standard formed beam systems by 3-4 orders. Composite PXWR has the emergent beam divergence $\Delta\theta<<2\theta_c$ at preservation of a total intensity. Schemes of diffractive and spectroscopic devices equipped by PXWR are considered. Data for X-ray beam diffraction on thin films at its grazing incidence and for focusing scattering scheme are presented. There are discussed X-ray fluorescence spectra collected at the grazing incidence on film targets of beams formed by PXWR. The model for the spectrum treatment taking into account PXWR using for the target excitation is formulated. PXWR application leads to falling of element detection limit more than one order in comparison of the standard TXRF spectrometer scheme. TXRF device with PXWR is more cheap, more simple in exploitation. PXWR can be used for TXRF study of Si wafers with d>300 mm and adapted for "in situ" measurements.

[1] V.K. Egorov, E.V. Egorov, T.V. Bil'chik, Investigation in Russia, v3, pp. 423-441 (2002). http://zhurnal.ape.relarn.ru/articles/2002/040e.pdf.

Biomaterials
Room: C-201 - Session BI+VT-MoA

Protein Surface Interactions
Moderator: D. Grainger, Colorado State University

2:00pm **BI+VT-MoA1 Self-Assembled Monolayers of Carboxy-Terminated Poly(ethylene glycol): Protein Resistance, Biospecific Functionalization and Application to Immunodiagnostics**, ***R. Dahint***, University of Heidelberg, Germany **INVITED**

The high specifity of antigen/antibody reactions has been widely exploited to develop accurate detection methods for biomolecules. Heterogeneous immunoassays, where proteins are selectively bound by immobilized antibodies and detected by the use of labeled secondary antibodies are a standard diagnostic technique. Also, a considerable amount of research has been focused on immunosensor development. A general problem in immunodiagnostics is non-specific protein adsorption: Macromolecules are not only bound to the substrate by specific antigen/antibody recognition, but also adhere due to non-specific interaction forces. Hereby, the accurate determination of antigen concentration may be significantly deteriorated. Moreover, non-specifically adsorbed proteins may even block and deactivate the immobilized receptors. The integration of specific receptors into a protein resistant matrix would, therefore, significantly improve quantitative analysis. Self-assembled monolayers (SAMs) of poly- and oligo(ethylene glycol) have proven to effectively prevent protein adsorption. We, therefore, synthesized a carboxy-terminated poly(ethylene glycol) alkanethiol ($HOOC-CH_2-(OCH_2-CH_2)_n-O-(CH_2)_{11}-SH$, n = 22-45) which facilitates covalent coupling of antibodies. In contrast to most other previous studies, where receptors have been coupled to SAMs formed from a binary mixture of differently functionalized molecules, only a single chemical functionality is involved. After characterizing the films by infrared absorption (FTIR) and X-ray photoelectron spectroscopy, ellipsometry and contact angle measurements, their performance as bioselective coatings with reduced non-specific adsorption has been tested in both FTIR and acoustic wave sensor experiments. The protein resistant properties of the films are put in context with previous results on oligo(ethylene glycol) alkanethiolate SAMs including neutron reflectivity studies on protein/surface interactions.

2:40pm **BI+VT-MoA3 ToF-SIMS and XPS Analysis of Enzymatic Digests of Adsorbed Protein Films**, ***M.S. Wagner***, *D.G. Castner*, University of Washington

Characterization of multicomponent adsorbed protein films is critical in understanding biological interactions with surfaces. We have previously shown that Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can quantify the composition of binary and ternary adsorbed protein films using the low mass ($0 < m/z < 200$) fragmentation pattern of the mass spectrum. However, quantification of more complex protein films using this method is limited to the most abundant proteins present in the films. Therefore, trypsin digestion of the adsorbed proteins was performed to generate tryptic fragments for subsequent analysis by ToF-SIMS. The tryptic fragments were identified by combining ToF-SIMS with matrices from Matrix Assisted Laser Desorption and Ionization Mass Spectrometry (MALDI-MS). Residual protein remaining on the substrate after digestion was detected using ToF-SIMS and X-ray Photoelectron Spectroscopy (XPS). This method provides unique fragments for the identification of adsorbed proteins by ToF-SIMS.

3:00pm **BI+VT-MoA4 Protein Adsorption on Colloidal Oxide Particles**, ***K. Rezwan***, *L.P. Meier*, *M. Textor*, *L.J. Gauckler*, ETH Zurich, Switzerland

Protein adsorption to surfaces of medical implants is an essential aspect of the cascade of biological reactions taking place at the interface between synthetic material and biological environment. The types and amounts of adsorbed proteins mediate subsequent adhesion, proliferation and differentiation of cells as well as deposition of mineral phases. Most metallic biomaterials are covered by a protective, stable oxide film such as titanium oxide on titanium. Hence proteins only interact with the oxide film and not with the underlying metal. Closer investigations of the protein - oxide interface are therefore of great relevance to the biomaterials field. In the past, protein adsorption and desorption has been investigated mostly on planar surfaces by in situ techniques such as ellipsometry, optical waveguide lightmode spectroscopy (OWLS) and quartz crystal microbalance (QCM). The drawback of these methods is the lack of direct information about surface charges, which are known to strongly affect protein adhesion and conformation at interfaces. We used colloid chemistry analysis methods such as colloidal vibration potential (CVP), X - ray disc centrifuge (XDC) measurements and UV â€“ spectroscopy (UVS) to study in detail the adsorption of proteins to well-defined colloidal particles of typically 100 - 200 nm diameter. Combining these methods, the adsorbed amount of proteins and its influence on the zetapotential and the isoelectric point of the particles were determined with great precision and across a wide pH range. Adsorption of bovine serum albumin was found to alter the zetapotential of the oxides Al2O3, TiO2 and SiO2 and their isoelectric points to an extent that depended on the adsorbed mass. Combining UVS and XDC, the volume density and the thickness of the protein layer could be determined. The thickness corresponded to a monolayer or less. The adsorbed mass of albumin turned out to be nearly independent of pH in the range from pH 2 to 12.

3:20pm **BI+VT-MoA5 Prediction of Adsorption Behavior of Fibronectin as a Function of Surface Functionality Using a Customized Protein Adsorption Force-Field**, ***R.A. Latour***, *K.A. Wilson,* Clemson University*, A.J. Garcia,* Georgia Institute of Technology*, S.J. Stuart,* Clemson University

The ability of a cell to bind to an adsorbed protein layer on a biomaterial surface is dependent on the structure and availability of the protein's cell binding domains following adsorption. A well-known example of this is integrin binding to the PHSRN and RGD sites located on the 9th & 10th type III repeats of fibronectin (Fn). The objective of this research was to utilize computational chemistry to predict the relative orientation and accessibility of these cell-binding domains in Fn after adsorption as a function of surface functionality (CH3, OH, NH3+, COO-). Modeling was conducted using an SGI O2/Onyx computational system with InsightII software (Accelrys). The Charmm force-field was used to simulate intramolecular interactions for the fibronectin, while a new set of force-field parameters was created to simulate the interactions between the fibronectin and the surface. The new force-field parameters were set to provide similar energy vs. surface separation plots for peptide residue-surface adsorption as determined by previous semi-empirical modeling studies using MOPAC/PM3/COSMO. Initial energy vs Fn orientation maps were generated followed by 50 ps molecular dynamics simulations at selected positions to assess initial adsorbed Fn behavior. Results suggest that the CH3 and COO- surfaces should most strongly inhibit integrin binding, but by different mechanisms; the CH3 surface by disrupting Fn structure and the COO- surface by blocking accessibility. The OH and NH3 surfaces were predicted to preserve binding site structure and accessibility. Results compare favorably with experimental studies and provide likely molecular mechanisms that help explain experimentally observed behavior.

3:40pm **BI+VT-MoA6 Analysis of Organic and Biological Materials in Ultra-High Vacuum**, ***D.G. Castner***, University of Washington **INVITED**

Ultra-high vacuum (UHV) surface science has a long, successful history in the fields of catalysis and microelectronics. The early adaptation of UHV-based tools in these fields was largely due to the fact that the materials involved (metals, ceramics, semiconductors, etc.) were readily vacuum compatible. This talk will address the challenges of adapting UHV surface analysis techniques for analyzing organic and biological materials. These include their higher vapor pressure, their increased susceptibility to X-ray, electron, and ion sample degradation, and vacuum induced changes in their structure. Some of the first organic surface analysis experiments were done on polymers. Since that time, these experiments have been extended to self-assembled monolayers (SAMs), biomaterials, and adsorbed biomolecules. Examples to be discussed from these areas will include the effect of polymer additives, surface rearrangement of polymers, the well-defined structure of SAMs, and preserving the conformation of adsorbed proteins.

4:20pm **BI+VT-MoA8 PEG-ylated Surfaces with Graded Protein Interactiveness : A ToF-SIMS, XPS and Optical Waveguide Sensor Study**, ***S. Pasche***, *S.M. De Paul, J. Vörös,* Swiss Federal Institute of Technology*, P. Hug, B. Keller,* Swiss Federal Laboratory for Material Testing and Research*, H.J. Griesser,* University of South Australia*, N.D. Spencer, M. Textor,* Swiss Federal Institute of Technology

Poly(L-lysine) grafted with poly(ethylene glycol) (PLL-g-PEG), a polycationic co-polymer positively charged at neutral pH, has been shown to spontaneously adsorb onto negatively charged surfaces, rendering them protein-resistant to a degree related to the PEG surface density. Since the PEG surface density is a function of polymer architecture (PEG molecular weight and grafting ratio expressed as number of lysine monomers per PEG side chain), it becomes feasible to control the interactiveness of a surface by varying the co-polymer architecture. Angle-dependent XPS and ToF-SIMS were used to investigate the surface-chemical properties. The adsorbed mass after serum exposure was determined by an optical sensor technique. Further colloid-modified AFM force measurements aim at studying the mechanical properties of the coated surfaces. PLL-g-PEG was adsorbed onto niobium oxide coated wafers, resulting in the formation of stable polymeric monolayers. The grafting ratio, g, of the polymer was varied systematically between 2 and 10, leading, upon surface adsorption, to highly different, but controlled PEG surface densities. PEG molecular weight was varied between 1000 and 5000. Polymer adsorbed mass was determined quantitatively by an in situ optical waveguide technique. A quantitative relationship was established between EG-monomer surface density, calculated from the known polymer architecture and the surface-adsorbed mass, ToF-SIMS intensities of PEG-, PLL- and substrate-related secondary ion peaks, and the amount of serum proteins that adsorbed onto the different polymer-coated surfaces. PLL-g-PEG surface-coating technology allows the fabrication of surfaces with tailored interactiveness and the establishment of design criteria for PEG-based, protein-resistant surfaces.

4:40pm **BI+VT-MoA9 Time-of-Flight Secondary Ion Mass Spectrometry Analysis of Conformational Changes in Adsorbed Protein Films**, ***N. Xia***, University of Washington*, C.J. May,* Yale University*, S.L. McArthur, D.G. Castner*, University of Washington

Characterizing the identity, composition, conformation, and orientation of adsorbed proteins is essential for the development of biocompatible devices. Static time-of-flight secondary mass spectrometry (ToF-SIMS) is a powerful surface analytical technique for analyzing adsorbed protein films. However, the ToF-SIMS experiment is done under vacuum, and drying adsorbed proteins for analysis can denature or change their conformation. In this study, trehalose coating was used to inhibit these conformational changes from occurring during sample preparation for ToF-SIMS analysis. Surface plasmon resonance (SPR) analysis showed that air-dried films of trehalose-stabilized antibodies retained a significant proportion of their hydrated antigen binding activity. In contrast, air-drying without trehalose protection resulted in the adsorbed protein films losing most of their antigen binding activity. Structural differences between trehalose-stabilized and unstabilized protein films were then analyzed with static ToF-SIMS. By application of principle component analysis (PCA) to the ToF-SIMS spectra, the biological activity difference observed in SPR was correlated to changes in protein conformation. Trehalose-protected proteins retained a greater degree of their original conformation than the unprotected proteins. This suggests that static ToF-SIMS has the capability to distinguish conformational differences in adsorbed protein films. Moreover, trehalose protection can be used for static ToF-SIMS analysis of adsorbed protein films to obtain structural information that is more relevant to the structure of the proteins in aqueous conditions.

5:00pm **BI+VT-MoA10 Study of the Adsorption Kinetics and Conformational Changes of Human Serum Albumin and Human Plasma Fibronectin using PM-RAIRS, Radiolabelling and Atomic Force Microscopy**, ***R.J. Manning***, *C.M.J. Fauroux, M.J. Pilling, P. Gardner, G.J. Leggett*, University of Manchester Institute of Science and Technology, UK

The kinetics of adsorption of proteins has been studied on self assembled monolayers (SAMs) on gold, formed by the adsorption of alkanethiolates with differing functional groups and varying alkyl chain lengths. The adsorption of human serum albumin (HSA) and human plasma fibronectin (HPF) has been studied using three complementary techniques: post modulation fourier transform reflection adsorption infrared spectroscopy (PM-RAIRS), radiolabelling, and atomic force microscopy (AFM). Initial adsorption kinetics of HSA and HPF were established using FTIR. It was found that monolayer coverage was reached faster on methyl terminated SAMs than on hydroxyl and carboxylic acid terminated hydrophilic monolayers. Tritium radiolabelling of HSA and HPF confirmed the trends observed with FTIR. The conformations of the adsorbed proteins were followed using PM-RAIRS, enabling quantitative monitoring of the percentage of α-helix, β-sheet, β-turn and random coils, indicating the degree of denaturation on differing surfaces over time. Finally, AFM was used to generate direct observations of layers of adsorbed proteins, providing useful insights into the distribution of proteins across the differing surfaces and enabling individual molecules to be observed. HSA was found to form a fibrillar network on methyl terminated SAMs at low concentrations and short adsorption times, whilst individual molecules were observed on hydroxyl and carboxylic acid terminated monolayers. This study demonstrates the complimentarity of FTIR, radiolabelling and AFM in understanding the adsorption of proteins on well-ordered SAMs.

Electrochemistry and Fluid-Solid Interfaces
Room: C-104 - Session EC+SS-MoA

Liquid-Solid Interfaces & Nanoscale Electrochemistry
Moderator: S. Morin, York University

2:00pm **EC+SS-MoA1 Femtosecond Spectroscopy at the Metal/Liquid Interface**, *S. Roke, M. Bonn,* ***A.W. Kleyn***, Leiden University, The Netherlands

Vibrational sum frequency generation spectroscopy is an ideal technique to study molecules at surfaces and at buried interfaces with a high degree of molecular specificity. The most powerful feature of this technique is its capability to monitor intramolecular vibrations of the first layer of molecules on the surface: it essentially allows one to look inside the molecules at the interface. The use of femtosecond laser pulses allows one to not only perform frequency domain measurements, but also time domain measurements. We have performed femtosecond time and frequency domain measurements on the acetonitrile/gold interface. Comparison of the time and frequency domain results showed that, although the two approaches are in principle equivalent they are sensitive to different physical aspects of the system. Time domain measurements are more clearly influenced by the inhomogeneity of adsorption sites, whereas frequency domain measurements are more subject to the homogeneous features of the spectral line broadening. To account for this we have extended existing models for calculating SFG spectra and free induction decay measurements. From the combination of the measurements and our model we have obtained information on the orientation and binding of acetonitrile to the gold surface and determined the nature and time scale of the decay of the vibrational polarization of the CH and CN stretch vibrations. The CN oscillators are distributed inhomogeniously across the surface and have a dephasing time of 1.65 ps. The CH stretch vibration however does not feel the inhomogeneity and dephases 2.5 times faster (T2 = 610 fs), because the methyl groups are further away from the interface.

2:20pm **EC+SS-MoA2 Studies of the Interphase Region for Liquid Hexadecane Near a Au Surface**, ***A.C. Oliver***, *J.E. Houston*, Sandia National Laboratories

In this presentation, we explore the formation and properties of a solid-like"interphase" region near Au surfaces immersed in liquid hexadecane using interfacial force microscopy (IFM). We measure variations of the normal and lateral friction forces, as well as the conductance behavior, as a function of the relative interfacial separation. We show that this interphase layer passivates the normally strong bonding between two Au surfaces even at high applied stresses. In addition, no conduction is seen for this normally insulating layer until appreciable stresses are applied. By placing a voltage between tip and sample, we determine the thickness of the organized film from the behavior of the electrostatic force as a function of relative separation up to film contact. We show that at room temperature the interphase-layer thickness is ~7 molecular diameters, which increases with larger bias voltages. In addition, the lateral force shows appreciable friction before film contact for the larger voltages, indicating that the field is causing a local film organization. Data taken as a function of temperature indicates a decrease in the film organization. We discuss the implication of these results in the general context of the interaction of surface in liquid environments. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:40pm **EC+SS-MoA3 Surface Forces at Electrified Interfaces**, *J. Frechette,* ***T.K. Vanderlick***, Princeton University

Electrodes specifically designed for the surface forces apparatus were developed to study adhesion between mica and polycrystalline gold at different applied potentials. Pull-off forces were a strong function of applied potential and dominated by electrostatic interactions. Adhesion measurements increased six-fold in a 150 mV window around the potential of zero charge. We compared these measurements using DLVO and JKR (Johnson-Kendall-Roberts) theory in the case of dissimilarly charged surfaces. We also investigated the effect of potential dependent adsorption, such as pyridine on gold, on electrostatic forces and adhesion. We observed a stronger influence of the adsorbate on adhesion measurements than on surface forces.

3:00pm **EC+SS-MoA4 A New View of Ion Adsorption at Mineral-Fluid Interfaces with Synchrotron X-Ray Scattering**, ***P. Fenter***, Argonne National Laboratory, *Z. Zhang,* Northwestern University, *M.L. Schlegel,* Commissariat a l'Energie Atomique, France, *C.Y. Park, L. Cheng,* Argonne National Laboratory, *K.L. Nagy,* University of Colorado at Boulder, *D.J. Wesolowski,* Oak Ridge National Laboratory, *M. Machesky,* Illinois State Water Survey, *M.J. Bedzyk,* Northwestern University, *N.C. Sturchio*, University of Illinois at Chicago **INVITED**

Ion adsorption at mineral-water interfaces is a key component of the electrical double-layer, a classic problem in surface science, and is fundamental for understanding the mobility of elements in the environment. We describe direct in-situ measurements of the systematic trends in ion adsorption near rutile- and muscovite-water interfaces using synchrotron X-ray scattering techniques (X-ray standing waves and X-ray reflectivity). These minerals represent two extremes in terms of location and origin of surface charge. The surface charge on rutile, an oxide, is determined by surface protonation reactions and is located above the mineral surface. In contrast, the surface charge of muscovite, a phyllosilicate, is determined by the permanent negative charge due to isomorphic lattice substitution below the mineral surface. The location of Zn^{2+}, Sr^{2+} and Y^{3+} ions were fully triangulated at the rutile(110)-water interface revealing unexpected differences in their adsorption geometries. Separate measurements were made of K^+, Cs^+, Ca^{2+}, Ba^{2+} and Zn^{2+} ion heights with respect to the muscovite(001)-water interface. Systematic trends in adsorption behavior will be discussed in the context of classical pictures of ion-mineral interactions (e.g., inner sphere vs. outer-sphere complexes) and by contrasting the different ion adsorption behavior at the rutile and muscovite surfaces. Research sponsored by the U.S. Department of Energy, Office of Basic Energy Science: Division of Chemical Sciences, Geosciences and Biosciences.

3:40pm **EC+SS-MoA6 Solution Composition Effects on Calcite Dissolution and Growth Processes**, ***A.S. Lea***, *J.E. Amonette, D.R. Baer, N.G. Colton*, Pacific Northwest National Laboratory

We have examined the influence of a number of solution impurities on step motion and shape of pits during dissolution and growth on the cleavage surface of calcite. Mg^{2+}, in contrast to the other impurities (Ca^{2+}, Mn^{2+}, Sr^{2+}, Co^{2+}, Mg^{2+}, and CO_3^{2-}) we have studied, exhibits unique behavior by uniformly enhancing dissolution rather than retarding dissolution. Of the impurities that retard dissolution, Sr^{2+} and CO_3^{2-} demonstrate selective sorption to the most sterically accessible step site resulting in a substantial slowing of dissolution of this type of step. Mn^{2+} and Co^{2+}, however, retard dissolution uniformly due to non-selective step sorption. For Mn^{2+}, Sr^{2+}, Co^{2+}, and Ca^{2+}, little impact on dissolution rate is seen until a threshold concentration is reached, whereupon near complete frustration of dissolution occurs upon further increase in impurity concentration. These results can be explained using a simple terrace-ledge-kink model that incorporates site-blocking and works equally well with metal ion or carbonate ion pair concentrations. This site-blocking model cannot explain the enhanced dissolution behavior of calcite in the presence of Mg^{2+}. In calcite growth processes, Ca^{2+} ions demonstrate preferred kink sorption sites, manifested by the unique pit shape observed during pit fill-in.

This work was supported by the Office of Basic Energy Science, Geosciences Research Program, U. S. Department of Energy. The work was conducted in the Environmental Molecular Sciences Laboratory, a U.S. Department of Energy user facility located at Pacific Northwest National Laboratory. .

4:00pm **EC+SS-MoA7 Investigation of Binary Oxide (V_2O_5) Thin Films as Electrodes for Rechargeable Micro Batteries using Li**, *A. Talledo, H. Valdivis,* Universidad Nacional de Ingenieria, Peru, ***C. Benndorf***, University of Hamburg, Germany

We report on the preparation of V_2O_5 thin films, their charcetrization and their application as electrodes in rechargeable micro batteries using lithium as counter electrode. The V_2O_5 thin films were deposited onto SnO coated glass by reactive rf sputtering of a V cathode using an Ar + O_2 atmosphere. The electrodes were characterized by their electrochemical behavior (IV-curves during charging and recharging using $LiClO_4$ +PC as electrolyte), X-ray diffraction (XRD), X-ray and UV induced photoelectron spectroscopy (XPS and UPS) and infrared (IR) measurements. XRD measurements demonstrated that unannealed V_2O_5 films were amorphous with no sharp reflexes. Annealing to 350°C was sufficient to produce crystalline β-V_2O_5. XPS spectra revealed the expected V/O ratio and the correct line positions. However, the O 1s peak was splitted into two components, one from the V_2O_5 component (530.8 eV). The other at 533.1 eV is attributed to the uptake of water from the atmosphere. The large uptake of water is consistent with a porous structure of the V_2O_5 thin film. The charged micro battery resulted in a maximum voltage of 3.4 V for the currentless circuit and a capacity of 34.5 mC/cm². With XPS we could demonstrate the migration of Sn into the V_2O_5 layer for the electrodes charged with Li. Further, UPS spectra from uncharged and charged V_2O_5 indicate a band gap narrowing due to the Li uptake, which is consistent with optical measurements. Our investigation contributes to the understanding and application of vanadium oxide thin films as cathodes for micro batteries.

4:20pm **EC+SS-MoA8 Creating Beakers without Walls: Formation of Deeply-Supercooled Binary Liquid Solutions from Nanoscale Amorphous Solid Films**, *P. Ayotte, R.S. Smith, G. Teeter, Z. Dohnálek, G.A. Kimmel,* ***B.D. Kay***, Pacific Northwest National Laboratory

Supercooled liquids are metastable and their lifetimes are dictated by the kinetics for crystallization. Traditional experimental studies have used a variety of methods to suppress crystallization while cooling from the liquid phase. An alternate approach is to heat an amorphous solid above its glass transition temperature, T_g, whereupon it transforms into a deeply-supercooled liquid prior to crystallization. We employ molecular beams, programmed desorption (both TPD and isothermal) and FTIR vibrational spectroscopy to synthesize and characterize compositionally tailored nanoscale films of glassy methanol and ethanol. We demonstrate that these films exhibit complete diffusive intermixing and suppressed crystallization when heated above T_g. Furthermore, the resulting container-less liquids evaporate as continuously mixed ideal binary solutions while retaining their solid-like macroscopic shapes. This approach provides a new method for preparing deeply-supercooled liquid solutions in metastable regions of their phase diagram and for studying the kinetics of their phase separation and crystallization as they approach thermodynamic equilibrium. The applicability of this technique for studying aqueous liquid solutions will also be presented and discussed. P. A. is an NSERC Postdoctoral Fellow. 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.

4:40pm **EC+SS-MoA9 Using NanomechanicaL Responses in Individual Systems from a Single C-C Bond to Single Cell**, ***J. Gimzewski***, University of California, Los Angeles **INVITED**

: The capability of the atomic force microscope has recently been extended as powerful tool to not only image molecules in real space in but also to explore the mechanical properties of single molecules in a wide range of environments ranging from ultra high vacuum to in vivo. In this talk I will present a series of experiments that span from individual cells in growth media to the forced rotation of a single carbon-carbon bond in a organic molecule, using AFM based techniques such as non-contact dynamic AFM. I will show that the ability to measure small forces and amplitudes in a range of environments enables unique insights into nanomechanical process such as the determination of the zepto Joule forces for molecular switches and the bility to monitor cell function. Additionally, I will also span these two extremes using liquid based nanomechanical probes of proteomic and genetic recognition processes.

Electronic Materials and Devices
Room: C-107 - Session EL+SC+MI-MoA

Metal-Semiconductor Interfaces
Moderator: C.J. Palmstrom, University of Minnesota

2:00pm **EL+SC+MI-MoA1 Spin Transport in Ferromagnet-Semiconductor Schottky Diodes**, ***P.A. Crowell***, *A.F. Isakovic, B.D. Schultz, J. Strand, C.J. Palmstrom*, University of Minnesota **INVITED**

We have completed an investigation of spin injection in semiconductor heterostructures using a Schottky contact between Fe and n-$Al_{1-x}Ga_xAs$ as an injector and an $Al_{1-x}Ga_xAs/GaAs/Al_{1-x}Ga_xAs$ quantum well (QW) as the detector. The injector and detector are combined in a single device in which the QW is placed in the depletion region of a p-n junction. The Schottky contact is δ-doped, so that a tunneling current can be obtained under moderate reverse bias.[1] The injected electrons recombine in the QW with holes from the p-contact, and the polarization of the resulting electroluminescence (EL) is used to infer the spin state of the recombining carriers. We demonstrate that the doping profile chosen for the QW has a dramatic effect on the apparent spin-detection efficiency. EL polarizations over 10% are obtained in optimally biased devices in which the QW is intentionally p-doped. The field-dependence of the EL polarization closely matches the magnetization of the Fe electrode. However, the largest polarizations are not observed from ordinary ground-state recombination in the quantum well. The maximum polarization observed from ground-state recombination is approximately 4% and appears to be less sensitive to the doping profile. In contrast, the EL polarization in control samples is less than 2%, does not track the magnetization of the ferromagnetic electrode and depends only weakly on bias voltage. The interpretation of these measurements will rely on a thorough understanding of the QW spin detector and the identification of background contributions. For example, we show using optical pumping measurements that the spin detection efficiency of the QW is a function of the bias voltage, as is the background photoluminescence polarization. This work was supported by DARPA, ONR, and NSF (MRSEC).

[1] H.J. Zhu et al., Phys. Rev. Lett. 87, 016601 (2001); A.T. Hanbicki et al., Appl. Phys. Lett. 80, 1240 (2002).

2:40pm **EL+SC+MI-MoA3 Characterization of an Fe/AlGaAs Tunnel Barrier Interface for Electrical Spin Injection**, *A.T. Hanbicki,* ***R.M. Stroud***, *B.T. Jonker*, Naval Research Laboratory

Electrical injection of spin-polarized carriers from a contact into a semiconductor is essential for the success of spintronic devices. Ferromagnetic metals are attractive contact materials because of their ample supply of spin-polarized electrons, but the use of these materials has been limited by small injection efficiencies in the diffusive transport regime.[1] The use of a tunnel barrier between a metal and semiconductor.however. should facilitate usable spin currents.[2] Recent experiments reported spin injection from Fe into a AlGaAs/GaAs-based LED which produced an electron spin polarization of 15% in the GaAs quantum.[3] This was attributed to tunneling through the Schottky barrier. We have characterized the Fe/AlGaAs contact reported in reference 3 to verify the tunneling nature of the contact and to investigate the physical nature of the interface. Samples were grown by molecular beam epitaxy and were specifically engineered to utilize the Schottky barrier between the Fe and the semiconductor as a tunnel contact. Current vs voltage measurements were made through the structure at different temperatures. The conductance shows an asymmetric parabolic dependence on the voltage. Further, there is a weak insulating-like behavior of the zero-bias resistance as a function of temperature, a reliable indication that this is a tunneling process based on the Rowell criteria for tunneling.[4] High-resolution TEM measurements indicate an atomically abrupt interface between the metal and semiconductor. Current-in-plane measurements and the relation of bias voltage to spin polarization will also be discussed. This work was supported by the DARPA SpinS program and ONR.

[1] G. Schmidt, et al, Phys.Rev.B 62, R4790 (2000)
[2] E.I. Rashba, Phys.Rev.B 62, R16267 (2000)
[3] A.T. Hanbicki, et al., Appl.Phys.Lett. 80, 1240 (2002)
[4] B.J. Jönsson-Åkerman, et al., Appl.Phys.Lett. 77, (2000).

3:00pm **EL+SC+MI-MoA4 A Schottky Tunnel Barrier Contact for Electrical Spin Injection into a Semiconductor**, ***B.T. Jonker***, *A.T. Hanbicki, G. Kioseoglou,* Naval Research Laboratory, *G. Itskos, R. Mallory, A. Petrou*, SUNY at Buffalo

Electrical injection of spin polarized electrons into a semiconductor heterostructure is a critical issue for semiconductor-based spintronic devices. While very encouraging results have been obtained using magnetic semiconductors as injecting contacts,[1] the desire for room temperature operation at low magnetic fields leads one to consider other materials and avenues. Ferromagnetic (FM) metals offer high Curie temperatures and can be rapidly switched (~ 300 ps) at low applied fields. However, theory has indicated that only very small spin injection (~0.01%) can be expected for typical FM metals as diffusive contacts.[2] We report here electrical spin injection from an Fe Schottky contact into an AlGaAs/GaAs LED structure, with spin injection efficiencies above 34% which extend to room temperature. These robust effects are attributed to spin tunneling[3] through the tailored Schottky barrier contact. The samples are grown by MBE, and the width of the depletion region at the Fe/AlGaAs interface is controlled by the semiconductor doping profile. Under reverse bias, electrons tunnel from the Fe into the semiconductor, and radiatively recombine in the GaAs quantum well. The circular polarization of the surface emitted electroluminescence (Faraday geometry) provides a quantitative, model independent measure of the QW spin polarization, and hence the injection efficiency.[1] The spin tunnel current is dominated by minority spin carriers, in contrast to previous work using Al_2O_3 tunnel barriers and a superconducting film detector. The temperature dependence of the polarization will also be discussed. These results will be compared with previous work[4] and theoretical modeling of Schottky barrier injection. Work supported by the DARPA SpinS program and ONR.

[1] R. Fiederling, et al Nature (1999); B.T. Jonker et al, PRB (2000)
[2] G. Schmidt et al, PRB (2000)
[3] E.I. Rashba, PRB (2000)
[4] H.J. Zhu et al, PRL (2001).

3:20pm **EL+SC+MI-MoA5 Contact Metallurgy for the Antimonide Based Compound Semiconductors**, ***S.E. Mohney***, *W.E. Liu, H.S. Wang, J.A. Robinson*, Penn State University **INVITED**

Antimonide based compound semiconductors are promising candidates for both high frequency, low power electronic devices and optoelectronic devices, and the performance of electrical contacts to these semiconductors is critical for some of the devices currently under development, particularly the electronic devices. Control of the interfacial reactions between the contact metals and the semiconductors is necessary during device processing and packaging since interfacial reactions between the metals and semiconductors occur at very low temperatures. Therefore, we have examined the condensed phase equilibria in the metal-III-Sb systems to guide our selection of shallow, thermally stable contact metallizations. We have performed thermodynamic calculations to estimate ternary phase diagrams in the transition metal-Ga-Sb, transition metal-In-Sb and selected metal-Al-Sb systems. We find that W, Re, and Os are the only transition metals predicted to be in thermodynamic equilibrium with both GaSb and InSb under the conditions considered in our calculations, while W is the only transition metal predicted to be in equilibrium with AlSb. Finally, we give an example of our use of the information we have gathered for the design of a very shallow, thermally stable low resistance ohmic contact to p-type GaInSb. Since we have observed using transmission electron microscopy that Pd reacts uniformly with GaSb at low temperatures, we chose a very thin layer of Pd as the first metal in our contact. We then deposited W because of our prediction that it would be in thermodynamic equilibrium with both GaSb and InSb and that it could serve as a diffusion barrier between layers. Finally, we capped the films with Au, which was important for lowering the metal sheet resistance. A contact resistance of 3 x 10^{-7} ohm-cm^2 was measured with good stability at 250 °C for 100 h, as verified using contact resistance measurements and Auger depth profiles.

4:00pm **EL+SC+MI-MoA7 Electrical Contact Behavior of Ni/C60/4H-SiC**, ***W. Lu***, Fisk University, *W.C. Mitchel*, Air Force Research Laboratory, *J.R. Landis*, University of Dayton Research Institute, *T.R. Crenshaw*, Fisk University, *S.R. Smith*, University of Dayton Research Institute, *W.E. Collins*, Fisk University

Ohmic contact formation of Ni/C60 film on n-type 4H-SiC was investigated. A C60 interfacial layer between Ni film and SiC improves ohmic contact properties significantly. The C60 film was deposited by Langmuir-Blodgett method prior to the Ni film deposition on SiC using DC sputtering method. High quality ohmic contact of Ni/C60/4H-SiC is formed after annealing at 800°C in Ar for two hours with a specific resistance of 1.6 x 10^{-6} Ωcm^2 for the SiC with a doping concentration of 1.8 x 10^{19}cm^{-3}. Raman spectra reveal that the formation of graphitic carbons by Ni catalytic effects result in the formation of ohmic contact on SiC, and the nano-size graphitic flakes identified by Raman spectroscopy play a key role for ohmic contact formation on SiC. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) show a direct relationship between the graphitized morphological features on the film and ohmic contact behavior.

4:20pm **EL+SC+MI-MoA8 Electrical Characterization of AlN MIS/MIM-structures**, ***F. Engelmark***, *J. Westlinder, I.V. Katardjiev, J. Olsson, S. Berg*, University of Uppsala, Sweden

The electrical properties of insulating ceramic films such as AlN, Ta_2O_5, HfO_2, ZrO_2, Al_2O_3, etc. are of substantial interest for a number of microelectronic and electro-acoustic applications owing to their chemical stability in harsh environments along with some very interesting electrical properties. In this work, emphasis has been put on the electrical properties of Aluminum nitride (AlN) films. Thin AlN films have been deposited onto Si(100) and Mo/Si(100) substrates. The sputter deposited Mo is polycrystalline, showing a predominant (110) orientation. AlN film growth is performed using different process conditions in a reactive PVD (Physical Vapour Deposition). Both fully textured (0002) polycrystalline and XRD amorphous films have been grown and studied. MIS- and MIM-structures have been fabricated and electrical properties such as dielectric constant, leakage current as well as their high frequency behaviour are investigated. The measurements indicate that the dielectric constant does not vary with crystallinity of the films, and remains constant at a value of 10. Further, the high frequency behaviour of the dielectric constant have been studied in the range 100 MHz to 20 GHz. The leakage current mechanism is also similar for different films and is believed to be Poole-Frenkel controlled. CV (Capacitance-Voltage) measurements for MIS structures revealed the presence of charges in the interface between the substrate and the dielectric layer. Trapped charge density was estimated to be 3.5*10^{10} cm^{-2}.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+NS-MoA

Self-Assembly and Nanomagnetism
Moderator: D. P. Pappas, DOC/NIST/EEEL/Magnetic Technology Division

2:00pm **MI+NS-MoA1 Self-assembly and Magnetism in Novel Core-shell Microspheres**, ***E.L. Bizdoaca***, *M. Spasova, M. Farle*, Halbleiterphysik und Optik, TU Braunschweig, Germany

We report on the fabrication and characterization of new composite core-shell particles with a defined shape, composition and multilayer shell thickness. These colloids can be produced by the layer-by-layer technique.[1] They consist of a core of a polystyrene (PS) microsphere (640 nm diameter) coated with consecutive shells of Fe_3O_4 nanoparticles (12 nm diameter) / polyelectrolytes /Au nanoparticles (15 nm). For the formation of the gold shell Au nanoparticles encapsulated in a very thin layer of silica (2 nm) were used. Composite core-shell particles were self-assembled into 1D periodic long-chain structure (up to 600 µm) by magnetophoretic deposition.[2] The length and separation of the chains were found to depend on the magnitude of the magnetic field and on the concentration of the water-based colloidal solution. The self-organization and the homogeneity of the colloidal coating were characterized by transmission electron and atomic force microscopy. Magnetic properties were determined by angular dependent ferromagnetic resonance (FMR) and SQUID-magnetometry between 5 and 300 K. FMR reveals long-range magnetic order at 300 K due to the dipolar coupling and an easy axis in plane, along the chains. We report a reduced magnetic moment in comparison with the magnetite bulk value. The remanence magnetization and the coercivity field (240 Oe) are not temperature dependent between 5 and 300 K. Supported by Deutsche Forschungsgemeinschaft. .

[1] F. Caruso et al, Chem.Mater.13 (2001) 109.

[2] E. L. Bizdoaca et al, J. Magn. Magn. Mater. 240 (2002) 44.

2:20pm **MI+NS-MoA2 Magnetic Resonance and X-ray Magnetic Circular Dichroism of Monodisperse Co Nanoparticles**, ***U. Wiedwald***, *M. Spasova*, Technical University Braunschweig, Germany, *M. Hilgendorff*, Hahn-Meitner-Institut, Germany, *M. Ulmeanu, E.L. Bizdoaca*, Technical University Braunschweig, Germany, *M. Giersig*, Hahn-Meitner-Institut, Germany, *M. Farle*, Technical University Braunschweig, Germany

Monodisperse Co nanoparticles with an medium diameter of 12 nm ($\sigma <$ 5%) are prepared by the thermolysis of $Co_2(CO)_8$.[1] After using a size-selective separation technique they are redispersed in toluene. For structural and magnetic investigations the samples are prepared by controlled evaporation of the solvent on various substrates. Detailed TEM analysis of the structure of Co nanoparticles shows that they consist of a 8-9 nm metallic Co core and a 1-2 nm thick CoO shell, both crystallized in fcc structure.[2] Angular dependent ferromagnetic resonance (FMR) of these arrays of Co nanoparticles reveals a remanent magnetization at 300 K that is due to long-range dipolar coupling between the nanoparticles.[3,4] A preliminary g-factor analysis yields a value of g = 2.15±0.02 that is close to bulk fcc value and in good agreement with the structural analysis. X-ray absorption fine structure (XAFS) shows a multiplet structure in the Co L_3 edge that is due to a superposition of metallic Co and Co in an oxidic environment. No evidence for x-ray magnetic circular dichroism (XMCD) at the $L_{2,3}$ edges is found for as prepared ex-situ samples for temperatures between 20 K and 300 K. After slight Ar^+ ion etching a well resolved XMCD signal with a strongly enhanced orbital-to-spin-moment ratio is observed. The results of the FMR and XMCD analysis will be compared and discussed in terms of the contributions from the antiferromagnetic CoO shell. This project is supported by the European Community, contract no. HPRN-CT-1999-00150 and the Access to Research Infrastructure action of the Improving Human Potential Programme. M. H. thanks the Deutsche Forschungsgemeinschaft, Az.: II C 10 - SPP 1072 for support.

[1] M. Hilgendorff et al., Aust. J. Chem. 54 (2001)

[2] M. Spasova et al., Proc. Spring MRS Meeting, San Francisco (2002), submitted

[3] U. Wiedwald et al., J. Vac. Sci. Technol. A 19 (2001)

[4] M. Spasova et al., J. Magn. Magn. Mat. 240 (2002)

2:40pm **MI+NS-MoA3 Surfactant-mediated Shape Control, Magnetism and Self-assembly of Cobalt Nanocrystals**, ***K.M. Krishnan***, *Y.P. Bao, M. Beerman*, University of Washington **INVITED**

Magnetic nanocrystals, monodisperse in size, shape and surface structure are now routinely synthesized by the rapid injection of an organometallic precursor into a hot coordinating solvent containing appropriate surfactants. The success of this method depends on temporally separating the nucleation and growth of the nanocrystals in solution and to control the precursor concentration to achieve size distribution focusing. In addition, careful choice of surfactant pairs that preferentially bond to different crystallographic planes of the growing nanocrystal can also be used to control the shape of the nanocrystals, including the preparation of high-aspect ratio particles or nanorods. For practical applications these nanocrystals must be organized into ordered arrays with well-defined inter-particle distances. In such nanocrystals, with a weak (van der Waals) attractive interaction between the metallic cores and a weak steric repulsion arising from the surfactant chains, entropy-driven self-assembly processes dominate. If particles of two different sizes are allowed to self-assemble, entropy driven wetting arising from depletion forces can be used to control the final organization. Use of solvent-nonsolvent pairs can be used to gently precipitate the nanocrystals into large scale ordered arrays. Details of the growth of Co nanocrystals with controlled size and shape, their subsequent self-assembly into ordered arrays, their characterization by a range of electron microscopy measurements and their isolated and collective magnetic behavior will be discussed.

3:20pm **MI+NS-MoA5 Structure and Magnetism of Colloidal Composite AgCo Nanoparticles**, ***M. Spasova***, Technishe Universität Braunschweig, Germany, *T. Radetic,* Lawrence Berkeley Laboratory, *N.S. Sobal,* Hahn-Meitner-Institut Berlin, Germany, *C. Raeder,* Technishe Universität Braunschweig, Germany, *M. Hilgendorff,* Hahn-Meitner-Institut Berlin, Germany, *U. Dahmen,* Lawrence Berkeley Laboratory, *M. Giersig,* Hahn-Meitner-Institut Berlin, Germany, *M. Farle*, Technishe Universität Braunschweig, Germany

Monodisperse, air-stable $Ag_{100-x}Co_x$ composite nanoparticles with a mean diameter of 12 nm have been synthesized by methods of colloidal chemistry.[1] The composition x was varied between 20 and 73 at.% Co. High resolution Transmission Electron Microscopy (TEM) and selected area electron diffraction have showed that the nanoparticles consist of precipitates of fcc Co and fcc Ag grains. No evidence for alloy formation was observed. Element-specific TEM images obtained by electron energy-loss spectroscopy and X-ray microanalysis indicate that Co is predominantly found in the surface region of the particles and the particles have an $Ag_{core}Co_{shell}$ structure. No Co oxide formation was observed in spite of Co being located at the particle surface. Magnetic properties of arrays of the nanoparticles on Si substrates were investigated by angular dependent ferromagnetic resonance and SQUID magnetometry between 5 and 300 K. The blocking temperature is found to depend on the particle composition. It increases with increasing Co content. At room temperature the nanoparticles containing 73 at.% Co are below and the $Ag_{55}Co_{45}$ nanoparticles are above their respective blocking temperatures. At lower temperatures contributions from additional magnetic phases are observed. The magnetization curves were analyzed as a function of temperature taking into account both paramagnetic and ferromagnetic contributions. The results are discussed in context to contributions from the Co/Ag interfacial and surface magnetism. The work has been supported through EC contract no. HPRN-CT-1999-00150.

[1] N.S. Sobal at el., Nano Letters, in press.

3:40pm **MI+NS-MoA6 Study of the Magnetic Cluster/Superconducitiviting Matrix Interface: the Co/Nb System**, ***V. Dupuis***, *L. Favre, M. Jamet, J. Tuaillon-Combes, P. Melinon, A. Perez*, DPM Lyon - France

Thin films consisting on pure Co nanoparticles embedded in a Nb superconducting matrix have been prepared from clusters preformed in the gas phase using the Low Energy Cluster Beam Deposition (LECBD) technique.[1] Such films are subsequently e-beam lithographied in view to prepare ultrahigh sensitivity Micro-SQUID magnetometer devices and to study the magnetization reversal mechanism of an individual nanocluster.[2] X-ray characterization experiments and Transmission Electron Microscopy performed on an assembly of cobalt clusters embedded in a niobium matrix have shown that such nanogranular films consist on crystallized fcc Co-grains in the form of 3 nm-diameter truncated octahedron (~ 1000 Co-atoms) randomly distributed in the polycrystalline niobium matrix. Sites of Co-atoms in the cluster core and at the cluster-matrix interface have been evidenced showing an alloyed Co-Nb interface concerned by almost one monolayer. On another hand, VSM magnetization measurements performed in the superparamagnetic regime evidenced a magnetic size of the Co-clusters lower than the one as deduced from TEM observations. So, in-situ complementary measurements under synchrotron radiation performed on Co/Nb bilayers grown in UHV confirm the presence of an alloyed Co_6Nb_7 interface which acts as a magnetically dead layer. Finally, from micro-SQUID measurements performed at 35 mK on one individual Co-cluster, we obtained a 3D-astroid shape corresponding to second order bi-axial anisotropy terms which can be attributed to surface anisotropy contributions ("Néel" model) underlying the main interfacial contribution in such nano-object.

[1] A. Perez et al. Materials Transactions, Special Issue on Nano-Metals 1, 42,1460 (2001).

[2] M. Jamet et al. Phys. Rev. Lett., 86, 4676 (2001).

4:00pm **MI+NS-MoA7 Magnetic Nanowires for Media and Devices Fabricated Using Copolymer Templates**, ***M.T. Tuominen***, *M. Bal, A. Ursache, Q. Xiao, J.T. Goldbach, T.P. Russell*, University of Massachusetts **INVITED**

Arrays of magnetic nanowires and nanowire devices were fabricated using nanoporous templates derived from self-assembling diblock copolymer films. Poly(styrene-methacrylate) (PS-PMMA) diblock copolymers as porous templates that were used to fabricate hexagonal arrays of vertical nanowires with densities of exceeding 1x10^12 per square inch. Electrodeposition within the template produces 10nm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanance making them potential candidates for ultrahigh-density perpendicular magnetic storage media. The internal crystal morphology of the nanowires, and consequently magnetic properties, can be manipulated and tuned by electrodeposition process parameters. The copolymer templates have been patterned laterally using conventional lithographic exposure to fabricate novel 3D magnetic nanowire devices. This includes current-in-plane magnetoresitive devices and current-through-wire switching field devices. Anisotropic magnetoresistance measurements show a sharp and complete magnetization reversal, indicating single-domain nanowire switching behavior. Such properties offer promising potential for new magnetic nanodevices built upon on single-domain elements. This work is supported by US National Science Foundation Nanoscale Interdisciplinary Research Team grant DMI-0103024 and Materials Research Science and Engineering Center grant DMR-9809365.

4:40pm **MI+NS-MoA9 Evolution of Fe Nanocluster Magnetism Grown on Pt(111)**, ***P. Bencok***, *S.S. Dhesi,* European Synchrotron Radiation Facility, France, *P. Ohresser,* Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, France, *N. Brookes*, European Synchrotron Radiation Facility, France

The magnetic structure of nanoparticles is a fascinating research area with many new and unexpected results. For the preparation of nanostructures one may use a well chosen system with appropriate growth modes. Room temperature deposition of submonolayer Fe ultrathin films on Pt(111) results in the formation of single layer clusters whose size increases with the amount of Fe. The structure of the stable pseudomorphic fcc clusters was studied using scanning tunnelling microscopy. The clusters were grown and measured in-situ by x-ray magnetic circular dichroism of Fe $L_{2,3}$ edge at beamline ID8 of the European Synchrotron Radiation Facility in Grenoble. Sum rule analysis was used to extract the magnetic spin and orbital moments with changing cluster size. The clusters show superparamagnetic behaviour with blocking temperature in the range 10-250 K increasing with cluster size. The easy axis of magnetization is perpendicular to the surface for all the range of cluster sizes studied. The orbital moment of the clusters as well as its angular anisotropy (related to the magnetic anisotropy energy) is enhanced in comparison with the bulk value and increases with decreasing cluster size. This enhancement is given by the increase in the number of perimeter atoms as the cluster radius diminishes. The perimeter atoms have reduced atomic coordination leading to the higher orbital moment. The magnetic spin moment per atom is lower than for bulk Fe. This behaviour can be explained by changes in the local atomic structure that is very sensitive to the atomic volume.

Manufacturing Science and Technology
Room: C-109 - Session MS-MoA

Control Issues in Electronics Manufacturing
Moderator: G.W. Rubloff, University of Maryland

2:00pm **MS-MoA1 Process Optimizations of Electrochemically Deposited Copper Films**, *H. Simka,* ***S. Shankar****, R.P. Chalupa, V.M. Dubin,* Intel Corporation **INVITED**

Electrochemical deposition (ECD) of copper interconnects in state-of-the-art microelectronic devices currently involves the use of organic additives in the electrolyte to achieve complete feature fill with good film properties. Optimization of this complex process typically requires extensive experimental efforts and time. We present a novel model-based ECD optimization approach, which involves investigations of the physical phenomena due to additive species interactions, and shape-evolution simulations of Cu films. A new model, which accounts for the transient surface interactions of additives and their effects in deposition rate, has been developed. The model uses a boundary element method (BEM) approach to solve the species diffusion equations in the electrolyte domain, and a Eulerian-Lagrangian approach to track the growing surface. The model has been successfully applied to explain two previously published, independent datasets of copper thickness SEM profiles in ECD with multi-component additive systems. A physically consistent description of the observed fill behavior at different process conditions will be presented. Factors that are critical in achieving optimal ECD Cu deposition will be discussed, including effects of feature dimensions, Cu seed-layer coverage, and process conditions. Analysis of the seed-layer requirements for good ECD performance at various feature dimensions will also be presented.

2:40pm **MS-MoA3 Real-Time Control of Ion Density and Ion Energy in Chlorine Inductively Coupled Plasma Etch Processing**, *C.H. Chang*, ***K.C. Leou***, *C. Lin, T.L. Lin, C.W. Tseng, C.H. Tsai*, National Tsing Hua University, Taiwan, ROC

The advanced semiconductor fabrication requires more tighten process monitoring and control to improve production yield and reliability. Recently, advanced process control (APC), an in-situ sensor based methodology, has been applied to achieve the desired process goals in operating individual process steps. For instance, in etching of polysilicon using chlorine discharges, in order to obtain a desired etch profiles, the process often is operated at the ion-enhanced regime where the etch rate and etched profile are strongly dependent on the total ion energy flux incident on the wafer surface. Therefore, a better process control can be achieved if one can implement the real-time control of ion energy flux in etch processing. In this study, we have demonstrated experimentally the real-time multiple-input multiple-output (MIMO) control of both ion density and ion energy in etching of polysilicon using chlorine inductively coupled plasma. To measure relative positive ion density, the optical emission at 750.4 nm from trace amounts of Ar is used which is proportional to the total positive ion density. An rf voltage meter is adopted to measure the peak rf voltage on the electrostatic chuck which is linearly dependent on sheath voltage. One actuator is a 13.56 MHz rf generator having a maximum power of 5 kW to drive the inductive coil seated on a ceramic window, along with a L-type matching network to minimize the reflected power. The second actuator is also a 13.56 MHz rf generator to power the electrostatic chuck via a matching network. The two rf generator is locked in phase. The MIMO controller is designed by using Quantitative Feedback Theory (QFT), which compensates process drift, process disturbance, and pilot wafer effect. This system has been used to etch unpatterned polysilicon and silicon oxide. The experiment results showed that the MIMO control system has a better reproducibility in etch rate and uniformity compared with current industrial practice.

3:00pm **MS-MoA4 Mathematical Approaches to Optimal Control of Transient Enhanced Diffusion**, ***M.Y.L. Jung***, *R. Gunawan, R.D. Braatz, E.G. Seebauer*, University of Illinois

Excessive transient enhanced diffusion (TED) of boron in silicon during rapid thermal annealing has been a major inhibitor to forming ultrashallow junctions for CMOS device applications. TED typically gives rise to a trade-off between junction depth X_j and sheet resistance ρ as a function of process variables. For example, increasing the ramp rate β or decreasing the maximum spike temperature T_M decreases X_j but increases ρ. This tradeoff suggests there are optimum values of β and T_M to produce the best X_j and ρ. The optimization of the temperature program is posed as a minimization problem with the objective function Φ, which is a function of the junction depth and the sheet resistance. The objective is selected such that: $\Phi=X_j(T(t)) + w\rho(T(t))$ where w is a weighting factor. The constrained minimization problem is solved using sequential quadratic programming. Although current technology employs linear temperature trajectories, different parameterizations of the temperature program are used in the optimization to elucidate the true optimal trajectory. The rate of cooling is also included in the parameterization. All these calculations are performed using the process simulator FLOOPS. We describe how the kinetic parameters in this simulator were obtained using firmly grounded procedures for estimating rate parameters using the Maximum Likelihood Method together with multivariate statistics to quantify accuracy. We also describe a rigorous parameter sensitivity analysis by the finite difference method to investigate TED model behavior. These approaches lead to vast improvements in the ability of simulations to match experiment.

3:20pm **MS-MoA5 Spatially Programmable Reactor Design: Toward a New Paradigm for Equipment Effectiveness**, ***Y. Liu***, *J. Choo, L. Henn-Lecordier, G.W. Rubloff, R.A. Adomaitis*, University of Maryland

Conventional single-wafer CVD reactor designs employ showerhead gas inlets which distribute impinging gases across the wafer in an attempt to achieve across-wafer process uniformity. However, it is difficult to maintain acceptable manufacturing uniformity as process parameters are changed, or to compensate for equipment asymmetries that influence uniformity. We have developed a new approach which exploits spatial programmability of impingment gas flux and stoichiometry, using a multi-segment showerhead design that accommodates gas inlet, exhaust, and sensing in each element of a 2-D array, with two goals: (1) to achieve across-wafer uniformity at any desired process design point; and (2) to intentionally introduce across-wafer nonuniformity so as to carry out multiple experiments on a single wafer (then followed by retuning to achieve uniformity at the optimized process design point). We have constructed a three-segment prototype for initial proof-of-concept, parameter identification, and model validation. Experimental results for W CVD demonstrate both inter-segment and intra-segment deposition rate tunability, in accord with expectations from modeling and simulation. Spatially programmability of reactor design, if scalable to higher integration levels with effective sensing, actuation, and control systems, could bring forth a new paradigm in equipment design that enables rapid optimization, higher process performance at high uniformity, and design scalability to larger substrates and multiple technology generations.

3:40pm **MS-MoA6 Monitoring and Control of Binary Gas Mixtures from Solid Phase MOCVD Sources using an Acoustic Sensor**, ***L. Henn-Lecordier***, *J.N. Kidder, G.W. Rubloff*, University of Maryland

In-line acoustic sensors have been used for several years in MOCVD source delivery systems to monitor and control the upstream composition of binary gas mixtures obtained from temperature- and pressure-controlled "bubbler" vessels. Since the vapor pressures of some commonly used MOCVD solid sources is low, extending into the sub-Torr range, it becomes difficult to maintain a constant - but minute - concentration of reagent in a high flow of carrier gas. In this study, an Inficon Composer acoustic sensor was implemented to measure and control the concentration obtained from two solid phase sources using H2 as a carrier gas, including (1) trimethylindium (TMI), which is used to grow GaInAs III-V compound semiconductors for optoelectronics, and (2) bis(cyclopentadienyl) magnesium (Cp2Mg) which is used in part as a p-type doping element in nitride-based compound semiconductors for blue LED's. Both sources are crystalline solids with low vapor pressures (2.5 and 0.04 Torr at 25°C respectively for TMI and Cp2Mg), which causes unstable sublimation/delivery rates and associated variability in composition and lattice mismatch. Using the acoustic sensor, reagent levels as low as 1.E-4 mol % in H2 were monitored and found in close correlation with the expected concentrations over a broad range of total pressure from 500 down to 60 Torr. This sensitivity suggests that source delivery control may be achievable to control (i.e., compensate for) variations in source delivery rate, e.g., adjusting the flow of the carrier gas through the source, diluting the binary mixture downstream of the source, or adjusting the gas density in the source.

4:00pm **MS-MoA7 Dynamic Simulation and Optimization at the Unit Process Level for Environmentally Benign Semiconductor Manufacturing**, ***S. Cho***, *W. Lei, G.W. Rubloff*, University of Maryland

Environmentally benign semiconductor manufacturing requires methodologies which enable co-optimization of manufacturing and technology metrics (such as process cycle time, consumables costs, and product quality) along with environmental (ESH) metrics. We have investigated this challenge at the unit process level, focusing on Cu CVD unit process and equipment, using a physically-based dynamic simulation approach which takes into account the process recipe and resulting time-dependent behavior of vacuum and gas flow, heat transfer, reaction chemistry, and equipment components and control systems. Higher temperature and pressure yield reduced cycle time and precursor consumption, producing a "win-win" situation for manufacturing and ESH metrics. In contrast, changes in precursor flow rate produce trade-off situations between these metrics; at higher temperatures, however, significant gain in precursor consumption is indicated at lower flow rate, with relatively small cycle time penalty. Energy consumption per unit film thickness is substantially reduced at higher temperature because the deposition rate of the thermally activated CVD process increases faster with temperature than does the heating power required at typical process conditions. These results at the unit process level demonstrate that the dynamic simulation approach (1) provides insights into complex physical/chemical system behavior and quantitative estimates for tradeoff analysis, and (2) reveals "win-win" situations in which ESH and manufacturing benefits may be achieved together. This work is supported by the U. Arizona NSF/SRC Center for Environmentally Benign Semiconductor Manufacturing.

4:20pm **MS-MoA8 Data Handling in Semiconductor Manufacturing: Overall Approach to Correlate Yield, Process and Equipment Parameters**, *M. Horn, H. Melzner, D. Knobloch*, ***F.H. Bell***, Infineon Technologies AG, Germany

Yield improvement in semiconductor manufacturing depends on several aspects. Major challenges are the robustness of design rules, improvement of the design for testability and stable manufacturing processes. For the later one, advanced process control (APC) featuring run-to-run control and Fault Detection and Classification (FDC) is seen as the most powerful technique to improve the in-line stability. However, correlation between yield (such as threshold voltage, saturation current, die functionality and reliability issues), process and equipment parameters suffer from economic handling of the huge amount of data. An overall approach from end-of-line electrical measurements to on-line process and equipment parameter detection is needed in order to simplify the data analysis. We show how the data analysis can be simplified using data extraction techniques, such as principal component analysis, that pre-selects the most significant yield related parameters and separates yield detractors with respect to sporadic and chronological events. These data can then be used to find possible root causes in process and equipment. Consequently, the APC parameters can then (1) be weighted towards yield significance and (2) be used to define the parameter set for run-to-run control and fault detection and classification. We will discuss examples that demonstrate how deviations in process and equipment parameters detracts yield, may cause reliability problems or does not influence yield and reliability at all. Examples are taken from aluminum metallization and EPI-Centura SiGe deposition processes.

4:40pm **MS-MoA9 Improved Tool Utilization and Process Capability Through Improved Flow Verficiation Technique**, ***S.A. Tison***, *S. Lu*, Mykrolis Corporation

Critical processes require accurate and reproduceable chemical delivery to acheive the necessary process capabilities. Continues reductions is device scaling requires improved process capabilities for high aspect ratios.[1]. Many dry etching processes require highly accurate and reproduceable delivery for flows below 10 sccm.[2] Historically, gas delivery reproduceability was acheived using rate-of-rise chamber verification techniques. Two of the most common techniques are refered to as "Flow Verification" and "Flow Cal". These techniques use the chamber as an accumulation tank and measure the pressure rise with time. Through the use of the gas equation of state they derive the average delivered gas flow. With the introduction of 300 mm processes the chamber volumes have increased and some critical gas flows have decreased. These effects have resulted in long times to complete the rate-of-rise measurements with the subsequent reduction in tool availability. Data is presented which shows that improved high resolution capacitance diaphragm gages can be used to make the necessary measurements with lower accumulation pressures and improve equipment availability. For a typical etch system the "Flow Verification" sequence can be reduce by one hour per chamber. These process improvements are enabled by reducing uncertainies associated with parasitic effects such as thermal transpiration[3] and other gage nonlinearities.

[1] J. Givens et al., J. Vac. Sci. Technol. B12, 427 (1994)

[2] M. Matsui et al., J. Vac. Sci. Technol. A20, 117 (2002)

[3] K. Poulter et al., Vacuum, 33, 311 (1983).

Nanometer Structures
Room: C-207 - Session NS+BI-MoA

Nanobiology
Moderator: V. Vogel, University of Washington

2:20pm **NS+BI-MoA2 Molecular Shuttles Based on Motor Proteins: Transporters for Nanotechnology**, ***H. Hess***, *J. Clemmens*, University of Washington, *C.M. Matzke, G.D. Bachand, B.C. Bunker,* Sandia National Laboratories, *J. Howard,* Max-Planck-Institute of Molecular Cell Biology and Genetics, Germany, *V. Vogel*, University of Washington

Active transport in cells, utilizing molecular motors like kinesin and myosin, provides the inspiration for the integration of active transport into synthetic devices. Hybrid devices, employing motor proteins in a synthetic environment, are the first prototypes of molecular shuttles - an active nanoscale transport system. The key problems for the construction of a molecular shuttle are guiding the direction of the motion, controlling the speed, and loading and unloading of cargo. Various techniques, relying on surface topography and chemistry as well as flow fields and electric fields, have been developed by us[1] and others[2] to guide the movement of molecular shuttles on surfaces. The control of ATP concentration, acting as fuel supply, can serve as a means to control the speed of movement. The loading process requires the coupling of cargo to the shuttle, ideally by a strong and specific link. Applications of molecular shuttles can be envisioned e.g. in the field of Nano-Electro-Mechanical-Systems (NEMS), where scaling laws favor active transport over fluid flow, and in the bottom-up assembly of novel materials. Recently, we demonstrated that the shuttles can be employed as self-propelled nanoscale probes to image surface topography.[3] The construction of an image relies on the tracking of the random movement of a large number of independent probes, a concept which is fundamentally different from e.g. the deterministic movement of a single tip in scanning probe microscopy. An aspect of our research is that devices using molecular shuttles can be based on mechanisms which are unique to the microscopic world. An example of this is the possible application of a Brownian ratchet for directional sorting.[4]

[1] Hess, H., et al., Nano Letters, 2001. 1(5): p. 235.

[2] Hess, H. and Vogel, V., Rev. Mol. Biotechn., 2001. 82: p. 67.

[3] Hess, H., et al, Nano Letters, 2002. 2(2): p. 113.

[4] Hess, H., et al., Appl. Phys. A, 2002. 75: p. 309.

2:40pm **NS+BI-MoA3 Nanomechanics of an Intrinsically Unstructured Protein**, *R. Mukhopadhyay*, ***J.H. Hoh***, Johns Hopkins School of Medicine **INVITED**

Microtubule-associated proteins (MAPs) are a class of proteins that bind to the surface of microtubules. These proteins are known to stabilize microtubules against depolymerization, and there evidence to suggest that MAPs play a role in maintaining spacing between adjacent microtubules and may play a role in cellular mechanics. MAPs are composed of two domains: the microtubule binding domain and the projection domains. Biophysical studies of the projection domain suggest that it is highly unstructured. We have recently developed a system to study the molecular mechanics of the projection domain of MAPs. In this system MAPs are end-grafted by their positively charged microtubule binding domains to a negatively charged surface. The properties of the projection domain are then probed by direct atomic force microscope (AFM) force measurements. These measurements show a long-range repulsive force that extends more than 100 nm from the surface, and is consistent with a polymer brush like interaction. A unique thrombin cleavage site at the boundary between the microtubule binding domain and the projection domain allows the projection domain to be proteolytically removed. This results in a total loss of the long-range repulsive force. The force is also sensitive to ionic strength, suggesting that, consistent with its sequence, the projection domain behaves as a polyelectrolyte. The polyelectrolyte nature of the projection domain and the large number of phosphorylation sites suggests a mechanism for regulating the mechanical properties of the protein. This notion is supported force measurements on phosphorylated and dephosphorylated MAPs. Thus phosphorylation of the MAP projection domain offers a biochemical mechanism for modulating the molecular mechanics of MAPS and the intermolecular forces between microtubules.

3:20pm **NS+BI-MoA5 Nanostructures for Analysis of individual Biomolecules**, ***H.G. Craighead***, *S.W. Turner, M. Foquet, J. Korlach, W. Zipfel, M. Levene, W.W. Webb*, Cornell University

We have used nanofabrication methods to create fine-scale fluid channels and optical devices for nano-scale spatial confinement of optical excitation for use in the analysis of individual biomolecules. Functional fluid systems with dimensions down to ~35 nm have been etched and created by use of sacrificial layer techniques. Narrow fluid channels have been used for DNA fragment sizing by single molecule analysis and used for fluorescence correlation spectroscopy with improved signal-to-noise ratios. Related lithographic approaches have been used to create regions of optical excitation, confined in all 3 dimensions, using metallic nano-constrictions or "zero mode waveguides" in which electromagnetic waves are exponentially attenuated. These devices enable practical studies of dynamic biochemical processes at the single molecule level. An example of such a process is the observation of the activity of a single DNA polymerase molecule during the replication of a DNA molecule. We have been able to optically observe the incorporation of individual bases in the DNA replication process. With optically differentiated base types, this could lead to high speed sequencing of single DNA molecules. These approaches may allow highly parallel observation and analysis of biochemical activity at the single molecule level. This work has been supported by The National Institutes of Health, the National Science Foundation through the NBTC and the Department of Energy. Fabrication of devices was done at the Cornell Nanofabrication Facility.

3:40pm **NS+BI-MoA6 Polyelectrolyte Multilayer Self Assembled Nanoparticles for Delivery of Transforming Growth Factor Beta**, ***C. Catuogno***, *M. Tabrizian*, McGill University, Canada

Biocompatible and biodegradable nanoparticles with additional high drug encapsulation efficiency and controllable targeting would form an ideal drug delivery system. Investigation of the possibility of making such vehicles is presented in this work. Such devices could be used in combination with polymeric bone scaffolds for delivery of transforming growth factor beta (TGF-b) in order to accelerate bone cell differentiation and bone formation in vitro. The particle shell is made of natural carbohydrate polymers namely chitosan or hyaluronic acid that are commonly used in tissue engineering. Chitosan is insoluble in water or in alkaline solutions but dissolves readily in dilute solutions of most organic acids. Chitosan has gel-forming ability at low pH and swells in acidic medium or in water. These proprieties added to those of hyaluronic acid have motivated the use of both materials to control TGF-b adsorption and release from the nanoparticles. Additionally, composite materials have been shown to improve mechanical properties of scaffolds. The nanoparticles are built from a succession of polyelectrolytes using the layer-by-layer method. Colloidal iron oxide particles are adsorbed on the polymer layers and encapsulated into the nanoparticles. This aims at inducing the guidance of nanoparticles using an external magnetic field to desired site of delivery when such device is used for in situ bone generation.

4:00pm **NS+BI-MoA7 Resolving Scanning Tunneling Microscopy Features of Oligomers Adsorbed on Si(100)**, ***B. Grandidier***, *Mathieu Dubois, C. Delerue, J.P. Nys, D. Stievenard,* IEMN, France, *J. Roncali*, IMMO, France

Scanning tunneling microscopy (STM) gives the possibility to observe complex organic molecules on silicon surfaces in ultra-high vacuum. Although the reactivity of the silicon surfaces often leads to the modification of the molecular electronic states, a clever synthesis of the molecules can keep their structures intact after adsorption. As a result, the molecules are imaged in their integrity and the contrast variation observed along the molecules is usually associated with the highest occupied and lowest unoccupied electronic states of the molecules. Here, we have investigated the STM imaging of conjugated oligomers on Si(100) by tight binding simulations. The molecules are physisorbed on the surface and extend over a few dimers rows. Due to coupling of the molecular states with the electronic states of the silicon surfaces, we show that the off-resonance tunneling process is the major contribution to the tunneling current in usual tunneling conditions. As a result, the potential barrier is lowered when the tip scans above a molecule and the contrast variation gives an enhancement of the Si dimer rows. Experimental STM images of conjugated oligomers confirm this theoretical prediction.

4:20pm **NS+BI-MoA8 Q-dots Patterned Surfaces for Cell Adhesion**, *A. Szucs*, ***J.P. Spatz***, University of Heidelberg, Germany

Highly luminescent semiconductor quantum nanodots (Q-dots) regularly patterned on different substrates, were synthesized and applied as binding sites for single cell receptors in order to study cell adhesion. CdS, CdSe and CdTe/ Q-dots in the size range of 2-8 nm in diameter were generated in Poly (styrene-b-2-vinyl-pyridine) (PS-P2VP)/inorganic hybrid reverse micellar system (RM). Solid Cd salts loaded polymer cores, constructed by the 2-vinyl-pyridine, were used as nanocompartments for preparation of uniform semiconductor nanoparticles. Particle size could be controlled by varying the diameter of the RM core, via the length of the core constructing polymer, and by changing the precursor salt loading in the polymer core. Different kinetics and structures were observed inside the RM core during the particle formation by using different precursor salts (Cd(ClO4)2, Cd(OAc)2). Photo luminescent properties of semiconductor nanoparticles were investigated by different methods (UV-VIS spectrophotometry, steady-state fluorescence, color luminescence imaging). "In situ" surface patterning on different substrates (Glass, Si-wafer etc.) by self-organization of the diblock copolymer micelles on the surfaces was monitored by AFM measurements.

4:40pm **NS+BI-MoA9 Cell Adhesion to Nanostructured Interfaces**, ***J.P. Spatz***, University of Heidelberg, Germany **INVITED**

Nanostructures with micrometer or nanometer spacings have been prepared through pure self-assembly of diblock copolymer micelles (formation and compartmental localization of metallic nanodots within block copolymer micelles) or in combination with a top-down approach (electron beam lithography). Within these structures, 7 nm Au particles can be positioned with a precision of < 10 nm and large freedom in pattern choice (periodic, aperiodic, dotes, lines). Specifically, this is obtained by casting a solution of HAuCl4 loaded block copolymer micelles onto the prestructured resist film. Due to capillary effects and steric hindering, the particles are centered within the prepatterned holes and at the edges of prestructured lines. Subsequent lift-off of the resist allows the removal of all micelles with the exception of those that are in direct contact to the underlying substrate. The block copolymer is then removed by plasma etching, which strips the polymer micelle and reduces the gold salt to gold thereby leaving behind nanoscopic dots or lines of gold in a defined array. These nanostructured interfaces are used as platform for biofunctionalisation of solid interfaces. The surfaces are used as a tool to investigate cluster formation of focal adhesion associated proteins of fibroblasts. Cultured human melanocytes allowed to study the regulation of cell shape through contact with interfaces offering different topography and biochemical pattern. The cellular morphology of melanocytes is a measurable indicator for cell reaction to the cellular environment. The characteristic cellular shape of different cell cultures was quantified by different shape parameters like the number and length of dendrites. A decreased signal-to-noise ratio was found for melanocyte cells concerning the number of dendrites and orientation of dendrites if cultured on biochemically and topographically structured substrates.

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-MoA

Nanotubes: Chemical Functionalization, Sensors
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

2:00pm **NT-MoA1 Photoenhanced Oxygen Adsorption in Carbon Nanotubes**, ***A.M. Rao***, Clemson Univeristy **INVITED**

Thermopower (TEP) measurements have been very effective for detecting trace amounts of absorbed gases in single walled carbon nanotube bundles (SWNTs). The dynamics of gas adsorption is extremely rapid with a short time constant (few seconds to hours) for achieving oxygen saturated TEP values of ~ +45 μV/K in SWNT bundles. Upon desorbing the oxygen from the sample, the TEP switches reversibly to ~ -45 μV/K. In this talk, we present TEP values in films of multiwalled carbon nanotubes (MWNTs) as a function of exposure to room air in the presence or absence of illumination from a UV lamp. The MWNT films were prepared on quartz substrates from a thermal decomposition of xylene-ferrocene mixtures at ~700 °C. In room air and room light, freshly prepared MWNT films exhibit a negative TEP value of ~ -12 μV/K that systematically changes to ~ +12 μV/K over a time period of ~ 4 months. Thus, MWNTs offer a unique opportunity to study photoinduced adsorption of gases in quasi one dimensional carbon system. Interestingly, upon UV illumination of the MWNT film in room air, the rate at which TEP sign reverses is drastically reduced to 7-10 days suggesting a photoenhanced oxidation phenomenon in carbon nanotubes. Based on our density functional calculations, we attribute this photoinduced phenomenon due to the lower energy barrier for adsorption of photogenerated singlet oxygen in the MWNT films. This work was done in collaboration with T. Savage, S. Bhattacharya, B. Sadanadan, J. Gaillard, T. M. Tritt, and Ya-Ping Sun (Clemson University), and S. Nayak (Rensselaer Polytechnic Institute). Research was supported by a grant from NASA Ames Research Center.

2:40pm **NT-MoA3 Strategies for Carbon Nanotube Functionalization**, ***S. Wong***, *S. Banerjee*, SUNY at Stony Brook

Understanding the chemistry of single-walled carbon nanotubes (SWNTs) is critical to rational manipulation of their properties. In one set of experiments, raw and oxidized SWNTs have been reacted with metal-containing molecular complexes. One of the molecular complexes studied was Vaska's compound. It has been found that Ir coordinates to these nanotubes by two distinctive pathways. With raw nanotubes, the metal attaches as if the tubes behaved as electron-deficient alkenes. With oxidized nanotubes, the reaction occurs by coordination through the increased number of oxygen atoms, forming a hexacoordinate structure around the Ir atom. Another compound analyzed was Wilkinson's complex. It has been found that the Rh metal similarly coordinates to these nanotubes through the increased number of oxygenated species. The functionalization reaction, in general, appears to significantly increase oxidized nanotube solubility in DMF (in the case of Vaska's) and in DMSO (with Wilkinson's). The derivatization process results in exfoliation of larger bundles of SWNTs and may select for the presence of distributions of smaller diameter tubes. An application has been made of this system as supports for homogeneous catalysis. In another set of experiments, oxidized SWNTs have been reacted with cadmium selenide nanocrystals (quantum dots) as well as with titanium dioxide nanocrystals to form nanoscale heterostructures, characterized by transmission electron microscopy and infrared spectroscopy. Based on the types of intermediary linking agents used, we have demonstrated a level of control over the spatial distribution of nanocrystals on these tubes. Optical data on the derivatized adducts suggest the possibility of interesting charge transfer behavior across the nanocrystal-nanotube interface.

3:00pm **NT-MoA4 The Fabrication and Characterization of Carbon Nanotube Nanoelectrode Array for Chemical/Biosensor Applications**, ***J. Li**, R. Stevens,* NASA Ames Research Center / Eloret Corp.*, H.T. Ng,* NASA Ames Research Center / SETI Institute*, L. Delzeit,* NASA Ames Research Center*, A. Cassell, C. Nguyen, B. Chen, J. Han,* NASA Ames Research Center / Eloret Corp.*, M. Meyyappan*, NASA Ames Research Center

Nanoelectrode arrays are attractive electroanalytical tools with the potential to provide much higher sensitivity for chemical and biosensor applications. So far nanoelectrode arrays/ensembles were prepared by template synthesis using nanoporous membranes or nanoscale defects created in the self-assembled organic monolayers on an Au surface. We report here on a new approach to fabricate solid-state nanoelectrode array/ensemble by bottom-up scheme using well-aligned multi-walled carbon nanotube arrays on a conducting substrate. Carbon nanotubes were grown on a substrate prepatterned with metal catalysts. The density can be controlled precisely with ebeam lithography. The alignment, diameter, and length can be controlled by plasma CVD process. Dielectric material such as SiO2 was then filled into the gap between carbon nanotubes by TEOS CVD to insulate the sidewall of the carbon nanotubes as well as the conductive underlayers. This method also provides an added advantage by which the mechanical strength of the carbon nanotube array is dramatically improved. An aggressive mechanical polishing can thus be applied to planarize the surface, resulting in a flat surface with only the ends of carbon nanotubes exposed. SEM indicates that carbon nanotubes remain their integrity during these processes. AFM shows that carbon nanotubes extend out of the insulating matrix by a few nanometers due to the higher mechanical strength. The electrical properties of individual carbon nanotubes in the array are thoroughly characterized with current sensing AFM and I-V measurements. Both of metallic and semiconducting properties were observed, strongly depending on the growth conditions. Thus fabricated carbon nanotube array is essentially an ideal nanoelectrode array with graphite edge-plane like nanoelectrodes distributed in a controlled way. The electrochemical properties and the application of these nanoelectrode arrays as chemical and biosensors will be discussed.

3:20pm **NT-MoA5 Investigation on the NO2 Sensitivity Properties of Multi-Wall Carbon Nanotubes Prepared by Plasma Enhanced Chemical Vapor Deposition**, ***C. Cantalini***, University of L'Aquila, Italy*, L. Valentini, I. Armentano, J.M. Kenny,* University of Perugia, Italy*, L. Lozzi, S. Santucci*, University of L'Aquila, Italy

The special geometry and unique properties of carbon nanotubes offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors.[1-4] The effect of gas environment on the electronic properties of carbon nanotubes have recently attracted certain attentions.[5,6] In the present work multi-wall carbon nanotubes (MWNTs) deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO2. The sensor design is a MWNT serpentine resistor, fabricated by photolithography defining a serpentine Si3N4 path upon silicon, and then growing MWNTs upon the Si3N4 structure. The electrical response has been measured exposing the films to NO2 (5 ppm) at different operating temperatures ranging between 50 and 250 Â°C. Upon exposure to NO2 the electrical resistance of MWNTs is found to decrease. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient conditions or by a higher recovery heating to 200 Â°C. Experimental findings revealed the chemisorption of oxidizer gas upon the surface of the NWNTs. Hence it appears that p-type semiconductor behavior is present in the MWNTs.

[1] Dresselhaus M S et al. 1996 Scienceof Fullerenes and Carbon Nanotubes (New York:Academic)

[2] Ebbesen T (ed) 1997 Carbon Nanotube: Preparation andProperties (Boca Raton, FL: CRC Press)

[3] Saito R et al. 1998 PhysicsProperties of Carbon Nanotubes (New York: WorldScientific)

[4] Lu J P et al. 1998 Int. J. High Electron. Syst. 9 101

[5] Kong J et al. 2000 Science 287 622

[6] Collins P G et al. 2000 Science 287 1801 .

3:40pm **NT-MoA6 Invited Paper**, ***R. Baughman***, University of Texas at Dallas **INVITED**

4:20pm **NT-MoA8 Surface Modification of Aligned Carbon Nanotube Arrays**, ***L. Dai***, The University of Akron

The excellent optoelectronic, mechanical, and thermal properties of carbon nanotubes have made them very attractive for a wide range of potential applications. However, many applications require the growth of aligned/micropatterned carbon nanotubes, along with their surface modification. We have developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate surface. We have also used photolithographic and soft-lithographic techniques for patterning the aligned carbon nanotubes with a sub-micrometer resolution. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest (e.g. polymer films for organic optoelectronic devices) in either a patterned or non-patterned fashion. The well-aligned structure further allows us not only to prepare novel aligned conducting polymer-carbon nanotube coaxial nanowires by electrochemically depositing a concentric layer of an appropriate conducting polymer onto the individual aligned carbon nanotubes, but also to develop a facile approach for modification of carbon nanotube surfaces via plasma activation followed by chemical reactions characteristic of the plasma-induced functionalities. These surface modification methods are particularly attractive, which allow surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be retained. In this talk, results from our recent work on microfabrication and chemical modification of aligned carbon nanotubes for certain device applications (e.g. biosensors) will be presented.

4:40pm **NT-MoA9 Comparing Light Gas Diffusion Rates in Carbon Nanotubes and Zeolites**, ***A.I. Skoulidas***, Carnegie Mellon University*, D. Ackerman, J.K. Johnson,* University of Pittsburgh*, D.S. Sholl*, Carnegie Mellon University

As in all microporous materials, the diffusion rates of molecules adsorbed in carbon nanotubes may have a large impact on the feasible applications of these materials. We have used atomistic simulations to compare the diffusion rates of H_2 and CH_4 in a range of defect-free single-walled carbon nanotubes with two silica zeolites with similar pore sizes, silicalite and ZSM-12. One advantage of comparing our results with these two zeolites is that we can validate the accuracy of our simulations against a large body of experimental data. We have used equlilibrium Molecular Dynamics and Monte Carlo methods to determine both the self diffusivity and the transport diffusivity of H2 and CH4 adsorbed as single components in carbon nanotubes. The transport diffusivity is the relevant quantity for describing macroscopic mass transfer in applications such as reversible adsorption cycles and membranes. We find that diffusion in carbon nanotubes is orders of magnitude faster than in the two zeolites over a broad range of pressure and temperature. These diffusivities are in fact among the fastest known for light gases in any environment, including bulk gas phases. This dramatic result can be understood in terms of the smoothness of the potential energy surface created by carbon nanotubes. We will discuss the implications of our results for using carbon nanotubes for highly permeable membranes.

Plasma Science
Room: C-103 - Session PS1-MoA

Dielectric Etch I
Moderator: S.H. Moon, Seoul National University, Korea

2:00pm **PS1-MoA1 Role of Fluorocarbon Radicals and Ions in SiO_2 Surface Etching Mechanism in Fluorocarbon-Based Discharges**, *X. Hua, L. Ling, X. Li, **G.S. Oehrlein***, University of Maryland, College Park*, M. Barela, H.M. Anderson*, University of New Mexico

To provide information on the synergistic and respective roles of FC radical and ion fluxes in SiO_2 and Si surface etching mechanisms, we measured the surface chemical changes of deposited/steady-state fluorocarbon (FC) films, etching rates of FC, SiO_2 and Si, and determined the absolute gas phase density of CF, CF_2 and COF_2 radicals as a function of RF bias and gas composition of C4F8/Ar inductively coupled discharges. Ar addition to C_4F_8 strongly increases the plasma density relative to pure C_4F_8 (~ 4x at 90% Ar), and results in a dramatic increase of the ion/neutral flux ratio for C_4F_8/90%Ar discharges relative to C_4F_8 (>20). Nevertheless, the x-ray photoelectron spectra of FC films formed on SiO_2 and Si surfaces without RF bias remain remarkably similar to those of films produced in pure C_4F_8 discharges at much lower ion/neutral ratio. Upon applying an RF bias, etching of FC, SiO_2 or Si commences. The C1s spectra of FC surface films for C_4F_8/90%Ar discharges become strongly fluorine-deficient relative to conditions without RF bias, whereas the C1s spectra of FC films formed in C_4F_8 change little. Infrared laser absorption spectroscopy was used to determine CF, CF_2 and COF_2 densities over SiO_2 and Si surfaces, with and without RF bias, and as a function of gas mixture. Without RF bias (FC deposition), the CF, CF2 and COF_2 densities do not vary with substrate type. With an RF bias, the CF_2 density over a SiO_2 surface is strongly reduced relative to a Si surface, and the change reflects the relative SiO_2/Si etch rate ratio. The composite of the results provide a fairly detailed view of the dominant surface etching mechanism and ion/neutral synergy.

2:20pm **PS1-MoA2 Characteristics of c-C_4F_8, c-C_4F_8/Ar and c-C_4F_8/O_2 Inductively Coupled Plasmas for Dielectric Etching[1]**, ***A.V. Vasenkov***, University of Illinois at Urbana-Champaign, *X. Li, G.S. Oehrlein,* University of Maryland, College Park, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Fluorocarbon plasmas are widely used for etching of silicon dioxide and other dielectrics. In particular, inductively coupled plasmas sustained in c-C_4F_8 with varying amounts of diluents such as Ar and O_2 are used to produce optimum fluxes of ions and radicals. To investigate plasma chemistry in these system, reaction mechanisms were developed for inductively coupled plasmas (ICPs) and reactive ion etching reactors sustained in c-C_4F_8, c-C_4F_8/Ar and c-C_4F_8/O_2 chemistries; and implemented into a 2-dimensional plasma equipment model. The limited electron impact cross-section data for the fluorocarbon species were collected and synthesized; and rate coefficients for gas phase chemistry were taken from independent studies in the literature or estimated fom measurements for related species. The final mechanisms involve 46 species and over 300 reactions. Parametric modeling studies were performed for ICPs at powers from 400 W to 1400 W and in a pressure range from 6 mTorr to 20 mTorr for c-C_4F_8, c-C_4F_8/Ar, c-C_4F_8/O_2 plasmas. The mechanisms were validated by comparing to measured ion saturation currents obtained with probes. The dominant reaction pathways and strategies to optimize desired radical fluxes will be discussed.

[1] Work supported by Semiconductor Research Corp., National Science Foundation and Sematech.

2:40pm **PS1-MoA3 Effects of Ar Gas Dilution on Precise SiO_2 Etching using CF_3I/ C_2F_4 Plasma**, *S. Samukawa,* ***H. Ohtake***, Tohoku University, Japan, *H. Ishihara, A. Koshiishi*, Tokyo Electron AT, Japan

The ϕ0.1µm high-aspect-ratio SiO_2 contact etching has successfully done using the parallel-plate commercialized etcher with the Ar-dilution C_2F_4/ CF_3I plasma. In the XPS analysis of deposition film, the radical-density ratio (for example, CF_3/ CF_2) in C_2F_4/ CF_3I does not change when Ar flow increases. However, it drastically changes in C_4F_8 gas chemistry. This could be because the C_4F_8 has complex dissociation processes. On the other hand, the radical-density ratio does not change with Ar dilution because the C_2F_4/ CF_3I gas chemistry has simple dissociation processes. Accordingly, the control of the radical densities in the C_2F_4/ CF_3I plasma could be easy by controlling the Ar flow. In this Ar/ C_2F_4/ CF_3I gas chemistry, the SiO_2 etching rate does not decrease even when Ar flow increases. However, the etching selectivity of SiO_2 to photo-resist increases when increasing the Ar dilution. Since the effect of the ion bombardment increase with Ar dilution, the C/F ratio in the deposited film on the photo-resist increases. As a result, the etching selectivity of SiO_2 to the photo-resist increases. With these conditions, the ϕ0.1µm, 10- aspect- ratio SiO_2 etching in C_2F_4/ CF_3I Ar plasma has successfully. Additionally, we investigated the leak current of MOSFET (L=0.1um, Tox: 20A) with multiple contact holes. In the threshold voltage and leak current measurement, the charging damages are not observed. Accordingly, the Ar dilution for C_2F_4/ CF_3I gas chemistry is very effective on the control of the radical densities and the increase of selectivity.

3:00pm **PS1-MoA4 Plasma Etching Chemistry and Kinetics for Silicon Oxide Thin Films**, ***O. Kwon***, *H.H. Sawin*, Massachusetts Institute of Technology

Surface kinetics study of silicon oxide etching with fluorocarbons in inductively coupled plasmas High density fluorocarbon plasma for silicon oxide etching has various ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity of photoresist. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as functions of ion bombardment energy, ion impinging angle, ion-to-neutral flux ration, which are necessary for profile evolution modeling of silicon oxide etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to differentially pumped side chambers. Surface reaction is studied by measuring etching and deposition rate with quartz crystal microbalance(QCM). At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. Etching or deposition rate is measured with QCM as functions of ion acceleration energy, ion impinging angle, ion-to-neutral flux ration with various fluorocarbon plasmas. With fluorocaron plasma, fluorocarbon deposition was observed at low ion energy, high ion impinging angle, low plasma power and high pressure. A model describing both deposition and etching regimes is suggested.

3:20pm **PS1-MoA5 Electrical Conductivity of Sidewall Deposited Fluorocarbon in SiO_2 Contact Holes**, ***T. Shimmura***, *S. Soda, S. Samukawa, M. Koyanagi, K. Hane*, Tohoku University, Japan

Predicting the feature profile evolution for high aspect ratio contact hole patterning requires quantitative measurements of the sidewall conductivity in contact holes. This paper reports on On-wafer monitoring of the sidewall current in holes. We were developed the device used for measuring the sidewall conductivity. A SiO_2 film (500 nm) was deposited between Poly-Si electrodes (300 nm). The holes were fabricated by HF wet etching or conventional ICP etching. The diameter of holes was 0.5 µm, and the numbers of holes were 240000. The sidewall current was measured by supplying the voltage of 20 V between electrodes. When the holes were formed with the wet etching, the sidewall current was 4.5 nA. Conversely, it was 276.8 nA in the case of ICP etching. By removing the deposited polymer, it decreased to 40.9 nA. To clarify the influence of the deposited polymer on conductivity, we also deposited polymer in the fabricated holes using C_4F_8 UHF plasma (5mTorr, UHF power: 500W). Then, deposited polymer was exposed Ar plasma (5mTorr, UHF power: 1000W). In XPS studies, the carbon to fluorine ratio of as deposited film was 0.91. After ion irradiation, it changes to 1.86. In FT-IR spectra, characteristic absorption peaks of fluorocarbon films are appearing in 1100 - 1400 cm^{-1}.[1] The absorption that appears in neighborhood 1700 cm^{-1} was increased and shifted to low wave number by ion irradiation. This result shows that ion irradiation causes defluorination and forms unsaturated bond. Additionally, the sidewall current increased to 2181.7 nA from 38.8 nA by ion irradiation. We had found that the high cross-linked and unsaturated fluorocarbon film caused increase in sidewall current.

[1] N.M.Makie, N.F.Dalleska, D.G.Castner, and E.R.Fischer, Chem. Mater., 9 349 (1997).

3:40pm **PS1-MoA6 Silicon Oxide Highly Selective Etching Using Novel Solid Gas Sources**, ***M. Nagai***, *M. Hori, T. Goto*, Nagoya University, Japan

Dry etching of silicon oxide (SiO_2) films is an essential process for fabricating deep contact holes in ultralarge-scale integrated circuits (ULSIs). This process has been developed by using high density plasma employing perfluorinated compound (PFC) gases such as CF_4, CHF_3, C_2F_6, C_4F_8, and so on. In this process, the high selectivity of SiO_2 over resist and underlayers and the vertical etching profile for high aspect ratio patterns are required. However, there has been a problem of the poor SiO_2/resist selectivity using PFC gas source. Additionally, PFC gases of high global warming potential cause a serious environmental problem. In this study, we have developed an environmentally begin etching process without PFC gases which enables to control the radicals independently, for example CF_2 radical, C atom and F atom. In this system, the etching was performed with magnetron plasma source. The top electrode of graphite was supplied with two rf powers of 13.56 MHz and 450 kHz, which were separated through a low-pass filter. The plasma was generated by 13.56 MHz and the incident ion energy on the graphite target was controlled by 450 kHz. The bottom electrode was supplied with rf power of 2 MHz as the substrate bias. Fluorine and carbon atom sources were employed instead of PFC gases. Ar and F_2 gases as a fluorine atom source were injected into the process chamber. Carbon species were generated by magnetron sputtering of the graphite plate using Ar and F_2 gas plasma. In this etching system, the etching characteristics of SiO_2 and resist were investigated. As a result, by controlling the carbon and fluorine species incident on the surface, we have obtained the SiO_2 etching rate of 420 nm/min and high SiO_2/resist selectivity of 10 with good pattern profile of the contact holes in environmentally begin etching system without employing PFC gases.

4:00pm **PS1-MoA7 Ion-enhanced Chemical Etching of ZrO_2 in a Chlorine Discharge**, ***L. Sha****, *J.P. Chang*, University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as ZrO_2, to enable their integration in sub-0.13 µm complementary metal oxide semiconductor (CMOS) devices. In the work, we aim to study the reaction kinetics of etching ZrO_2 in chlorine chemistry in an Electron Cyclotron Resonance (ECR) high-density plasma reactor. The gas phase species, including the reactants (Cl_2, Cl_2^+, Cl, Cl^+, Cl^-, â€¦) and the etching products (zirconium chlorides and chlorine oxides), were identified with optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS). The etch rate was determined to scale linearly with the square root of ion energy in the higher ion energy regime ($E_{ion} > 60$ eV), indicating that it is limited by the momentum transfer to the etched film. At low ion energies, the etch rate was quite constant, likely due to reactive sputtering of the metal oxides. The etching products were found to be predominantly $ZrCl_3$ (>70%) at low ion energies. However, $ZrCl_4$ became dominant at much higher ion energies. This is likely due to the enhanced surface chlorination under higher ion energy impact. This is in good

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agreement with X-ray photoelectron spectroscopy (XPS) measurements, which revealed increased surface chlorine content in the film etched at higher ion energy. The concentrations of the gas phase species will be quantified with actinometry and QMS, as a function of the chlorine pressure, ion energy, and the microwave power. The etching mechanism will be proposed and the reaction rate coefficients will be calculated based on a CSTR model. CHEMKIN will be used to simulate the etching process and the results will be compared with the experimental measurement. Finally, BCl_3 will be introduced to assess its effects on the etching selectivity of ZrO_2 to Si.

4:20pm **PS1-MoA8 Ferroelectric Etching Characteristics in Ar/Cl_2 and in Ar/SF_6 Mixtures**, ***L. Stafford***, *J. Margot*, Universite de Montreal, Canada, *M. Chaker*, INRS-Energie et Materiaux, Canada

Ferroelectric materials such as barium-strontium-titanate (BST) and strontium-bismuth-tantalate (SBT) are promising for many applications, including high-k DRAMs, FeRAMs and microwave components in the millimeter wavelength range. In order to integrate these materials to various devices, the development of reliable and efficient patterning processes is a crucial issue. In this context, it was recently shown that excellent etching characteristics for BST and SBT could be achieved using a pure argon high-density plasma, provided it is operated in the very low-pressure regime (i.e. 1 mTorr or less).[1] However, scientific literature indicates that the use of reactive fluorinated or chlorinated plasmas may still improve the process. For this reason, we have investigated the etching of BST using Cl_2-Ar mixtures. The emphasis is put on the influence of the experimental conditions (total gas pressure and Cl_2 percentage in Ar) on the etch rate and on the selectivity over HPR-504 photoresist. The etching results are correlated to the plasma characteristics, including positive ion density, ion energy and reactive neutral atom concentration as obtained from various plasma diagnostics (Langmuir probes, mass spectrometry on ions and neutrals, and actinometry). Our results show that the etch rate is directly proportional to the positive ion density, whatever the experimental conditions yielding that density. This indicates that in the range of pressures investigated, the etching mechanism is dominated by sputtering. Thus, considering the fact that for given experimental conditions, the ion density in chlorine is significantly lower than in argon, the use of argon thus appears more advantageous than Cl_2 to achieve high etch rates together with a good selectivity. These results will also be compared to those obtained in Ar/SF_6.

[1] L. Stafford et al., J. Vac. Sci. Technol. A, 20(2), pp. 530-535 (2002).

4:40pm **PS1-MoA9 Measuring Vacuum Ultraviolet Radiation-Induced Damage**, ***J.L. Lauer***, *J.L. Shohet, R.W.C. Hansen*, University of Wisconsin-Madison

During plasma processing, UV(ultraviolet) and VUV (ultraviolet) radiation is present, but its effects are difficult to separate from those due to charge particles incident on the wafer. To isolate the radiation effects, unpatterned oxide-coated wafers and Charm-2 wafers were exposed to UV/VUV radiation at the University of Wisconsin-Madison synchrotron. The contribution of UV/VUV photon irradiation to gate-oxide damage, and damage to dielectric materials in general, were examined using two measurement techniques that may predict the possibility of damage. They are (1) surface potential measurements and (2) electrically erasable read-only memory transistors (Charm-2 Wafers). In addition to these measurements, the current flowing to the wafer and the voltage on the substrate, were monitored during photon irradiation. Two processes, photoemission and photoconductivity, can create currents flowing across the dielectric layer, while only photoemission occurs in conductors. Positive charge appearance on the surface of dielectrics and conductors by VUV photoemission results in extraneous charge measurements with both techniques. As a result, it can become difficult to interpret the net amount charge on surfaces. In addition, it was determined that the UV monitors on Charm-2 wafers do not respond to VUV radiation.[1] Thus, the results from both damage measurement techniques must be analyzed carefully, especially in situations where VUV generation is important, such as in processing plasmas.

[1] The authors are grateful to W. A. Lukaszek of Wafer Charging Monitors and John Hu of LSI for loaning us the Charm-2 wafers and providing the analysis of the UV/VUV exposures. This work was supported in part by the National Science Foundation under grant DMR-0084402

5:00pm **PS1-MoA10 Transfer of Resist Roughness into Substrates during Plasma Etching**, ***A.P. Mahorowala***, *D.L. Goldfarb, G.M. Gallatin, D. Pfeiffer, K.E. Petrillo, K. Babich, M. Angelopoulos*, IBM T.J. Watson Research Center

Traditionally photoresists have been evaluated on the basis of their lithographic process latitude and etch resistance. For sub-150 nm process technologies, this is inadequate because the deviations in linewidth caused by a photoresist's inherent roughness and transferred into the substrate during etch can be comparable to the maximum allowable tolerance. The photoresist roughness issue has been exacerbated by the introduction of 193 nm photoresists whose films are not only thin but whose etch resistance is poorer than the 248 nm photoresists widely used. The photoresists used in conjunction with 157 nm and EUV lithographies are expected to be even thinner. This paper systematically studies the roughness transfer into an oxide substrate when using 248 nm, 193 nm and 157 nm photoresists in conjunction with organic and inorganic anti-reflective coatings/hard masks. Photoresist thickness, minimum feature size, plasma etch chemistry and time were varied as a part of this study. The analysis is based on cross-sectional and top down SEM micrographs and careful measurement of the sidewall roughness using AFM. The relative contributions of the photoresist material, development conditions, and the etching conditions to the roughness of the final image are determined and explained. Recommendations to prevent roughness transfer into the substrate are made.

Plasma Science
Room: C-105 - Session PS2-MoA

Plasma Processing for Large Area Substrates
Moderator: D. Leonhardt, US Naval Research Laboratory

2:00pm **PS2-MoA1 Ion Flux Uniformity in Large Area High Frequency Capacitive Discharges**, ***A. Perret****, *P. Chabert, J. Jolly, J.P. Booth, J. Guillon*, Ecole Polytechnique, France

Etching and thin film deposition using capacitive RF discharges at 13.56 MHz are routinely used for Flat Panel Display fabrication. The current trend in FPD technology is to increase the substrate size (> 1m2) while keeping high throughput (> 50 glass/hour). Very High Frequency (VHF) plasma excitation promises to provide faster processes whilst avoiding damage due to high energy ion bombardment. However, the reactor size may no longer be negligible with respect to the wavelength of the RF electromagnetic wave, causing non-uniformity in the plasma density across the reactor. The physical origin of this phenomenon is the beginning of a spatial standing wave within the reactor. The standing wave effect will become more important as the frequency is increased. Other phenomena causing non-uniformity will appear if the skin depth become small compared to the reactor size. We will present an experimental study of the ion flux uniformity of a plasma created in a large area capacitive discharge driven at frequencies of 13.56 to 60 MHz. The discharge was produced between two square plates (40cm x 40cm) separated by a distance of 8 cm. The ion flux variation across the reactor is measured by a system composed of 64 electrostatic probes inserted in the grounded upper electrode and biased negatively. The probes are regularly spaced and the time to read all probes is less than 2 seconds. The experimental results will be compared with a recently proposed model (Lieberman et al. Plasma Sources Science and Technology, accepted 2002).

2:20pm **PS2-MoA2 Electrical Characterization of Linearly Extended Inductively Coupled Plasma Sources for Large Area Processing**, ***Y.J. Lee***, *K.N. Kim*, Sunkyunkwan University, South Korea, *S.E. Park, J.K. Lee*, Pohang University of Sci. and Tech., South Korea, *G.Y. Yeom*, Sunkyunkwan University, South Korea

In order to achieve the performance required for high resolution flat panel display (FPD) devices, especially for TFT-LCD of next generation, improved dry etch processes currently indispensable technology for semiconductor industry are required for volume manufacturing and superior critical dimension control. The plasma sources developed to date for the production of high-density and large-area plasmas mainly focused on the spiral-type planar external ICP sources. However, due to its large inductance with the scale-up to larger areas and the cost and the thickness of its dielectric material, the conventional ICP source using an external spiral antenna may have reached its limit in extending the process area. Therefore, in this study, a plasma source utilizing inductive coupling of linear extended internal antennas has been used as a candidate for the efficient large area high-density plasma source. To minimize the inherent electrostatic coupling effect in the internal inductive linear antenna configurations, various internal-type linear antenna designs have been used in a square shaped (830mm*1,020mm) plasma chamber. Characterization of the system impedance for the various internal-type antenna schemes were achieved by measuring the current, the voltage, and the phase angle difference at 13.56MHz using a V/I probe (ENI). It was found that there was a significant change in inductance depending on the type of linear antenna designs. A simple modeling and simulation with a 2-D fluid code were also used to

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analyze the optimum arrangement and the distance of the each line source. In this presentation, the effects of various arrangements of the linear antennas and process conditions on the plasma characteristics 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 and the results were compared with the simulation data.

2:40pm **PS2-MoA3 Optimization of Source Modules in ICP-Helicon Multi-Element Arrays for Large Area Plasma Processing**, ***J.D. Evans***, *F.F. Chen*, University of California, Los Angeles

Optimization studies of compact inductive rf-source modules for use as individual elements of a multi-element ICP-helicon source array, with sufficient density N and spatial N(R) profile uniformity for plasma processing of arbitrarily large substrates, is described. Attention is restricted to a low-magnetic-field (low-B) regime (B < 250G), within which a local maximum (low-B peak) in N vs B is routinely observed and exploited for optimum plasma production efficiency. Proof of principle experiments that exploit this low-B peak have been successfully performed [PSST 10, 236 (2001)] in Ar and Cl. Arrays consisted of 7 cylindrical Pyrex tubes (o.d. = 5cm) plus antennas, with center-to-center spacing = 2d, mounted in a honeycomb pattern on top of a magnetic bucket. Optimization of individual modules of various aspect ratios and sizes are the focus of the present work. Static Bo is provided by a combination of coils and ring-shaped permanent magnets in close proximity to each module, designed such that they can fit in a usable multi-element source of arbitrarily large area. Measurements of N(R) vs B, at RF powers Prf < 1.6kW and neutral pressures Po = 1-25 mTorr, as well as radial N(R) profiles obtained from Langmuir probes vs axial distance are obtained. Anomalous enhancement of N(R) uniformity is observed when the low-field peak condition is met, with "flat" density profiles extending 5 tube radii, at axial distances < 2 tube diameters below the mouth. The implications for large area plasma processing applications are discussed.

3:00pm **PS2-MoA4 Scaling up of a Magnetic Pole Enhanced Inductively Coupled Plasma Source (MAPE-ICP)**, *P. Colpo*, ***T. Meziani***, *F. Rossi*, European Commission, Joint Research Centre, Italy

The principles of a Magnetic Pole Enhanced Inductively Coupled Plasma are presented. Plasma characterisation made on a 200mm source show that the electrical coupling efficiency is increased by a factor 4 as compared to a conventional flat coil configuration. Scaling up of the reactor to the dimension of 800x800mm poses several technological problems that have been solved and are presented. Characterisation of the large scale source show that a plasma density of 2 to 4 E11cm-3 with an Ar plasma at 2MHz is obtained and an homogeneity of the ion current density better than 20% over 800mm. Application of the source to the etching of SiO2 layers is presented. Etching rates of the order of 100nm/mn are obtained over the whole area. Results of plasma characterisation and chemistry are presented.

3:20pm **PS2-MoA5 Plasma Processing for Large Area Substrates**, ***V. Cassagne***, *M. Elyaakoubi*, UNAXIS France **INVITED**

In the liquid crystal flat panel display industry, the large area has another meaning than in semiconductor business. First, in size , the starting generation in the early 90's was in the range of 300x400mm glass substrate, now (5th generation) the average size is 1100x1250 mm (higher productivity, higher flexibility). Second is the generation cycles : in 12 years, the market generated 6 size generations without real sizes standards. Now with more than 1.4m^2 substrates, in parallel of economic and production pressure, we have to face Physics challenges in addition to standard engineering issues. Both for PECVD, PVD and dry etching processes, we have to deal with new phenomenon linked to the dimensions. There are first mechanical (loading 0.5mm thick substrate, thermal expansion, atmospheric pressure stress), then thermal (temperature process uniformity, heating/cooling power and time), gas flow (as diffusion length is smaller than reactor size local defaults are exhibited), RF electric field uniformity (now electrode dimensions start to be not negligible compare to RF wavelength, local field disturbances affect the process uniformity due to diffusion limitation). In addition, production trends require higher throughput (higher deposition rate, faster plasma cleaning), higher yield (low particles, lower defaults), higher up-time (higher reliability, easier maintenance), smaller footprint (compact solution, parallelism). It leads to R&D programs like plasma uniformity (gas flow, RF field, plasma chemistry), arcing-free plasma, up-scalable concepts and target utilization optimization for PVD and PECVD and high density source for Dry Etching. All these topics are evaluated by numerical modeling and experimental set-up. Advanced materials, laboratory tests and prototyping are used in order to prepare new plasma system generations.

4:00pm **PS2-MoA7 High-rate Large-area Plasma Deposition using Multiple Expanding Thermal Plasmas**, ***M. Schaepkens***, *C.D. Iacovangelo*, General Electric Global Research Center

A unique, high rate, large area plasma deposition process has been developed to generate various functional coatings on polymeric substrates. The process relies on the integration of a plurality of individual expanding thermal plasma sources into a multi-source setup. In this work we will discuss the effects of various hardware (e.g. reagent injection configuration) and process (e.g. pressure, reagent flow, preheat) parameters on the performance of a dual-source system that has been used to apply abrasion resistant coatings to polycarbonate substrates. It will be shown that a properly engineered dual-source system can generate transparent, organosilicon-based coatings that provide uniform, glass-like abrasion resistance across substrates up to 30 cm x 30 cm. Multi-source systems comprising more than two plasma sources hold promise for generating even larger area uniform coatings.

4:20pm **PS2-MoA8 Reflective Enhancement of Distributed Helicon Sources**, ***F.F. Chen***, University of California, Los Angeles

In Ref. 1 it was shown that large-area substrates can be covered uniformly with dense plasma by using a plurality of short helicon sources.[1] In this source use was made of the "low-field peak" (LFP), a density peak occurring near B = 50G which had been observed in several helicon devices.[2] A very quiet, stable discharge could be obtained in the neighborhood of this peak.[3] This feature was not predicted by standard helicon theory and was unexplained. In the latest version of the code HELIC developed by Arnush,[4] it is possible to model a short helicon source bounded at one end. The LFP is produced by constructive interference by the reflected wave from an end plate near the antenna and not, for instance, by a resonance of the Trivelpiece-Gould mode. This mechanism can also explain previous observations[5] of density enhancement by flaring magnetic fields or inserted blocks. This knowledge permits design of more compact helicon reactors.

[1] F.F. Chen, J.D. Evans, and G.R. Tynan, Plasma Sources Sci. Technol. 10, 236 (2001).

[2] F.F. Chen, X. Jiang, J.D. Evans, G. Tynan, and D. Arnush, Plasma Phys. Control. Fusion 39, A411 (1997).

[3] F.F. Chen, J. Vac. Sci. Technol. A 10, 1389 (1992).

[4] D. Arnush, Phys. Plasmas 7, 3042 (2000).

[5] G. Chevalier and F.F. Chen, J. Vac. Sci. Technol. A 11, 1165 (1993).

Surface Engineering
Room: C-111 - Session SE+NS-MoA

Nanoparticle and Nanofiber Surface Technologies
Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE+NS-MoA1 Investigation of Erbium Dispersion in Electrospun Nanofiber Matrices**, *W. Kataphinan*, ***R.D. Ramsier***, *E.A. Evans, D.H. Reneker*, University of Akron

Thermally stable nanofibers can be doped with molecular and atomic species. As an example, electrospun nanofibers made from polydiphenoxyphosphazene (PDPP) have been doped with erbium (Er) using Er(III) nitrate hydrate dissolved in ethanol. The Er/PDPP matrices are thermally stable up to 150 C in air for extended periods of time. Nanofibers electrospun from ceramic precursors are stable up to much higher temperatures. Infrared spectroscopy, electron microscopy and other techniques are used to quantify the influence of the electrospinning parameters (voltage, solvent, concentration, etc.) on the structural and spectral properties of the nanofibers and the dispersion of the Er-based dopants. Differences between methods for doping the fibers will be described based on these results. These results expand the useful operating temperature range of polymer nanofiber systems as well as the use of nanofiber matrices as a support for the dispersion of molecular and atomic scale dopants.

2:20pm **SE+NS-MoA2 Grafting of Poly (N-isopropylacrylamide) in Surfactant Templated Mesoporous Silica Films and Particles**, *Q. Fu*, ***G.V. Rama Rao***, *J. Huang, G.P. Lopez*, The University of New Mexico

Surface-initiated atom transfer radical polymerization (ATRP) is an effective and versatile method used to generate grafted polymers on surfaces. We report grafting of a poly (N-isopropylacrylamide) (PNIPAAM), a thermally responsive polymer, into a mesoporous silica matrix using the ATRP technique. PNIPAAM exhibits a lower critical solution temperature (LCST) at 32°C in water, below which it is in an expanded conformation and soluble in water. Above the LCST, PNIPAAM is in compacted state and insoluble in water. Synthesis of mesoporous films and monodisperse microparticles was carried out through an acid catalyzed sol-gel process using a surfactant template approach. We used a non-ionic surfactant (Pluronic-P123) and a cationic surfactant (cetyltrimethyl ammonium bromide) for the present study. The LCST of the hybrid films was established by static contact angle measurements. These hybrid materials exhibited thermo responsive behavior by changing from hydrophilic to hydrophobic state with change in temperature. X- ray diffraction and transmission electron microscopic studies on the films and particles confirmed the presence of an ordered porous structure before and after ATRP. The grafting of the polymer onto the pore surface was confirmed by drastic decrease in pore volume of the particles after ATRP. Pore opening and closing due to contraction and expansion of PNIPAAM was studied by fluorescent dye uptake behavior of particles by monitoring the fluorescence intensity in flow cytometry experiments. It was found that the uptake of the dye into the pores was obstructed below LCST, and above LCST, the polymer was collapsed and facilitated the passage of dye into the mesopores. The dye in the pores was entrapped by cooling the particles to below LCST and subsequently the dye was released by washing with water above LCST. These materials have potential application in controlled release, chemical separation and control of fluidic transport.

2:40pm **SE+NS-MoA3 Structural, Optical and Photocatalytic Properties of Nd^{3+} Doped TiO_2 Nanoparticles**, ***W. Li***, *S.I. Shah*, *C.-P. Huang*, University of Delaware, *O. Jung*, Chosun University, Korea

TiO_2 nanoparticles, with Nd^{3+} dopant concentration ranging from 0 to 1.5 at.%, were synthesized using metallorganic chemical vapor deposition. The dopant concentration and TiO_2 stoichiometry were verified by x-ray photoelectron spectroscopy and energy dispersive x-ray spectroscopy. Particle size and crystal structure were obtained by x-ray diffraction and high-resolution transmission electron microscopy which showed the nanoparticles are polycrystalline anatase with 22 nm average particle size. Red shifts of TiO_2 absorption edge with the increase of Nd^{3+} concentration were observed by spectrophotometery. 1.5 at.% Nd^{3+} shows ~0.15 eV red shift. The photoreactivities of Nd^{3+} doped and undoped TiO_2 were measured by studying the degradation of 2-chlorophenol solutions under ultra violet radiation. Nd^{3+} position in TiO_2 lattice critically affects the photocatalytic activity of TiO_2 nanoparticles. Nd^{3+} position in TiO_2 lattice was studied by using XRD peak shifts. The results of these studies will be presented.

3:00pm **SE+NS-MoA4 Computational Studies of Gas-Phase Growth of Soot Nanoparticles Using Fully-Integrated Integrated Molecular Dynamics and Kinetic Monte Carlo Methods**, ***A. Kubota***, *W.J. Pitz*, *C.K. Westbrook*, Lawrence Livermore National Laboratory

Combustion under fuel-rich gas conditions leads to the formation of soot nanoparticles. We study this process of carbon nanoparticle formation through the use of fully-integrated kinetic Monte Carlo and molecular dynamics methods. Rule-based polymerization and gas-surface kinetics are used in the chemical kinetic mechanism. This mechanism includes competitive H-abstraction and H-addition, as well as carbon-species addition, termination and cyclodehydrogenation and ring-closure reactions. We demonstrate that nanoparticle structure, morphology and rates are strongly coupled to the chemical kinetics as well as the gas-phase conditions. We compare modeling results with available experimental measurements.

3:20pm **SE+NS-MoA5 Enhancement of High Temperature Oxidation Resistance of Fe-Cr-Ni Alloys Using Nanocrystalline CeO2 Coating Synthesized by Microemulsion Technique**, ***S. Seal***, *S. Patil*, *S. Kuiry*, University of Central Florida

Fe-Cr-Ni alloys are usually subjected to high temperature oxidation during their various processing stages like rolling, forging and heat treatment. Extensive scaling losses are found to occur in these components in such aggressive environments at elevated temperatures. Therefore, development of coating that imparts oxidation resistance to Fe-Cr-Ni alloys is important not only for applications of these alloys at elevated temperatures but also to protect the oxidation losses during high temperature processing. The present study investigates the effectiveness of nano-sized CeO2 coating to enhance high temperature oxidation resistance of Fe-Cr-Ni alloys. Nanocrystalline CeO2 particles were synthesized with micro-emulsion technique using AOT [sodium bis(2-ethylhexyl) sulphosuccinate] as a surfactant. Kinetics of high temperature oxidation was studied on both bare and coated rectangular specimens in dry air. The scale cross section and surface morphology were characterized by using SEM, EDS, XPS and HRTEM studies.

4:00pm **SE+NS-MoA7 Formation and Optical Properties of Peridically Arranged Silver Nanoparticles by Irradiation with Linear Polarized Ultrashort Laser Pulses**, *A. Heilmann*, *A. Kiesow*, ***D. Katzer***, Fraunhofer-Institute for Mechanics of Materials Halle, Germany, *A. Podlipensky*, *G. Seifert*, *H. Graener*, Martin-Luther-University Halle, Germany

We report on a new and simple method to generate periodically ordered metallic, wire-like structures in an organic polymer-like matrix by irradiating thin films with series of ultrashort laser pulses. The films, which were deposited by alternating plasma polymerization and metal evaporation, are characterized by a two-dimensional particle size and shape distribution, i.e. all silver particles are arranged on one plane within the plasma polymer matrix. After laser irradiation with linearly polarized ultrashort (pulse duration < 150 fs), the nanostructure of the film changes from a relatively uniform particle distribution to a formation of an ensemble with metal particle nanowires. This was demonstrated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Material ablation during laser irradiation was not observed. The individual nanowires are between 100 to 250 nm wide with equal line space ratio. The obtainable structure size is not a function of the focusability of the laser and is significantly smaller than the laser wavelength used. The orientation of these wire-like structures is correlated to the linear polarization of the laser pulses, and is independent on the write direction of the laser beam. This dependence on laser polarization results in anisotropic optical properties. The optical extinction spectra were measured by locally resolved optical spectroscopy and by using linearly polarized light. The shift of the extinction peak depending on different steps of nanowire formation was analyzed. The optical spectra were correlated with the different nano-structures and various models were discussed to explain the material transport in the film.

Surface Science
Room: C-108 - Session SS1-MoA

Surface Reactions: CO and NO
Moderator: G. Fisher, Delphi Research Labs

2:00pm **SS1-MoA1 Bridging the Pressure Gap at the Atomic Level: CO/Pt(110) and CO/Pt(111)**, ***E.K. Vestergaard***, *P. Thostrup*, *T. An*, *B. Hammer*, *F. Besenbacher*, University of Aarhus, Denmark

We have studied the adsorption of CO on Pt(111)[1] and Pt(110)[2] over 12 orders of magnitude, up to 1 bar, using high-resolution scanning tunneling microscopy.[3] Here we demonstrate the possibility of bridging the pressure gap for these systems at the atomic level. For both surfaces, our new high-pressure STM results show that the adsorbate structures formed at high CO pressures are identical to high-coverage structures observed at low temperatures under vacuum conditions. Our findings are at variance with previous STM results where it was concluded that new structures develop at the platinum surfaces at high CO pressures. From these and other pertinent cases we attempt to extract general directions for making conjectures as to the high-pressure response of chemisorption systems.

[1] E. Kruse Vestergaard, P. Thostrup et al., submitted to Phys. Rev. Lett.

[2] P. Thostrup et al., Phys. Rev. Lett. 87, 126102 (2001)

[3] E. Laegsgaard, P. Thostrup et al., Rev. Sci. Instr. 72, 3537 (2001).

2:20pm **SS1-MoA2 Fluctuations and Bistability in CO Oxidation on Nanoscale Facets**, ***D.-J. Liu***, *J.W. Evans*, Iowa State University

Recent experiments of catalytic surface reactions, especially CO oxidation on nanoscale Pt field-emitter-tips,[1] provides tremendous new possibilities for modeling of surface reactions and for comparison with stochastic theories of chemical reactions. Particularly, in a chemical reaction with bistability, fluctuations can induce transitions between the two stable states for sufficiently small systems. We analyze a "hybrid" atomistic model mimicking CO oxidation on nanoscale facets of metal(100) catalyst surfaces. The model, which incorporate infinite CO diffusion and superlattice ordering of immobile O, display bistability for an infinite system. We focus on the probability distribution for the populations of adsorbed species, as well as dynamics of the fluctuations-induced transitions. An effective potential picture emerges from our analyses of kinetic Monte Carlo simulations. Qualitative behavior can be approximated by traditional master equation and Fokker-Planck equations, where the system size dependence and the approach to the critical point can be characterized by the mean-field behavior. Analysis of a generalized model with finite CO diffusion reveals the role of CO diffusion in the crossover from the mean-field to the equilibrium Ising-like behavior.

[1] Y. Suchorski et al., Phys. Rev. Lett. vol. 82, 1907 (1999).

3:00pm **SS1-MoA4 In situ Monitoring of the Catalytic CO + NO Reaction on Pd(111) at 240 mbar: The Formation of Isocyanate**, ***Ch. Hess***, *E. Ozenzoy, D.W. Goodman*, Texas A&M University

The CO + NO reaction to form CO_2, N_2O and N_2 has been studied on a Pd(111) surface at pressures up to 240 mbar by using in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS). At a pressure ratio of $P_{CO}/P_{NO} = 1.5$ and temperatures above 500 K, i.e., under reaction conditions, besides CO and NO, isocyanate is adsorbed on the surface as evidenced by isotope experiments. Below 0.1 mbar total pressure, however, no isocyanate formation was observed. The role of the isocyanate in the CO + NO on Pd(111) is discussed by comparison of the spectroscopic and kinetic results. In addition, kinetic measurements of the CO + NO reaction between 590 and 650 K showed an increase in the N_2O selectivity, a result of temperature-dependent changes of the ratio $[NO]_a/[CO]_a$. Within this temperature range, the apparent activation energy of the reaction was determined to be 54 ± 21 kJ/mol.

3:20pm **SS1-MoA5 Fundamental Studies of Function and Deactivation of NOx Storage Catalysts**, ***E. Fridell***, *A. Amberntsson, P. Broqvist, J. Dawody, A.W. Grant, L. Olsson, M. Skoglundh*, Chalmers University of Technology, Sweden **INVITED**

We have investigated the function of the different components in so called NOx storage catalysts regarding both the storage/reduction of NOx and deactivation by sulphur. These types of catalysts are used in lean burn applications for trapping NOx as nitrates, which in turn are reduced during lean conditions We have investigated model samples containing Ba compounds for storage of NOx and Pt and Rh as catalysts for oxidation and reduction reactions. We find that NO2 plays an important role in the storage mechanism as an oxidising agent. Two different mechanisms for this are discussed: The formation of surface peroxides and the oxidation of nitrites to nitrates. FTIR studies show that NOx is stored as surface nitrates. The stability of these species is also confirmed by first principle calculations. The sulphur deactivation is found to be more severe when SO2 is added during the rich phase than when SO2 is added during the lean period. This observation is found to be connected to the interaction between Pt and SO2. FTIR shows the formation of bulk sulphates both under lean and rich conditions. The influence of the choice of noble metals for the deactivation and regeneration was also investigated. It is found that Rh plays an important role for the regeneration after sulphur deactivation. Further, XPS studies show that the formation of platinum oxides is significant in the presence of NO2, especially for the Ba-containing samples. This has strong implications for the reactions.

4:00pm **SS1-MoA7 Nitrite and Nitrate Formation from NO and NO2 Adsorption on Alkaline Earth Metal Oxide Surfaces**, ***M. Miletic***, University of Michigan, *P.J. Schmitz, W.F. Schneider*, Ford Research Laboratory, *J.L. Gland*, University of Michigan

Alkaline earth oxides surfaces are currently being explored as a means of trapping NOx species under excess oxygen conditions typical of lean burn (e.g. diesel) engine exhaust. These metal oxides have been proposed as active components in automotive NOx abatement strategies because of their role in effectively storing and releasing NOx under lean/rich exhaust cycling. However, molecular understanding of the adsorption and reactions of NO, and NO2 on alkaline earth oxide surfaces remains incomplete. A series of temperature programmed studies of NO and NO2 on alkaline earth oxide surfaces are reported here. These experiments, coupled with XPS and ab-initio studies, indicate that reactive chemisorption plays a unique, adsorbate-specific role for both low and high temperature desorption. The effect of coverage on the molecular species is unexpected both in reactive adsorption and desorption on these oxide surfaces. Experimental and computational Density Functional Theory results are coupled, highlighting the importance of reactive configurations, charge transfer, surface-adsorbate Lewis acidity/basicity, and surface oxidation/reduction processes. Together, these approaches are used to form an integrated understanding of the driving forces behind nitrite and nitrate formation on alkaline earth oxide surfaces.

4:20pm **SS1-MoA8 Adsorption and Reaction of NO on $SrTiO_3$ Surfaces**, ***S. Azad***, *L.-Q. Wang, M.H. Engelhard, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

The adsorption and reaction of NO on metal oxide surfaces has recently received considerable attention in relation to the efficient removal of toxic pollutants from automobile exhaust. In this study, the reactivity of NO on $SrTiO_3$ surfaces has been investigated using temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). On oxidized surfaces containing predominantly Ti^{4+} cations NO was found to be much less reactive and desorbed mainly as molecular NO around 250 K. Similar TPD spectra obtained for NO adsorption on $SrTiO_3$ prepared by sputtering or annealing the surface to 750 K, 850 K and 900 K in vacuum and in O_2 suggested that thermal annealing of this surface did not affect the reactivity of NO with Ti^{4+} cation sites. However, a significant number of defects containing mainly Ti^{3+} (observed by XPS) that was created by Ar^+ ion bombardment greatly increased the reactivity of the surface towards the adsorbed NO molecules. NO is reduced by the Ti^{3+} sites on these defected surfaces and the major decomposition products are N_2 and N_2O. Co-adsorption of NO with CO on both reduced and oxidized surfaces has also been examined. The results of NO on $SrTiO_3$ surfaces will be compared with the results of ongoing studies of NO adsorption on $Ce_{1-x}Zr_xO_2$/YSZ(111).

4:40pm **SS1-MoA9 Structural and Chemical Properties of Ti/Pt(100)-c(2x2) Second Layer Alloy - Evidence for Strong Ligand Effects**, *S. Hsieh, T. Matsumoto*, University of Southern California, *M. Batzill*, Tulane University, ***B.E. Koel***, University of Southern California

We have investigated the structure and chemisorption properties of a Ti/Pt(100) surface alloy using AES, XPS, LEED, STM, XPD, ALISS, and TPD of CO and H_2. Samples were prepared by evaporating Ti onto a clean Pt(100)-hex reconstructed surface at 300 K. After annealing the sample to 800 K, a c(2x2) ordered LEED pattern was observed that sharpened as the temperature was increased to 920 K. Further annealing to 1000 K caused the LEED pattern to become diffuse, due to onset of disorder in the surface layers resulting from Ti diffusion into the bulk. Using XPD and ALISS, we have determined that Ti atoms in the Ti/Pt(100)-c(2x2) surface alloy are not present in the topmost layer, but instead, in the second layer. Thus, the surface layer is pure Pt. XPS results showed that the Ti $2p_{3/2}$ peak from the surface alloy is shifted about 1.4 eV from a thick Ti film, and the Pt 4f peak is shifted 0.1 eV, consistent with the formation of strong intermetallic bonds upon alloying. CO adsorbed reversibly on the alloy, desorbing in a broad peak with a maximum at 376 K, showing a strong downward shift of 132 K compared to CO desorption from clean Pt(100). Thermal desorption of H_2 was also studied and a similar peak shift toward lower temperatures was observed. In addition, much less H_2 adsorbed on the Ti/Pt(100)-c(2x2) surface than on Pt(100). These results show that the second-layer Ti atoms exert a strong "ligand effect" on the Pt atoms at the surface, and this is a good model system for studying pure ligand effects at alloy surfaces.

5:00pm **SS1-MoA10 Dissociation/Dehydrogenation of Hydrocarbons on NiAl(100)**, *K.A. Layman*, ***Y. Jiang***, *J.C. Hemminger*, University of California, Irvine

HREELS has been used to study the reactivity of CO, CO_2, acetone, and pyridine on NiAl(100) as a function of surface coverage and temperature following adsorption at 140 K. While CO adsorbs primarily associatively at low CO exposures, we observe that CO begins to dissociate on the NiAl(100) substrate after very high CO exposures (100-1000 L), as indicated by the formation of a predissociation CO stretch at ~1366 cm^{-1}. In addition, CO_2 interacts very strongly with the NiAl(100) surface, as indicated by the shifting of the asymmetric CO_2 stretch to ~2027 cm^{-1}. This shift is observed for CO_2 exposures as small as 0.1 L. In contrast, the adsorption of acetone and pyridine on the NiAl(100) substrate is non-dissociative. Upon annealing the NiAl(100) surface after exposing the NiAl(100) single crystal to CO_2, acetone, or pyridine, the adsorbate begins to dissociate and/or dehydrogenate. After annealing the surface to approximately 260 K, the hydrocarbons begin to dehydrogenate. Further annealing to approximately 500 K results in the cleavage of the C-O or the C-N bond, forming Al_2O_3 or Al_xN_y thin films. The thin films of Al_2O_3 follow the phase temporal regimes exhibited for Al_2O_3 thin films grown by exposing the NiAl(100) single crystal to oxygen. Further annealing of the Al_xN_y thin films results in a similar ordering/phase change as observed for the Al_2O_3 thin films.

Surface Science
Room: C-110 - Session SS2-MoA

Nucleation & Growth of Metals on Oxides & Semiconductors

Moderator: D.Y. Petrovykh, Univ. of Maryland/Naval Research Lab

2:00pm **SS2-MoA1 The Effects of Copper on the Hydrogen-Passivation of Si(001)**, ***A.R. Laracuente***, *L.A. Baker, L.J. Whitman*, Naval Research Laboratory

Foreign adsorbates can alter the morphology of surfaces and often have a dramatic impact on film growth. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates, it is important to understand how adsorbates affect the surface morphology of

H-terminated Si surfaces. Currently, we are studying how copper modifies the morphology of monohydride-terminated Si(001). In the experiments, clean Si(001) surfaces are first exposed to 0.3 monolayer of Cu and then passivated with atomic H under conditions that produce a monohydride surface. The samples are characterized at room temperature using scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). We find that the main effect of Cu pre-exposure is the formation of pits on the surface. The pits are about 3 nm x 3 nm in size and one atomic layer deep. It appears that Cu induces Si etching during the atomic H exposure. Furthermore, the "pitted" H-terminated surface is subsequently dosed with Cu to investigate the effects of the pits on the growth of Cu. We will present our STM and AES results, and an analysis of the pit size distribution.

2:20pm **SS2-MoA2 Competing Classical and Quantum Effects in Shape Relaxation of a Metallic Island**, ***H. Okamoto***, *D. Chen,* Rowland Institute for Science, *T. Yamada,* NASA Ames Research Center

Pb islands grown on a silicon substrate transform at room temperature from the initially flattop facet geometry into an unusual ring shape with a volume-preserving mass transport process catalysed by the tip electrical field of a scanning tunnelling microscope. The formation of such ring shape morphology results from the competing classical and quantum effects in the shape relaxation. The latter also leads to a sequential re-growth on alternating strips of the same facet defined by the underlying substrate steps, showing for the first time the dynamical impact of the quantum size effect on the stability of a nanostructure.

2:40pm **SS2-MoA3 Formation of Monodispersed Cobalt Nanoclusters on the Si$_3$N$_4$(0001)-4x4 Surface**, ***C.-L. Wu***, *T.-B. Chou, S. Gwo, W.-C. Lin,* National Tsing-Hua University, Taiwan, ROC, ***M.-T. Lin***, National Taiwan University, Taiwan, ROC

A novel phenomenon of forming monodispersed Co nanoparticles at room temperature on a single-crystal Si$_3$N$_4$ dielectric thin film is presented. Results of very narrow size distributions with an average size of ~30 Co atoms have been obtained. We have found that cobalt clusters deposited on Si$_3$N$_4$ are stable with respect to cluster agglomeration/coalescence and thermal decomposition. Also, we have confirmed that the average size of Co clusters is independent of the deposition time and insensitive to the magnitude of the deposition flux. Therefore, their areal density can be controlled by the deposition time. The motivation for using a single-crystal Si$_3$N$_4$ support is two-fold. First, the dielectric support reduces chemical intermixing and electronic coupling (Si$_3$N$_4$ is an excellent diffusion barrier with a bandgap energy of 4-5 eV) between metal clusters and the substrate compared with situations using semiconductor or metal surfaces. Second, the defect-free Si$_3$N$_4$ surface provides us a unique opportunity to study the formation of metal clusters without the influence of surface defects. Consequently, quantum effect can play an important role in the size control.

3:00pm **SS2-MoA4 The 'Three-Dimensional' Schwoebel-Ehrlich Barrier in Ag Crystallite Growth on Si(111)**, *W.X. Tang, K.L. Man,* Hong Kong University of Science and Technology, *H. Huang,* Hong Kong Polytechnic University, ***M.S. Altman***, Hong Kong University of Science and Technology

Growth morphology will be affected, or even dictated, by kinetic limitations that may be present during growth. One such limitation, which has received a great deal of attention, occurs in growth at surfaces when there is a Schwoebel-Ehrlich (SE) diffusion energy barrier to atomic motion descending a monolayer height step. We present evidence of an analogous 'three-dimensional' (3D) SE energy barrier to atomic diffusion across the ridge that separates two facets on a three-dimensional crystal. The 3D SE barrier stems from the reduced coordination at the ridge. Differences of the adatom formation energies on adjacent facets cause the 3D SE barrier to be asymmetric. Kinetically limited growth shapes of Ag crystallites on the Si(111) surface have been studied with low energy electron microscopy (LEEM) and diffraction (LEED). These growth shapes are in agreement with expectations from the asymmetry of the 3D SE barriers. LEEM observations of the modification of growth shapes caused by codeposition of surfactants are also consistent with modification of the 3D SE barrier caused by surface passivation. The 3D SE barrier is expected to be relevant to diffusion in the presence of multilayer height steps on surfaces, and is therefore also important for the development of film texture.

3:20pm **SS2-MoA5 Self-organization of Semimetal Bi on Si(111)**, ***T. Nagao***, Tohoku University, Japan, *T. Kogure,* University of Tokyo, Japan, *J.T. Sadowski,* Tohoku University, Japan, *T. Sekiguchi, S. Hasegawa,* University of Tokyo, Japan, *T. Sakurai,* Tohoku University, Japan

We have studied the self-organization of epitaxially grown semimetal bismuth on Si(111) surfaces by in situ reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), and 4-probe conductivity measurement. On the 7x7 surface, up to around 4ML, the system grows in a S-K like manner: [102] oriented flat-top islands grow after completion of disordered wetting layer. Sharp height distribution of these flat-top islands peaked at 1.2nm was clarified in a wide growth temperature range (290-550 K) as well as wide deposition rate (0.1-2.0 ML/min), which indicates the significance of the electronic effect in the film growth. After the connection of the flat-top islands, the growth mode switches to a nearly perfect FvM growth, and the connected layer self-organizes into a single-crystal ultrathin film with Bi(001)-1x1 surface as evidenced by in situ RHEED and ex situ XTEM. Four-probe measurements showed the largest resistance drop at around 4 ML followed by another gradual drop around 4-10 ML and finally approached to a conductivity only several times lower than the bulk value, unusual value for such thin films. The initial drop was associated with the percolation of the flat-top islands. The following gradual drop was assigned to the reduction in the (surface and bulk) roughness scattering, due to self alignment in the crystal orientation via drastic interfacial glide and mass transport of the flat-top nanocrystals which are initially loosely bound on the disordered wetting layer. The origin of this new type of electronic growth and its self-organization into perfectly ordered ultrathin film will be discussed in detail.

3:40pm **SS2-MoA6 Controlling Island Size Distributions for Metals on Oxides: Cu and Ni Islands on TiO$_2$(110)-(1x2)**, *J. Zhou, B.T. Long,* ***D.A. Chen***, University of South Carolina

Metal islands deposited on oxide surfaces are frequently used as model systems for understanding heterogeneous catalysts. In order to investigate how the surface chemistry of the metal islands may change as a function of island size, it is first necessary to produce islands with narrow size distributions. In these studies, Cu and Ni have been vapor-deposited onto a partially reconstructed TiO$_2$(110)-(1x2) surface and characterized by STM under UHV conditions. The key to achieving a uniform island size distribution for Cu on TiO$_2$(110)-(1x2) is a low D/F ratio, where D is the diffusion rate for Cu on the surface and F is the Cu deposition or flux rate. When rate of deposition is high relative to diffusion, the incoming Cu atoms have a greater probability of encountering another Cu atom and forming a new island before they are able to diffuse across the surface and contribute to the growth of an existing island; in this case, small islands of uniform sizes are formed with high island densities. When the rate of diffusion is high relative to flux, the incoming Cu atoms are more likely to diffuse to an existing island before encountering other Cu atoms; in this case, Cu islands of varying sizes with lower island densities are formed. We have varied the D/F ratio by changing both the deposition rate and the temperature of the surface during deposition. In all cases, the lower D/F ratio yields a more uniform size distribution. Notably, the Cu islands grown on this partially reconstructed TiO$_2$(110)-(1x2) surface produce high island densities (~5x10^{12}/cm^2 at 2 ML) due to high defect densities on the titania surface itself. Larger islands Cu (~100 Å diameter) with uniform size distributions can be produced by deposition at room temperature followed by annealing at higher temperatures. Investigations of Ni island growth on the reconstructed titania surface are currently underway.

4:00pm **SS2-MoA7 Surface Nanostructuring to Control Size and Composition of Individual Oxide Supported Nanoparticles**, ***A. Kolmakov***, University of California, Santa Barbara, *D.W. Goodman*, Texas A&M University

A key to the technological utilization of oxide supported metal nanoparticles as an active element in gas sensing devices and catalysts is an atomic level understanding of their role in the chemical reaction. The chemical and physical properties of nanoparticles dispersed on oxide surfaces exhibit a marked dependency on their size, shape, composition and electronic interaction with the support. To explore this avenue a umber of methods of producing and delivery of size selected clusters from the gas or liquid phase to the oxide surfaces have been developed during the last decade. Alternatively, recent achievements in single molecule and clusters spectroscopy with NSOM and SPM and TEM proved the feasibility of so called individual approach where instead of probing the ensemble of size selected particles, imaging and spectroscopy of the individual oxide supported nanoparticles with different sizes and composition is performed and compared during the single experiment. Using Ag, Au and alloy clusters supported on TiO$_2$ (110) as a model system, we demonstrate several experimental schemes for studying individual supported metal clusters using oxide surface nanostructuring in conjunction with SPM. Namely, on slightly reduced TiO$_2$ we create laterally confined and precisely located areas with controllably modulated defect densities by exploiting a "tip shadowing" technique to synthesize a nanostructured mask. Since the diffusion length of the adsorbate atoms and eventually the cluster nucleation density are strongly mediated by surface defect densities in these areas, a well-defined and controllable variety of cluster sizes is accessible for imaging and spectroscopy within the field of view of the SPM. A similar procedure is applied for tuning the doping level of individual, metal particles. The spectroscopic and morphological changes of the individual clusters were probed in situ while exposuring the sample to elevated pressure of reactive gases.

4:20pm **SS2-MoA8 Nucleation and Sintering Kinetics of Pd on** a-**Al_2O_3(0001)**, ***S.L. Tait, Jr.***, *L.T. Ngo, Q. Yu, S.C. Fain, Jr., C.T. Campbell*, University of Washington

Low-temperature methane combustion for applications in electric generator turbines is catalyzed by Pd nanoparticles to minimize NO_x pollution. The reaction depends on the dissociation of methane molecules on the Pd surface. Nanoscale Pd particles contain coordinatively unsaturated Pd atoms, making them more active for the dissociation of CH_4. We have studied the growth of Pd nanoparticles on the α-Al_2O_3(0001) surface. The alumina single crystal was cleaned by annealing in air and in vacuum. The cleanliness and structure of the surface were verified by XPS and LEED. Experiments were conducted on the unreconstructed 1x1 and the reconstructed $\sqrt{31}\times\sqrt{31}$ R±8.9° surfaces. Wide terraces were observed on the surface with non-contact atomic force microscopy (NC-AFM). Sub-monolayer doses of Pd were deposited by vapor deposition. NC-AFM was used to observe the growth of Pd nanoparticles upon annealing. These measurements provide information about the Pd particle size, number density and morphology. The Pd showed a tendency to cluster at step edges. To measure Pd particle sintering kinetics and size effects thereon, temperature-programmed ion scattering spectroscopy was used to monitor the fraction of the surface covered by Pd particles continuously as the surface was heated at 1 K/s. The number density of the Pd particles was measured before and after heating using NC-AFM. Curiously, large regions of the surface were found to be void of clusters even at step edges. A mechanism involving the various elementary steps in atom and cluster migration is being developed to model the kinetics of sintering with physically reasonable parameters. Work supported by DOE-OBES Office of Chemical Sciences and the M. J. Murdock Charitable Trust. LTN supported by the IGERT Nanotechnology Fellowship.

4:40pm **SS2-MoA9 The Domain Boundary Barrier on Intermixed SbGe(001)**, *M. Li*, ***E.I. Altman***, Yale University

The nucleation and growth of epitaxial Ge structures on the intermixed SbGe(001) surface below the Sb segregation temperature was studied using scanning tunneling microscopy (STM). The drastic changes in the density, shape and size of the epitaxial structures as a function of Sb concentration in the Ge(001) substrate reveal the favored nucleation of Ge ad-dimers on Ge instead of Sb. The lack of Ge epitaxial structures on Sb suggests the enhanced surface diffusion on Sb-passivated surface. The Ge epitaxial structures always situate in the proximity of domain boundary between mainly bean-shaped Sb dimer domains and Ge dimer domains in the substrate. A one-directional repulsive potential barrier at the Sb-Ge domain boundary is proposed that inhibits the diffusion of Ge dimers from Ge domains to Sb domains and thus the nucleation of epitaxial structure is confined to Ge domains.

Thin Films
Room: C-101 - Session TF-MoA

Transparent Conductive Coatings
Moderator: C. Stoessel, Consultant

2:00pm **TF-MoA1 Polaron Conductors with Infrared Transparency**, ***G.J. Exarhos***, *C.F. Windisch, Jr., K.F. Ferris*, Pacific Northwest National Laboratory, *S.K. Sharma*, University of Hawaii **INVITED**

Mixed transition metal spinel oxide films (AB_2O_4) deposited from solution or by means of reactive magnetron sputtering are found to exhibit resistivities on the order of milliohm-cm and optical transparency to wavelengths approaching 16 micrometers. These extraordinary properties are achieved when metal cations selected from group VIII in the periodic table are resident within the spinel lattice. Results from temperature-dependent Raman spectroscopy, Hall and Seebeck measurements, XPS, and x-ray diffraction indicate the importance of cation disorder on the conductivity and suggest processing avenues to further tailor film properties. These include partial substitution of lithium for cations resident on the tetrahedral lattice sites and gross replacement of first row transition metal cations with those deeper in the periodic table. Electronic structure modeling approaches provide a rational path to optimizing properties in these materials. Charge transport processes in p-type spinel oxides will be contrasted with those of free-carrier driven TCO films such as cation-doped ZnO. Prospective applications of the spinel films to applications requiring high transmissivity at long wavelengths will be discussed.

2:40pm **TF-MoA3 p-Type Semiconducting Cu_2O-CoO Thin Films Prepared by Magnetron Sputtering**, ***S. Suzuki***, *T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

In this report, we describe the preparation by magnetron sputtering of p-type semiconducting thin films consisting of a new multicomponent oxide, Cu_2O-CoO. The Cu_2O-CoO films (thickness, 200-450 nm) were deposited on glass substrates at a temperature of 200 to 400°C by r.f. magnetron sputtering using a powder target. The sputtering deposition was carried out at a pressure of 0.2 to 4.0 Pa in an Ar+O_2 gas atmosphere with an r.f. power up to about 80 W. A mixture of Cu_2O and CoO powders calcined at 1000°C in air for 1 h was used as the target: CoO contents of 0 to 100 mol.%. The obtained electrical and optical properties were strongly dependent on the deposition conditions as well as the CoO content of the target. The resistivity of Cu_2O-CoO thin films deposited at 200°C in a pure O_2 gas atmosphere at a pressure of 2.0 Pa with an r.f. power of 80 W decreased as the CoO content was increased, reached a minimum at about 80 mol.%, and then increased markedly with a further increase in CoO content. A minimum resistivity of $3.9X10^{?3}$Ωcm was obtained in a Cu_2O-CoO thin film prepared with a CoO content of 80 mol.% and identified as the polycrystalline delafossite $CuCoO_2$ by x-ray diffraction analyses. However, the resistivity exhibited a spatial distribution on the substrate surface that depended on the deposition conditions. The multicomponent oxide Cu_2O-CoO thin films prepared in the CoO content range from 0 to 100 mol.% found to be p-type, or positive hole conduction, as evidenced from Seebeck effect. From transmission spectra measurements, the band-gap energy of Cu_2O-CoO films are roughly estimated to be about 1.8 eV. This is the first report of the preparation of new p-type semiconducting Cu_2O-CoO thin films.

3:00pm **TF-MoA4 CVD Formed p-type ZnO Thin Films**, ***X. Li***, *Y. Yan, T.A. Gessert, C. Perkins, H.R. Moutinho, T.J. Coutts*, National Renewable Energy Laboratory

We have fabricated zinc oxide (ZnO) films that demonstrate a p-type behavior by using a metalorganics chemical vapor deposition (MOCVD). In our low pressure MOCVD, without any plasma enhance, the Zn precursor: diethylzine (DEZ) is reacted with the oxygen and nitric oxide (NO) gas at the temperature range between 200° and 500°C. The p-type behave is only observed on those films formed by DEZ and NO gas. In this reaction, the NO gas is used to supply both O and N to form an N-doped ZnO (ZnO:N) film. The highest N concentration obtained in our ZnO:N films is ~3 at.%, which is highest N-incorporation level reported for ZnO:N films. Hole concentrations of the films are in the range of $1.0x10^{15}$ cm^{-3} - $1.0x10^{18}$ cm^{-3}, with mobility varied from the values of 260 cm^2 $V^{-1}s^{-1}$ to 0.7 cm^2 $V^{-1}s^{-1}$. The minimum film resistivity achieved is ~20 Ω-cm.

3:20pm **TF-MoA5 Raman Spectra of Cobalt Nickel ITCO Films**, ***C.F. Windisch Jr.***, *K.F. Ferris, G.J. Exarhos,* Pacific Northwest National Laboratory, *S.K. Sharma*, University of Hawaii

Cobalt-nickel spinel oxide films have recently shown promise as infrared transparent conducting oxide (ITCO) materials, with resistivity as low as 10^{-3} ohm cm and transmittance (for a 100 nm-thick film) approaching 80% at 5 µm. While our current research is focused on optical behavior, the materials have been the subject of previous study, mainly due to their capacity to catalyze the water electrolysis reaction. Attempts to characterize the underlying structural and mechanistic causes for the remarkable electrical and magnetic properties, however, were only partly successful. In particular, there is still uncertainty regarding not only the electrical conduction mechanism, but also the identities of the various charge states of the Ni and Co ions and their distributions among the octahedral and tetrahedral sites in the spinel lattice. In all likelihood, the characteristics of the ions and the specifics of the conduction mechanism are intimately related. In order to understand how the unique electrical and optical properties of the cobalt-nickel spinel oxide films result from chemical structure, Raman spectra were obtained as a function of temperature and composition. Shifts in peak frequencies and changes in bandwidth as a function of temperature and laser power, particularly under cryogenic conditions, could not be explained by simple heating effects alone. Details of this behavior, as well as the spectral changes observed as a function of the Co/Ni ratio in the spinel, point to the presence of a localization of charge states and the important role of small polaron hopping in the electrical conduction mechanism. This work was supported by the Materials Sciences Division of Basic Energy Sciences through the DOE Office of Science and the ARO through DARPA contract AO J209/00. Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

3:40pm **TF-MoA6 Plasma Chemistry Aspects versus Material Properties Related to Textured Zinc Oxide Deposition and Etching using an Expanding Thermal Plasma**, ***R. Groenen***, *E.R. Kieft, M. Creatore,* Eindhoven University of Technology, The Netherlands, *J.L. Linden,* TNO, The Netherlands, *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. As recently shown, a new approach for low temperature ZnO deposition is developed, using an expanding thermal argon plasma created with a cascaded arc.[1] (Co)precursors are oxygen and diethylzinc. Films are deposited on glass substrates at a temperature from 300 down to 150°C at a rate up to 1 nm/s. A rough surface texture, which is essential for application as front electrode in thin film solar cells, is obtained during deposition. Quadrupole mass spectrometry is used to correlate film properties and gas phase composition. Gas specific calibrations have been performed to make quantitative measurements of the stable reaction product concentrations. First insights into the chemical processes taking place in the plasma have been obtained. There appears to be a close relation between detected species and the observed texture development, which allows for further improvement of the material light trapping properties. Especially the role of hydrogen is under investigation. In this respect, a new method for dry ZnO etching using an expanding thermal argon - hydrogen plasma created with a cascaded arc has been demonstrated, obtaining etch rates up to over 10 nm/s. In-situ ellipsometry, as well as ex-situ FTIR, AFM, SEM, and Hall measurements have been applied to characterize the effect of etching on film properties.

[1] R. Groenen, et al., Appl. Surf. Sci. 173 (2001) 40.

4:00pm **TF-MoA7 Super-Smooth Indium-Tin Oxide Thin Films by Negative Sputter Ion Beam Technology**, ***M.H. Sohn***, *D. Kim, N.W. Paik, S.J. Kim,* Plasmion Corporation, *S. Gupta*, KDF

A new ionized PVD, Negative Sputter Ion Beam technology, is described for the deposition of super-smooth indium-tin oxide (ITO) thin films with highly transparent and conductive properties at near-room temperature deposition. A limited amount of cesium vapor injected onto a conventional sputtering target surface lowers the work function of the target and produces a negatively charged sputter ion beam. The negative sputter ion beam carries the kinetic energy defined by the potential difference between the cathode and substrate. A negatively-charged sputter ion beam was produced by retrofitting an ITO magnetron sputtering cathode with a cesium vapor injector capable of releasing controlled amounts of cesium vapor into the plasma during deposition. Experiments were performed in a down-sputtering scanning batch tool (KDF 902GT). Using this highly energetic deposition process, ITO thin films have been obtained at near-room temperature (less than 50 °C) with super smooth surface (< 1 nm RMS), resistivity of 4 x 10^{-4}Ωcm, and transmittance higher than 90% (at wavelength 550 nm). Baseline ITO depositions were also carried out under the same sputtering conditions with no cesium injected, as a comparison. In this paper, film properties such as resistivity, transmittance over the visible spectrum, and surface roughness will be detailed as a function of cesium partial pressure during deposition. The significance of a high quality, low temperature ITO coating process applied to polymer substrates will be discussed.

4:20pm **TF-MoA8 ZnO Thin Film Synthesis and Device Application**, ***R.S. McLean***, *M.H. Reilly, P.F. Carcia*, DuPont Central Research and Development

ZnO is a wide bandgap, n-type semiconductor that can be doped degeneratively with Group III elements, making it useful as a transparent conducting electrode. Recently, there have been reports of successful p-type doping of ZnO, which would enable device applications ranging from uv lasers to transparent thin film transistors. ZnO is also attractive because polycrystalline films can be grown at low temperatures, compatible with temperature-sensitive plastic substrates, thus presenting the opportunity for fabricating good quality electronic devices on flexible substrates. In this paper we discuss synthesis and electronic properties of ZnO films on polyester substrates and device application. ZnO films were grown by rf magnetron, rf diode, and ion beam sputtering on substrates ostensibly at room temperature. Films grown at low oxygen partial pressure, p(O_2), had the lowest resistivity, ~0.01 ohm-cm, with a dependence of resistivity on p(O_2) that was exponential-like. Hall effect mobility measured in films with resistivity between 0.01 and 10 ohm-cm, was ~ 6-12 cm^2/V-s, independent of deposition technique. All film were polycrystalline with prominent c-axis orientation and small, uniform grain size, ~ 25 nm. Film stress increased with p(O_2) and more energetic deposition conditions, suggesting that bombardment by negative oxygen ions likely caused high stress. Finally we fabricated a ZnO, transparent, thin-film transistor, and its properties will also be discussed.

4:40pm **TF-MoA9 ITO Films with Low Resistivity and Low Internal Stress**, ***S. Takayama***, Hosei University, Japan

Indium tin oxide (ITO) is widely used to make transparent conducting films for various display devices. Recently, ITO films with low resistivities, low internal stresses, and high optical transmittance are required in relatively low-temperature processes for use in future display applications. However, to my knowledge, there are no reports of ITO films with both low resistivity and low internal stress having been successfully obtained in relatively low-temperature processes at less than 200°C. For this purpose, in this report, Indium tin oxide (ITO) films (260 to 280 nm in thickness, prepared by d.c.magnetron sputtering on a glass substrate at room temperature) were annealed in air, vacuum, and oxygen gas atmosphere. The structure of all the present as-deposited ITO films was not amorphous, but poly-crystalline. The electronic properties were measured by Hall effect measurements using the Van der Pauw method at room temperature. The internal stress was measured by using a thin-film X-ray diffractometer (XRD, Rigaku RINT 2500). It was found that, among the above post-annealing treatments, oxygen gas annealing significantly reduced both the resistivity and the internal stress in ITO films at fairly low temperatures of 100°C -150°C. Resistivities and internal stresses as low as 7 x 10^{-4}Ωcm and 38 MPa, respectively, were obtained by annealing in oxygen gas atmosphere at 100°. It was also revealed that the (111) crystal orientation becomes dominant and that whole grains grow dramatically as a result of post-oxygen-annealing, even at 100°C. It was tentatively concluded that the decrease of both resistivity and internal stress of post-annealed ITO films in oxygen gas atmosphere resulted from a large grain growth at relatively low temperatures. Finally, the optical transmittance of all of the post-annealed films in oxygen gas atmosphere was measured and found to be nearly 90% in the visible region of the solar spectrum.

Applied Surface Science
Room: C-106 - Session AS-TuM

Polymer Characterization
Moderator: J.E. Fulghum, Kent State University

8:20am **AS-TuM1 Chemical Bonding of Perfluoropolyether End Group with Carbon Overcoat Surface by Irradiating Visible Laser Light**, ***L. Zhu***, *J. Zhang, T. Liew, K. Ye,* Data Storage Institute, Singapore

A thin lubricant film was applied on a magnetic hard disk carbon overcoat to reduce friction force, resist corrosion and minimize wear. Further treatment of the lubricant is to improve one or more of its properties for its compatibility with increasing magnetic recording densities. In this paper, we investigate the chemical bonding of perfluoropolyether lubricant molecules with carbon overcoat surface by irradiating visible laser light. A Nd:YAG laser with a wavelength of 532nm was used to irradiate the lubricant film (2 nm) on carbon overcoat surface in ambient environment. Samples were analyzed using the time-of-flight secondary ion mass spectroscopy. We found that with increasing laser energy, the ion yield of the end group CF2CH2OH decreases indicating the formation of chemical bonds of the end group with the active sites on the carbon overcoat surface. Secondary ion mapping of the laser irradiated area shows that fluorine and backbone fragments COF2 and C2OF4 are concentrated in the bonding area. This is in sharp contrast with our previous results with UV laser irradiation on the lubricant where the abundance of the end group remains almost constant with increasing laser energy and two unique backbone peaks are generated, indicating direct scission of the lubricant molecules in UV regime.

8:40am **AS-TuM2 TOF-HREELS and AFM Characterization of Highly Oriented Teflon (PTFE) Films**, ***Z. Yang***, *G. Bernhardt, R.L. Jackson, L.J. LeGore, P. Kleban, W.N. Unertl, B.G. Frederick,* University of Maine

Highly oriented polytetrafluoroethylene (PTFE) films are potentially useful as substrates for anisotropic growth of organic and bio-materials and as model surfaces for studying surface modification. High resolution electron energy loss spectroscopy (HREELS) has advantages of surface specificity, sensitivity and the possibility of non-dipolar interaction mechanisms, but has required relatively long data acquisition times. We have developed a novel time-of-flight (TOF-HREELS) spectrometer, which utilizes a throughput advantage to dramatically reduce acquisition times.[1] PTFE films were deposited onto sputtered films of gold and platinum on oxide-covered Si wafers by the friction transfer process.[2] The samples were studied by AFM to characterize the film roughness and thickness. The AFM images reveal long, straight ribbons of PTFE parallel to each other when deposited at a substrate temperature of 220 °C and a pressure of 1kg/8 mm^2. Comparisons are made between HREELS spectra obtained by the conventional instrument and the TOF-HREELS spectrometer.

[1] R. H. Jackson, et al., Surf. Sci. (2002), in press; L. J. LeGore, et al., ibid.

[2] P. Bodö, M. Schott, Thin Solid Films 286 (1996) 98.

9:00am **AS-TuM3 Surface Analysis of Poly (dimethylsiloxane) using Time-of-Flight Secondary Ion Mass Spectrometry**, *J.A. Gardella,* ***R. Rey-Santos***, The State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful techniques for surface analysis. ToF-SIMS has been used to study the secondary and tertiary structures of polymers. The Langmuir-Blodgett technique has been used to prepare thin films of poly (dimethylsiloxane) (PDMS) monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FT-IR) has been used to identify the surface structure of PDMS films. The use of the statistical chain breaking model of poly (alkyl methacrylates) by Zimmerman, Hercules, and Benninghoven published in Analytical Chemistry in 1993, helped us to determine the statistical chain breaking model for PDMS. Our goal is to use polymers as model systems to investigate the ion formation mechanisms and provide information about the long-range forces between polymer chains.

9:20am **AS-TuM4 Surface Analysis of Novel PDMS-Containing Amphiphilic Graft Copolymer by X-Ray Photoelectron Spectroscopy**, ***L. Chen***, *P.L. Valint, J.A. Gardella*, State University of New York at Buffalo

The surface composition 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 has been determined by angle dependent X-Ray Photoelectron Spectroscopy (XPS). The effects of PDMS graft length, PDMS bulk content and Molecular Weight Distribution (MWD) on the surface composition were investigated. It was found that the PDMS surface concentration increased with the increase of PDMS bulk content, but the effect of the bulk content on PDMS surface concentration for copolymers with long graft chains is much smaller than that for copolymers with short graft chains. For a given PDMS bulk content, a longer PDMS graft gave a surface richer in siloxane. The dominating factor in defining the siloxane surface segregation is not bulk content but graft length for these copolymers. PDMS surface concentration of copolymers with narrow MWD was observed higher than that with broad MWD, this could be explained by the purification process the copolymers went through during preparation.

9:40am **AS-TuM5 Embedding of Noble Metal Nanoclusters into Polymers as a Potential Probe of the Surface Glass Transition : Study with XPS**, ***V. Zaporojtchenko***, Christian-Albrechts University of Kiel, Germany

Embedding of noble metal nanoclusters into polymers is introduced as a novel method with a strong potential to follow the polymer glass transition at the surface.[1] X-ray photoelectron spectroscopy (XPS) in combination with transmission electron microscopy (TEM) was used to characterize the formation of nanoclusters during the noble metals (Au and Cu) deposition onto different polymers and to study the embedding of nanoclusters into polymers. The size of the metallic clusters and an embedding depth were determined using a mathematical correction of the XPS intensity.[2] This procedure is based on the measurement of the ratio of two XPS lines of the same metal with different binding energies and their attenuation length. X-ray photoelectron spectroscopy (XPS) has been applied to study the embedding of Cu and Au nanoclusters into polycarbonate, nylon as well as polystyrene films with different molecular weight by annealing the polymer films above the glass transition temperature Tg . It is shown that the temperature dependence of the embedding depth is clearly correlated to the glass-transition temperature of the polymer. Our investigations strongly support a depression of Tg at the surface compared with that of the polymer bulk. This supports the view that the molecular motion is enhanced near the surface due to the additional degrees of freedom. The enhancement of the surface glass transition temperature was observed due to Ar ion treatment of the polymers. The changes of Tg , which are qualitatively related to cross-linking, depend on the ion fluencies in the range of 10E13 - 10E14 cm^{-2} .

[1] V. Zaporojtchenko, T. Struskus, J. Erichsen, F. Faupel, Macromolecules 34(5) (2001) 1125.

[2] V. Zaporojtchenko, K. Behnke, T. Struskus, F. Faupel, Surf. Interface Anal. 30 (2000) 439.

10:00am **AS-TuM6 Surface Composition in Isotopic Polymer Mixtures Based on ToF-SIMS and Neutron Reflectivity**, *A. Takahara, D. Kawaguchi,* ***K. Tanaka***, Kyushu University, Japan, *S. Tasaki,* Kyoto University, Japan, *M. Tozu, T. Hoshi,* Ulvac-Phi, Inc., Japan, *T. Kajiyama*, Kyushu University, Japan

Surface composition in blend films composed of monodisperse polystyrene (hPS) with the number-average molecular weight, Mn, of 19.7k and deuterated monodisperse polystyrene (dPS) with Mn of 847k was examined by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) in conjunction with neutron reflectivity (NR). Although hPS has higher surface energy than dPS, ToF-SIMS and NR revealed that hPS was enriched at the outermost surface of the films. The surface segregation of hPS can be accounted for by the molecular weight disparity for both components, that is, an entropic effect.

10:20am **AS-TuM7 SPM Structural Study of Phase Segregation, Thermal Behavior, and Aging of Poly(Ester Urethane) Compression Molded Samples**, ***M.E. Hawley***, *E.B. Orler, D.A. Wrobleski, R.P. Hjelm*, Los Alamos National Laboratory

Only a limited number of structural studies have been performed on segmented poly urethanes using tapping mode scanning probe techniques to determine both the nanostructure and the corresponding nanophase segregation of hard and soft segments within the samples. This type of information is needed to better understand the mechanical and thermal properties of these materials and to facilitate modeling efforts. In order to address these issues, we have fabricated a compression molded segmented poly(ester urethane) samples with varying hard (HS) to soft segment (SS) ratios. Samples were examined using scanning probe phase imaging techniques to obtain the topography and map the corresponding HS and SS segregation before and after heating to over 100 °C both ex-situ and in-situ to and correlate those results with thermal absorption data. Changes in structure were followed as a function of time to address aging issues. A number of significant differences were observed before and after these thermal plastic samples were heat treated. Variations in structure and heat-induced morphological changes were directly related to HS content. Fine 10 to 10 nm thick lamellar- or fibril-like structures were most prominent in samples with lower HS content while harder, thicker elongated structures seen to a limited extent on all samples dominated the surface of high HS samples. The disappearance of the fine structures appears to be related to a peak in the endothermal data. The reappeared emanating from the large rod-like structures first as short branching then completely covering the surface after less than 2 days. Surface roughness increased in the process by approximately 10x.

10:40am **AS-TuM8 Surface-induced Ordering of Poly(ethylene terephthalate) Studied with In-situ Grazing Incidence X-ray Diffraction**, ***J.E. Macdonald***, *M. Durell, D. Trolley,* Cardiff University, UK, *P.C. Jukes, A.M. Higgins, R.A.L. Jones*, University of Sheffield, UK

Grazing incidence x-ray diffraction has been performed during in-situ annealing of a polymer thin film for the first time to investigate the molecular configuration at the surface of poly(ethylene terephthalate) (PET) films during crystallisation. The structural ordering at the surface of the film was compared directly with that in the bulk of the film by employing incident angles at and above the critical angle for total reflection. Ordering was observed at the surface at annealing temperatures of 85-95°C, while the bulk of the film remained amorphous. Parallel in-situ atomic force microscopy studies give direct images of the spherulites formed at the surface. Both techniques in tandem thus yield the structure and kinetics of ordering at the surface and in the bulk of the film.

11:00am **AS-TuM9 A Novel Micromechanical Platform to Measure the Surface Stress Produced by Electroactive Polymers**, ***V. Tabard-Cossa***, *M. Godin, O. Laroche, B. Seivewright,* McGill University, Canada, *A. Badia,* Universite de Montreal, Canada, *B. Lennox, P. Grutter,* McGill University, Canada

A novel platform to measure the surface stress produced by ionic electroactive polymer (EAP) materials is presented. In order for these materials to be used as conventional microactuators, it is important to accurately characterize them and, in particular, quantify the surface stress associated with the applied potential, so that their mechanical limitations and advantages can be determined. Micromechanical cantilever-based sensors, with their high sensitivity and fast response, are ideal tools for the characterization of these molecular scale electromechanical actuators. A standard, three-probe, electrochemical system is used, with an Ag/AgCl reference electrode and a Pt counter electrode, in a combined apparatus with a surface stress AFM cantilever-based sensor, where the cantilever simultaneously serves as the working electrode to obtain surface stress data in parallel with cyclic voltammetry (CV). The instrument, capable of integrating the electrochemical setup with the surface stress sensor requirements, will be described. The experimental setup, with the optimal cell geometry, necessary electronics and required software and hardware components will be shown. Dodecyl benzenesulfonate-doped polypyrrole (PPy(DBS)) in an aqueous solution of Na(DBS) is the EAP studied. Potentiostatic growth results of polypyrrole films on gold coated AFM cantilevers and their characterization by cyclic voltammetry and AFM/SEM will be presented. In addition, bending of the PPy/Au coated cantilever bilayer structure is measured as a function of applied potential. The equation used to calculate the surface stress induced during cyclic voltammograms circumvents the need to know the cantilever's Young's modulus by using readily measurable cantilever properties.[1] Finally, surface stress as a function of applied potential will be shown and its correlation with oxidation and reduction peaks addressed.

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[1] M. Godin et al., Appl. Phys. Lett. 79, 4 (2001).

11:20am **AS-TuM10 Photoelectron Spectroscopy of Conjugated Polymers**, *R. Friedlein,* Linköping University, Sweden, *S.L. Sorensen,* Lund University, Sweden, *W. Osikowicz, M.P. de Jong,* ***W.R. Salaneck***, Linköping University, Sweden **INVITED**

Conjugated polymers have been studied by photoelectron spectroscopy and other related surface science techniques for over two decades. In the past few years, however, several advances have been made in classical techniques. Some aspects of X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), as applied to conjugated polymers, will be hi-lighted. New results on high quality conjugated polymers will be presented.

Advancing Toward Sustainability Topical Conference Room: C-210 - Session AT-TuM

Aerosols and Climate Change, Growing Energy Demands, and Benign Semiconductor Manufacturing

Moderator: R.L. Bersin, Emergent Technologies Corporation

8:40am **AT-TuM2 Individual Particle TOF-SIMS Imaging Analysis of Aerosol Collected During the April 2001 Asian Dust Event**, ***R.E. Peterson***, *B.J. Tyler,* University of Utah

Time of Flight Secondary Ion Mass Spectroscopy can provide information regarding the surface chemistry, including both organic and inorganic compounds, of individual atmospheric aerosol in the micrometer size range. X-ray analysis has commonly been used to analyze the composition of single particles but has several important limitations. Principally, X-ray analysis cannot be used to study organic compounds in the aerosol, it offers low sensitivity for light elements common in crustal material and it cannot distinguish isotopes. TOF-SIMS has the potential to provide superior performance in these areas. We have developed statistical image processing methods to allow extraction of individual particle spectra from TOF-SIMS images. In mid April 2001 a strong Asian dust event was tracked by satellite across the Pacific Ocean and into the continental United States. While Asian dust deposition is common in Hawaii, strong events characterized by significant visibility degradation have been much less frequently reported in the Rocky Mountain west. Samples were taken during and after the event at the University of Utah in Salt Lake City, Utah. Size segregated samples were collected on aluminum substrates using an 8 stage Graseby-Anderson cascade impactor and total aerosol samples were collected with 47 mm Fluoropore filters. Surface and depth profile analysis of the particles was performed using a Phi Trift I TOF-SIMS instrument. Statistical methods, including PCA, mixture models and neural networks, were used to extract spectra of individual particles from the TOF-SIMS images and to classify particles based on their surface chemistry and depth profiles. Differences in both the chemistry and size distribution of the particles could be seen between the aerosol collected during the Asian dust event and aerosol collected post-event at the University of Utah site.

9:00am **AT-TuM3 Atmospheric Aerosol Detection, Analysis and Transformation**, ***P.H. McMurry***, University of Minnesota **INVITED**

Atmospheric aerosol particles scatter light, deposit on surfaces and in lungs, and participate in chemical transformations. This lecture will focus on the formation of new particles in the atmosphere by homogeneous nucleation, and on the chemical and physical properties of such freshly nucleated particles. It is important to understand nucleation since it affects the number concentrations of particles in the atmosphere. Number concentrations, in turn, determine the extent to which clouds form, and clouds play a central role in the earth's radiation balance. Our understanding of nucleation has progressed rapidly in the past few years due to recent advances in measurement. Routine measurements of aerosol size distributions down to 3 nm are now possible. Such measurements have shown that nucleation is ubiquitous in the atmosphere. We now are carrying out measurements that will help us understand what species are responsible for the formation and growth of new atmospheric particles. We have developed techniques to measure properties of freshly nucleated (3-10 nm) particles, including their tendency to absorb water, their volatility as a function of temperature, and their chemical composition. In this lecture these new measurement methodologies will be described, and our recent measurements will be discussed.

9:40am **AT-TuM5 Future Environmental Issues Associated with the Generation of Electricity**, ***J. Stringer***, EPRI **INVITED**

Over the next twenty to forty years the world-wide demand for electricity will increase substantially. In part, this is because of the increasing energy demand, particularly in the developing countries, and the increasing fraction of this energy that will be provided as electricity. In part, it is because of the increase in the global population, with most of this increase taking place also in the developing countries. Certainly for the immediate future, this demand will be met largely by the burning of fossil fuels. This will result in significant environmental challenges, and the major challenge is probably the emission of CO_2. It is not the object of this paper to discuss the issue of global warming: it is enough that there will almost certainly be a continuing global political pressure to limit these emissions. The current situation will be reviewed, with special emphasis to the United States, and the probable global developments will be discussed. The current options will be described, including methods that are being proposed for the capture and sequestration of the emitted CO_2. The major issues relate to the separation of the CO_2 from the relatively dilute concentration of the gas in the very large volume of the combustion off-gas, and the transport of the concentrated gas to a repository. The security and permanence of the various proposed repositories clearly must also be clearly defined and monitored. Alternative paths, including the decarbonization of the generation of electricity, will also be discussed. This decarbonization has been in progress for many years, and clearly the end-point in terms of combustion-based generation is represented by the use of hydrogen as the fuel. Production of hydrogen, either by separation of hydrogen from a hydrocarbon such as methane, or by reforming, presents significant issues, and the transportation and storage of the hydrogen are also issues which have still to be solved. Non-combustion based methods - nuclear fission, hydroelectric generation, biomass combustion, wind-power, and photovoltaic generation - will be briefly reviewed in terms of their possible contributions within the time scale defined above. Other aspects of the overall problem include improved efficiencies in the generation of electricity, reduced losses in transmission, and continued improvements in the efficiency of end use. Most importantly, all of this must be achieved with a minimum economic impact

10:20am **AT-TuM7 The Challenge of Relating Basic Research to the Solution of Environmental Problems**, ***D.R. Baer***, Pacific Northwest National Laboratory

Many members of the research community have enthusiastically redirected their research efforts to address important national problems. This paper examines the difficulties researchers face in actually having an impact on solving these problems. Several examples demonstrate the willingness of researchers to undertake environmentally related research projects and to participate in efforts that help define a critical scientific agenda. However, evidence indicates that the transfer of new scientific information to environmental technology and application is a more difficult challenge. There are several barriers to the rapid transfer of new scientific information to technological practice. Barriers include the nature research funding, an accepted (mis)understanding of the relationship between pure and applied research, the challenges of basic scientists and engineers working on multidisciplinary teams and working with non-technical people and organizations who have a vested interest in the problem and solution. To have a significant impact on environmental problems, technologists need to become involved in many activities, well beyond those associated with laboratory research.

10:40am **AT-TuM8 ESH Performance Plays a Vital Role in Sustaining the Growth of the Semiconductor Industry**, ***C. Miller***, *W. Worth*, International Sematech **INVITED**

Rapid technology advances and rapid growth have historically been the basis for the success of the semiconductor industry. Over the last twenty five years the industry has enjoyed a growth rate (~15%) which far exceeds the growth rate of the U.S. economy overall (3-4%). To ensure that this rapid growth rate can be sustained into the future, it is important that the industry makes efficient use of natural resources, minimizes any impact on the environment, and ensures the protection of its workers and the communities in which it operates. It has been repeatedly shown that resource efficiency is linked to lower operating costs and better environmental performance. International SEMATECH's Environment, Safety and Health (ESH) division is engaged in several projects that are aimed at enabling continued, sustainable growth for the industry. These include energy and water conservation, perfluorocompound (PFC) emissions reduction as well as early ESH assessment of the multitude of new chemicals and materials being considered for 157nm photolithography, ultra-low dielectrics, and advanced gate stacks. The timely assessment of any potential ESH impacts associated with these novel materials is essential to ensure that they are used in a safe and environmentally sound manner through cost-efficient ESH solutions and controls. This paper will describe the approach and results of SEMATECH's efforts in the areas of resource conservation, PFC emissions reduction and early identification of potential ESH impacts associated with the next generation semiconductor chemicals and materials.

Biomaterials
Room: C-201 - Session BI+SS-TuM

Platforms for Non-fouling and Patterned Surfaces
Moderator: D.G. Castner, University of Washington

8:20am **BI+SS-TuM1 Molecular Assembly and Micro-/Nanopatterning Techniques on Oxide-based Surfaces for Controlling Non-specific and Specific Interactions**, ***M. Textor***, ETH Zürich, Switzerland **INVITED**

The assembly of multifunctional molecules at surfaces has become an important technique to design interfaces for biosensor applications and model surfaces for cell-biological studies. While alkanethiol self-assembled monolayers on gold surfaces are routinely used today, corresponding systems for oxide-based surfaces had first to be developed. The objective is to produce interfaces via cost-effective, robust techniques that allow the elimination of non-specific protein adsorption and the addition of ligands in controlled density to sense the biological environment. Poly(ethylene glycol)-grafted polyionic copolymers assemble spontaneously from aqueous solutions at charged interfaces resulting in well-defined, stable monolayers. The degree of interactiveness of the resulting surface with the bioenvironment can be controlled quantitatively through the design of the polymer architecture. If the polymer is functionalized with bioligands such as biotin, biosensor interfaces with quantitative control over ligand density can be efficiently produced. Chemical patterning of surfaces into adhesive and non-adhesive areas has become an important tool to organize in a controlled manner biological entities such as cells and biomolecules at interfaces. A novel surface modification technique is presented that uses a lithographically pre-patterned, inorganic substrate, which is subsequently converted into a pattern of biological contrast via area-selective molecular assembly processes. Biologically meaningful patterns of protein-adhesive and non-adhesive areas in a size range from micrometers to as small as 50 nm could be produced. Fluorescence microscopy, XPS, ToF-SIMS and AFM were used to control ex situ each surface modification step, while the kinetics of the surface reactions including the interaction with biological media were monitored in situ with an optical sensor (OWLS) and the quartz crystal microbalance (QCM-D) technique.

9:00am **BI+SS-TuM3 Orientation in Oligo(ethylene glycol) Functionalised Self Assembled Monolayers Adsorbed on Gold Depending on the Oligomer Length**, ***M. Zwahlen***, University of St Andrews, UK, *S. Herrwerth, W. Eck, M. Grunze*, University of Heidelberg, Germany, *G. Haehner*, University of St Andrews, UK

Oligo(ethylene glycol) (OEG) functionalised self-assembled monolayers (SAMs) have attracted considerable attention due to their protein repelling properties. The underlying mechanism is of high scientific relevance for future applications but has not yet been completely resolved. 'Steric repulsion', which describes the resistance to non-specific protein adsorption in the case of the polymer PEG does not explain the mechanism in densely packed SAM structures sufficiently. It has been suggested that one crucial parameter for the interaction of OEG-modified surfaces with their environment is the orientation in the organic adlayer. This has motivated a number of structural investigations on OEG-SAMs. As a contribution to the ongoing discussion, we present a study of the orientation in OEG-functionalised SAMs adsorbed on gold. It was measured as a function of the number of EG units in the molecule using soft X-ray absorption spectroscopy (NEXAFS). The results and their implications on the vacuum structure of the OEG-films will be discussed. The data will be compared to those obtained with complementary experimental techniques under similar as well as under different environmental conditions.

9:20am **BI+SS-TuM4 DOPA: A Novel Anchor for PEGylation of Biomaterials**, ***J.L. Dalsin***, *P.B. Messersmith*, Northwestern University

It is widely recognized that modification of biomaterial surfaces with biocompatible polymers is a useful strategy for controlling protein adsorption and cell interactions with materials. The physical or chemical immobilization of poly(ethylene glycol) (PEG) has routinely been used to limit biological fouling of surfaces. Many of the current PEGylation methods, however, are limited by high costs and complexity of synthesis. Most importantly, each of the present strategies vary widely depending on the characteristics of the substrate, and are typically different for metal, metal oxide, and polymer substrates. We are developing a new biomimetic strategy for anchoring PEG to biomaterial surfaces. Our approach is to utilize linear and branched PEGs end-functionalized with DOPA. DOPA is found in significant quantities in the adhesive proteins secreted by marine mussels for attachment to underwater surfaces, and recent evidence suggests that the presence of DOPA promotes strong and durable adhesion of these proteins to metal, metal oxide, and polymer surfaces. Recently, it has been shown that DOPA-containing peptides adhere strongly to gold surfaces, mediated by metal-oxygen bonds formed between the catechol group of DOPA and Au atoms at the metal surface. In this study, we report our findings on the use of DOPA as an anchor for PEGylation of biomaterial surfaces. A variety surfaces were modified by adsorption of DOPA-modified-PEGs from solution, and the presence of PEG on the surface was confirmed with a number of surface characterization techniques, including XPS and TOF-SIMS. The behavior of cells on modified and unmodified gold surfaces was evaluated in an attempt to optimize the conditions for DOPA-mediated PEGylation of metals, metal oxides, and polymers.

9:40am **BI+SS-TuM5 Characterization of Non-Fouling Surfaces by Matrix-Assisted Laser Desorption / Ionization Mass Spectrometry**, ***G.R. Kinsel***, *J. Zhang, R.B. Timmons, M. Li*, University of Texas at Arlington

Matrix-Assisted Laser Desorption / Ionization (MALDI) mass spectrometry 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. An attractive feature of this analytical approach is the relative simplicity of the sample preparation. In principle, all that is required is that the analyte of interest be mixed with an appropriate "matrix" (typically a small, functionalized aromatic compound) and the two compounds allowed to co-crystallize on some type of support. In recent work, however, we have shown that the nature of the support can have a marked effect on the magnitude of the analyte MALDI ion signal. Specifically, we have shown that as the binding affinity of the support for the analyte increases, the analyte MALDI ion signal decreases. This relationship has been used to develop a quantitative method for the determination of the protein binding affinity of various materials based on a MALDI standard additions approach. In the present studies the MALDI method has been used to quantitate the protein binding affinity of a number of "non-fouling" surfaces. These surfaces include plasma polymerized PEO, plasma polymerized CH3OH, PEO-PU block copolymers, and PEO grafted surfaces. The "non-fouling" properties of these surfaces are compared with the protein binding affinity of other conventional polymers including PTFE, LDPE, etc. In addition, the binding properties of the various surfaces are examined with relation to a variety of peptides and modest sized proteins.

10:00am **BI+SS-TuM6 Polymerized Planar Biomembrane Assemblies**, ***S. Saavedra***, University of Arizona

The utility of planar supported lipid bilayers (PSLBs) as protein-resistant coatings in molecular device technologies is hampered by the chemical and mechanical instability of these structures relative to (for example) alkylsiloxane self-assembled monolayers. We have been investigating cross-linking polymerization of diene-functionalized lipids as a strategy to enhance the inherent instability of PSLBs. The membranes are self-assembled by vesicle fusion, then polymerized in situ by a redox-initiated chemistry. In contrast to diacetylene-based materials, these new diene-based materials contain relatively few defects. They are stable to conditions that would destroy a fluid membrane (e.g. exposure to air, surfactants, solvents), yet retain the characteristic protein resistance of a fluid PSLB. Thus these structures appear to possess both the stability and inertness required for implementation of PSLBs in many technological applications. This talk will focus on preparation, characterization, and protein functionalization of diene-based PSLBs.

10:20am **BI+SS-TuM7 Protein Binding at Biomembrane Interfaces**, ***P.S. Cremer***, Texas A&M University **INVITED**

We have used a combination of lithographic patterning techniques and microfluidics to spatially address fluid phospholipid bilayers at the liquid/solid interface. These systems are capable of multivalent ligand-receptor attachment chemistry. Moreover, on-chip designs allow for high throughput temperature, concentration, pH, and ionic strength measurements in an environment which closely mimics a cell membrane interface.

11:00am **BI+SS-TuM9 Surface Characterisation of Supported Lipid Layers**, ***S.L. McArthur***, *M.W. Halter, V. Vogel, D.G. Castner*, University of Washington

The boundaries of biological cells and organelles are defined by complex and dynamic membranes constructed from an array of lipids, proteins and carbohydrates. These interfaces have a range of specific functions and properties, one of which is their ability to prevent non-specific protein adsorption, making membrane mimics an attractive option for a variety of in vivo and in vitro biomedical implant and diagnostic applications. The development and characterization of complex biomimetic surfaces presents a challenge in terms of their initial formation, long-term stability and integrity in a variety of environments and the maintenance of bilayer fluidity. In this study we detail the development and chemical characterization of supported lipid monolayers. The structure was formed by coupling HEMA to a glass support and subsequently activating it with CDI to couple the headgroups of the lipid, dimyristoyl ethanolamine (DMPE). The success of the immobilization procedure was investigated by XPS and ToF-SIMS. A number of different lipid transfer regimes were explored. Results illustrated that the samples produced using Langmuir-Blodgett transfer at high pressure (20 mN/m) had the largest fraction of the transferred lipids remaining at the surface after 5 minutes sonication in ethanol. Fluorescence microscopy of the lipid layers showed that the presence of this limited number of anchored lipids acted to stabilize the monolayer and maintain its integrity without having a detrimental effect on layer fluidity.

11:20am **BI+SS-TuM10 Purification of Mobile, Membrane-tethered Proteins in Micropatterned Supported Lipid Bilayers**, ***L. Kam***, *T.D. Perez, W.J. Nelson, S.G. Boxer*, Stanford University

Supported lipid bilayers are a unique system for studying fluidic membranes in a controllable in vitro format. A variety of methods for tethering proteins to supported bilayers provide a powerful reductionist model of cell-cell recognition and activation. However, contemporary methods for preparing membrane-tethered protein systems typically incur an immobile fraction; this population complicates and, at worst, subverts interpretation of experimental results. Here, we present a method for separating a population of mobile, GPI-tethered protein from an immobile fraction in a supported lipid bilayer. A GPI-modified protein based on the cell-cell adhesion protein E-cadherin was introduced into Egg PC vesicles by detergent dialysis. On a glass substrate, two adjacent and connected regions of supported lipid bilayer were created using a converging flow configuration. One region contained both mobile and immobile populations of GPI/cadherin while the other contained Egg PC alone. An electric field applied tangentially to the surface induced migration of the mobile, but not immobile, protein into the region of Egg PC, generating a purified population of these proteins which may then be isolated for analysis or further experimentation free from the immobile fraction. Importantly, this method is independent of the specific factors influencing protein mobility and thus generally applicable.

11:40am **BI+SS-TuM11 Spatial Control of Cell Attachment Using Micropatterned Plasma Polymers**, ***S.A. Mitchell***, *N. Emmison*, The Robert Gordon University, Scotland, UK, *A.G. Shard*, Sheffield University, England, UK

In recent years, there has been increased interest in the spatial control and regulation of cellular attachment and growth. Several techniques have been developed to produce surfaces with a well-defined chemical heterogeneity that are suitable for the rapid adhesion, spreading and proliferation of cells. Spatial control and sub-cellular pattern resolution has been successfully demonstrated by techniques such as micro-contact printing of self-assembled monolayers.[1] However, the labour intensive, time consuming preparation and ready oxidation of these surfaces limit the utility of these devices. Additionally, they are only applicable to substrates that are rarely used in biomedical devices. We have employed plasma polymerisation as an alternative method for the chemical patterning of surfaces, although the chemical composition of these surfaces is more difficult to control, this one-step procedure is rapid and cost effective.[2] The resulting surfaces have both a chemical functionality and a pattern resolution comparable to alternative techniques.[3] They may be applied to virtually any substrate, including relatively rough surfaces such as tissue culture polystyrene, greatly increasing their applicability. We describe the patterned deposition of plasma polymers onto a variety of substrates and outline some of the advantages and limitations of the technique. Physicochemical characterisation of the plasma polymers is performed with XPS, AFM and contact angle analysis. The culture of mammalian cells on patterned substrates demonstrates their ability to spatially regulate cell attachment and spreading.

[1] M Mrksich and G M Whitesides, Tibtech, 13, 228-235(1995)

[2] N A Bullett, R D Short, T OLeary, A J Beck, C W I Douglas, M Cambray-Deakin, I W Fletcher, A Roberts, C Blomfield, Surf. Interface Anal., 31, 1074-1076(2001)

[3] L Dai, H J Griesser, A W H Mau, J. Phys. Chem. B, 101, 9548-9554(1997).

Electronic Materials and Devices
Room: C-107 - Session EL+SC-TuM

Heterojunctions
Moderator: R.S. Goldman, University of Michigan

8:20am **EL+SC-TuM1 Epitaxial Growth and Characterization of CdS Layers Grown on InP (001) using Molecular Beam Epitaxy from Atomic Sulfur Beam and Thermally Evaporated Cd**, ***J.W. Choi***, *M.-A. Hasan, A. Bhupathiraju*, University of North Carolina at Charlotte

Recent progress in epi-ready InP(E_g=1.35 eV) wafer growth has prompted new applications of heterojunction devices and quantum structures based on closely lattice matched epitaxial films on InP. Cadmium sulfide (CdS), a direct bandgap material (E_g=2.5 eV), has a small lattice mismatch to InP (0.63%) that can facilitate optoelectronic integration on InP. In this work, growth of CdS on InP (001) substrates is investigated using modified molecular beam epitaxy (MBE). Two growth methods are investigated. In the first method, epitaxial growth is conducted by atomic sulfur (S) beam from an RF atomic source with H_2S as the source gas while Cd is supplied from a cracker cell. The RF source is operated at 13.56 MHz and produces an intense monoatomic sulfur beam (λ= 930.5 nm emission peak measured by plasma spectroscopy). In the second method, deposition is performed using CdS sublimation from a solid CdS using a conventional Knudsen cell. Rinsing by methanol is used to clean the epi-ready InP (001) substrates. Final substrate cleaning is achieved by thermal desorption (530-550°C) in vacuum. RHEED shows InP (001) 2x1 surface after thermal cleaning. In both methods, in-situ RHEED measurement indicates epitaxial growth of zincblende CdS; Auger electron spectroscopy (AES) shows stoichiometric CdS within the AES resolution limit. AES depth profiles also indicate an abrupt InP/CdS interface for all temperatures investigated. The growth rate of CdS is primarily governed by Cd flux as indicated by the activation energy measured from the flux-dependence of the growth rate. Atomic force microscopy (AFM) shows measurable dependence of surface roughness on growth method. For growth using an RF atomic source, average surface roughnesses of 1-2 nm is measured for all growth temperatures, layer thicknesses, and flux ratios with no evidence of island formation; higher roughness values (10-20nm) were typically measured for growth from solid CdS.

8:40am **EL+SC-TuM2 Structure of InAs/InP Interfaces Formed During Metalorganic Vapor-Phase Epitaxy**, ***D.C. Law***, *Y. Sun, C.H. Li*, University of California, Los Angeles, *S.B. Visbeck*, Siemens & Shell Solar Gmbh, *G. Chen, R.F. Hicks*, University of California, Los Angeles

We have studied the initial stages of heterojunction formation during the metalorganic vapor-phase epitaxy of indium arsenide on indium phosphide. Exposing an InP (001) film to 10 mTorr of tertiarybutylarsine below 500 °C results in the deposition of a thin InAs layer from 1.5 to 5.0 atomic layers thick (2.3 to 7.5 Å). The surface of this epilayer remains atomically smooth independent of arsenic exposure time. However, in an overpressure of tertiarybutylarsine at or above 500 °C, the arsenic atoms diffuse into the bulk, creating strained InAsP films. These films form three-dimensional island structures to relieve the built-up strain. The arsenic transport into InP can be described by a constant-source diffusion model with the arsenic number density given by: $N_{As} = 0.5\ N_T \mathrm{erfc}\ (x/2\sqrt{(D_{eff}t)})$. The activation energy and pre-exponential factor for arsenic diffusion into indium phosphide are: $D_o = 2.3\pm1.0 \times 10^{-7}\ cm^2/s$ and $E_d = 1.7\pm0.2$ eV.

9:40am **EL+SC-TuM5 Device Quality III-V Compound Semiconductor Epitaxy on Si Via SiGe Interlayers**, ***S.A. Ringel***, *C.L. Andre, A. Khan, M. Gonzalez, M.K. Hudait*, Ohio State University, *E.A. Fitzgerald*, Massachusetts Institute of Technology, *J.A. Carlin, M.T. Currie, C.W. Leitz, T.A. Langdo*, AmberWave Systems Corporation **INVITED**

Integration of III-V compounds with Si using direct epitaxial approaches has been an area of intense interest for years. Achieving this would enable a complement of electronic and optoelectronic capabilities that would generate new circuit functions with higher speed, and potentially simpler architecture. There is also substantial interest in III-V/Si integration where the primary purpose for Si is as an alternative substrate for III-V solar cells, which are conventionally grown on Ge or GaAs substrates. Compared to Si, these substrates are expensive, brittle and heavy, which are issues for this application. For both of these directions, the materials issues of how to integrate III-V compounds with Si without degrading electronic properties due to the mismatch in structural, thermal and chemical properties so that high performance devices can be achieved are the same. Here we show that growth of compositionally graded SiGe interlayers to accommodate lattice strain between a Si wafer and III-V epitaxial structures, coupled with monolayer-scale control over the formation of the initial III-V/IV interface to eliminate anti-phase domain disorder and block interface diffusion, together yield high quality AlGaAs/GaAs and InGaP/GaAs layers, heterostructures and minority carrier devices. Time resolved photoluminescence measurements of III-V double heterostructures reveal record high minority carrier lifetimes for GaAs on Si in excess of 10 nanoseconds, which is attributed to the simultaneous elimination of anti-phase domains and reduction of residual threading dislocation densities to below $1\times10^6\ cm^{-2}$. SIMS and capacitance-voltage measurements show that autodoping is effectively eliminated for GaAs grown on Ge/SiGe/Si, with no additional background impurities detected in the GaAs layers grown on these substrates. Solar cells are used as examples of minority carrier devices to show that high performance comparable to similar devices grown on conventional substrates has been achieved, with record voltage output for III-V cells grown on Si.

10:20am **EL+SC-TuM7 Interdiffusion, Alloying, and Defect Formation at GaN-Sapphire Interfaces**, ***X.L. Sun***, *S.T. Bradley, G.H. Jessen, L.J. Brillson*, The Ohio State University

The chemical and electronic structure at GaN/sapphire interfaces has a major influence on the electronic quality of epitaxial GaN films. In particular, degenerate doping usually occur near hydride vapor phase epitaxy (HVPE) grown GaN/sapphire interfaces that can affect lateral transport in overgrown devices. Near the interface, impurity diffusion, alloying, and related defect formation can occur at the high (1150°C) growth temperatures that is important to understand and control. We have used Auger electron (AES) and cathodoluminescence (CLS) spectroscopies in a UHV scanning electron microscope (SEM) to probe the chemical and electronic features at the HVPE GaN/sapphire interface in cross section in a nanometer scale. Specimens were cleaved and Ar sputtered in UHV to prepare clean interfaces with well-defined AES, CLS, and secondary electron images. AES images reveal dramatic evidence for diffusion of O from sapphire typically decreasing exponentially ~ 1 µm into GaN from 60% to the detection limit of < 1% surface coverage. The AES O intensity line profile mirrors corresponding SIMS O depth profiles and a donor level CLS emission vs. depth normal to the interface found in similar samples. Conversely, N with plateau concentrations of ~5 % extend ~ 2 µm into the sapphire and correspond spatially to a 3.8 eV defect emission attributed to Al-N-O complexes. While Ga exhibits no strong diffusion, interface Al decreases from 10% to < 1% over ~1 µm into the GaN and support evidence for AlGaN alloy formation, based on ~3.6 eV CLS emission above the GaN band gap at the buried interface. Depending on surface pretreatment and growth conditions, such interfaces can be abrupt to < 200 nm or can exhibit interdiffusion on a micron scale. These results illustrate a new approach to probe chemical and electronic interactions at semiconductor heterojunctions and reveal that both interdiffusion and alloying can occur and lead to extrinsic electronic effects.

10:40am **EL+SC-TuM8 Growth and Characterization of Heterjunction Diode Made of AlN on Si(111)**, ***K. Sundaresan***, *M. Jenkins, M.-A. Hasan*, University of North Carolina, *M. Sardela Jr.*, University of Illinois

Single crystalline hexagonal AlN(001) was grown on Si(111) using surface-reconstruction induced epitaxy. The Si(111)7x7 surface, generated under thermal etching under UHV, was first passivated by deposition of ~0.3 monolayer (ML) of Al at 650-700 °C. Each Al atom bonds to 3 Si atoms on the surface, which give rise to the well-known Si(111)root3xroot3 surface. The well ordered, Al-passivated Si(111)root3xroot3 surface was then used as a template to initiate epitaxial growth of AlN on Si. The growth was conducted by using an atomic N flux from a RF atomic source and thermal Al evaporation. X-ray diffraction showed single crystalline hexagonal AlN(001) with a full width at half maximum (FWHM), measured from the layer peak, equal to that of the Si substrate indicating highly oriented AlN layer. Epitaxial growth was achieved over a wide range of Al/N flux ratio and growth temperatures extending from 350 to 850 °C. AlN/Si heterojunction diode, fabricated using this method showed a breakdown voltage in excess of 350 V and a leakage current below 100 nA indicating high quality interface.

11:00am **EL+SC-TuM9 Observation of a Long-range Strain Field under SiO_2/Si Interface by using Multi-wave X-ray Diffraction**, ***W. Yashiro***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *K. Sumitani, T. Takahashi*, The University of Tokyo, Japan, *Y. Yoda*, Japan Synchrotoron Radiation Research Institute (JASRI), *K. Takahashi, T. Hattori*, Musashi Institute of Technology, Japan

In order to further improve the speed of VLSI circuits, new materials and device structures are being proposed in recent year. In particular there has been considerable interest in strained Si because it can lead to high-performance metal-semiconductor (MOS) devices. Transmission electron microscopy (TEM) is a technique to investigate local strains, e.g. around a dislocation at a phase boundary. In contrast with TEM, x-ray diffraction is powerful to investigate long-range ordered structures in crystals. In the present paper, we propose a new method that is sensitive to very small and long-range strains near surfaces of crystals by using multi-wave x-ray diffraction technique. To date, the Bragg reflection of x-ray diffraction is used to investigate such long-range strain fields. Recently Emoto et al. have indicated using the Bragg reflection that there exist very small strain fields on the side of the Si substrates if even ultra-thin layers are formed on them.[1] Our method is also a method using the Bragg reflection, but with the important distinction that we use a phenomenon, intensity modulation of the CTR scattering under a Bragg condition. This makes it possible to determine total displacements due to small lattice distortions, rather than local lattice spacing. The method was applied to a Si(001) wafer whose surface is covered with an oxide layer about 5 nm thick formed by microwave-excited high density Kr/O_2 plasma oxidation. We found that the total displacement of -0.18 Å in the direction normal to the surface exists under the interface between the oxide layer and the substrate.

[1] Emoto et al. Surf. Sci. 493 (2001) 221-226.

11:20am **EL+SC-TuM10 Measurement of Fermi Level Pinning Kinetics at Si-SiO$_2$ Interfaces: Implications for CMOS Transistor Manufacture**, ***K. Dev***, *M.Y.L. Jung, R. Gunawan, R.D. Braatz, E.G. Seebauer*, University of Illinois

Excessive transient enhanced diffusion (TED) of boron in silicon has been a major inhibitor to forming ultrashallow junctions for CMOS device applications. Current technology for junction formation relies on ion implantation into Si through SiO_2 to introduce dopants into the substrate, followed by rapid thermal annealing. We have investigated a previously unknown effect in this process sequence: charge build-up at the Si-SiO_2 interface and the resulting Fermi level pinning that can occur just after implant. Fundamentally, the charge build-up occurs in response to the ion-induced formation of dangling bonds that introduce energy states into the Si surface bandgap. The present work uses the optical technique of photoreflectance to demonstrate experimentally that these effects indeed exist and to measure their evolution kinetics. Photoreflectance is one of a class of modulation spectroscopies in which a semiconductor is periodically perturbed, and the resulting change in dielectric constant is detected by reflectance. The presence of a photoreflectance spectrum demonstrates unequivocally the existence of Fermi level pinning. The spectral amplitude scales linearly with the magnitude of built-in surface potential. Thus, we can deduce the pinning kinetics from the variation in amplitude. Our data demonstrate the existence of substantial pinning just after implant with 500 eV ions. Healing begins to occur in the vicinity of 400°C - within the temperature stabilization step in which interstitial clusters form. TED simulations using electrostatic boundary conditions derived from the photoreflectance experiments show that pinning deepens the pn junction significantly by transforming the Si-SiO_2 interface into a reflector of charged bulk interstitials.

11:40am **EL+SC-TuM11 Effects of Interface Properties on Degradation and Reliability of CMOS Devices with RPECVD Stacked Oxide/Nitride and Oxynitride Dielectrics**, *G. Lucovsky*, ***Y. Lee***, North Carolina State University, *Y. Wu*, Advanced Micro Devices, *C. Bae, J.G. Hong*, North Carolina State University

The effects of interface properties on device degradation and reliability of sub-2nm stacked oxide/nitride and oxynitride gate dielectrics prepared by the remote plasma enhanced CVD (RPECVD) technique under constant voltage stress (CVS) are investigated. Time evolutions of the transient SILC effect and threshold voltage (Vt) changes have been demonstrated to illustrate the breakdown behaviors and charge trapping during stress. More negative Vt shifts were observed for both P- and N-MOS devices, indicating the increases of hole trapping at the Si/SiO_2 interface. The p-channel transistors with stacked gate dielectrics received interface N_2/He nitridation and effectively suppress positive off-state leakage current, resulting in less device degradation as compared to the transistors without interface nitridation. This improvement is attributed to approximately one monolayer of N at the Si/SiO_2 interface which suppresses hole trapping. In addition, the influence of remote-plasma-assisted oxidation (RPAO) thickness on oxynitride device degradation and reliability is also studied. It is found that the devices with 0.6 nm RPAO exhibit improved GV characteristics, lower post-breakdown current and higher TDDB reliability compared to the devices with 0.8 nm RPAO. The generation of interface states and the correlation between carrier conduction mechanism and TDDB are also discussed.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+EL+SC-TuM

Ferromagnetic Semiconductors
Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI+EL+SC-TuM1 ab initio Magnetic Exchange Interactions in DMS and TiO$_2$**, ***M. van Schilfgaarde***, Arizona State University **INVITED**

The electronic structure of TM-doped TiO2 is studied within the ab initio local spin-density approximation and compared to more traditional TM-doped III-V DMS semiconductors. The conduction band of TiO2 consists mainly of Ti d character. Substituting a 3d TM for Ti, localized levels split off the conduction band; they are spin-split by an on-site exchange interaction and are responsible for the magnetism. The deepest level is of t2 symmetry and sweeps deeper in the gap in the series TM=V,Cr,Mn,Fe,Co. In the dilute alloy, the impurity level broadens into a narrow band. Thus the conductivity is expected to occur through a hopping mechanism, increasing with decreasing temperature as is observed in Co:TiO2. The character of this level is compared to TM d levels in the III-V DMS alloys (Cr,Mn,Fe):(Al,Ga,In)(N,P,As). Using a linear-response technique, the LSDA is mapped analytically onto a magnetic hamiltonian, which was used to investigate exchange interactions in random TM:TiO2 and (Cr,Mn):(Al,Ga,In)(N,P,As) alloys. Several novel phenomena will be described in the DMS case; for example Tc is predicted to increase monotonically with concentration for Cr:III-V, while for Mn:III-V Tc reaches a maximum at about 10% Mn concentration. The exchange interactions are found to have elements in common with both the carrier-mediated model and the double exchange/superexchange model, but also show important differences. For (V,Cr,Mn,Fe,Co):TiO2, the filling, magnetic moment and exchange interactions change systematically and are well described by a double exchange/superexchange model. However, for Tc to reach the observed RT in Co:TiO2, a source of holes is needed.

9:00am **MI+EL+SC-TuM3 Co$_x$Ti$_{1-x}$O$_2$ Anatase Heteroepitaxy on Si(001)**, ***T. Droubay***, Pacific Northwest National Laboratory, *A.C. Tuan*, University of Washington, *S.A. Chambers*, Pacific Northwest National Laboratory

With a Curie temperature above 700K, high remanence, and respectable coercivity, Co-doped TiO_2 anatase ($Co_xTi_{1-x}O_2$) is one of the more magnetically robust dilute magnetic semiconductor (DMS) materials currently under investigation. The future of this material for near-term device use as a spin injector requires deposition on and compatibility with traditional semiconductors such as silicon. Successful growth of crystalline oxides on silicon without oxidizing the underlying substrate is a formidable challenge. Our goal in this work is to grow epitaxial $Co_xTi_{1-x}O_2$ on Si(001) by using a suitable template layer, and then determine the resulting magnetic and electronic properties. We have previously shown that polycrystalline $Co_xTi_{1-x}O_2$ grown on Si(001) with its native oxide is ferromagnetic at room temperature. We are now working on $Co_xTi_{1-x}O_2$ heteroepitaxy on Si(001) using an ultrathin epitaxial $SrTiO_3$ buffer layer to prevent formation of titanium silicide and SiO_2 at the interface that result from a thermodynamic instability. An added benefit of the $SrTiO_3$ buffer layer is to generate a nearly zero conduction band offset to Si, which is essential for efficient n-type spin injection. A detailed analysis of the growth and properties of this heteroepitaxial system will be presented.

9:20am **MI+EL+SC-TuM4 Epitaxial Growth and Properties of Co-doped TiO$_2$ Anatase on LaAlO$_3$(001)**, ***S.A. Chambers***, *T. Droubay, C.M. Wang, S.M. Heald, S. Thevuthasan, A.S. Lea, C.F. Windisch, Jr.*, Pacific Northwest National Laboratory, *R.F.C. Farrow, L. Folks, J.-U. Thiele, M.G. Samant, R.F. Marks*, IBM Almaden Research Center

We are investigating Co-doped TiO_2 anatase heteroepitaxy on $LaAlO_3$(001) by oxygen plasma assisted molecular beam epitaxy. This material is of considerable interest because it is ferromagnetic well above room temperature. Thus, it may be a useful DMS for spintronics. The use of a higher growth rate (0.04 nm/sec) results in the nucleation of nanocrystals of rutile, the more stable form of TiO_2, within the continuous anatase film. The density of rutile nanocrytals increases as the quality of the substrate surface decreases. A lower growth rate (0.01 nm/sec) results in a much better film morphology, although a low density of smaller nanocrystals remains. Unlike the fast-grown films, these films show no evidence for any phase other than anatase. A number of techniques reveal that Co substitutes for Ti in the lattice and exhibits a +2 oxidation state; there is no evidence for elemental Co in any form. Each Co(II) substitution for Ti(IV) requires an O^{-2} anion vacancy in order to maintain charge neutrality, and evidence for such a vacancy is forthcoming from preliminary Co K-shell EXAFS. Such vacancies do not generate free carriers because they are uncharged. Hall effect and XPS measurements show that the films are n-type, the most likely cause being the presence of O atom vacancies that form during growth. These vacancies are independent of the presence of Co, and are negatively charged, thereby providing a source of free electrons from shallow donor states. The magnetization depends critically on free carrier concentration, as expected for a DMS. The exact Curie temperature is currently being determined, but appears to be in excess of 700K.

9:40am **MI+EL+SC-TuM5 Ferromagnetism in Mn-implanted Single Crystal Oxides**, ***D.P. Norton***, *S.J. Pearton, B.S. Jeong, Y.W. Heo, A.F. Hebard, N.A. Theodoropoulou,* University of Florida, *L.A. Boatner,* Oak Ridge National Laboratory, *Y.D. Park,* Seoul National University, Korea, *R.G. Wilson*, Consultant

Several semiconducting oxides, including ZnO, offer significant potential in providing spin-based functionality. Theoretical predictions suggest that room-temperature carrier-mediated ferromagnetism should be possible in Mn-doped p-type ZnO. In this paper, we report on the synthesis and properties of magnetically-doped semiconducting oxides, including ZnO. While previous efforts report no ferromagnetism in Mn-doped ZnO that is n-type due to group III impurities (consistent with theory), we find ferromagnetism in n-type ZnO that is co-doped with Mn and Sn. Hysteresis was observed in magnetization versus field curves for Mn-implanted n-type ZnO:Sn. Differences in zero field-cooled and field-cooled magnetizations persists up to ~ 150 K for Sn-doped ZnO crystals implanted with 3 at % Mn. These results indicate that ZnO doped with Mn and Sn may prove promising as a ferromagnetic semiconductor for spintronics.

10:00am **MI+EL+SC-TuM6 Self-compensation in Manganese-doped Ferromagnetic Semiconductors**, ***S.C. Erwin***, *A.G. Petukhov*, Naval Research Laboratory

We present theoretical evidence that the observed hole compensation in manganese-doped ferromagnetic semiconductors is due to interstitial manganese. We show that under the non-equilibrium conditions used during growth, interstitial Mn is readily formed near the surface by a simple low-energy adsorption pathway. In GaAs, isolated interstitial Mn impurities are electron donors, each compensating two substitutional Mn acceptors under p-type conditions. We show that partial compensation is a prerequisite for ferromagnetic order below the metal-insulator transition, and that the Curie temperature is highest when 1/6 of the Mn is interstitial.

10:20am **MI+EL+SC-TuM7 Ferromagnetic Semiconductor Heterostructures**[1], ***N. Samarth***, Penn State University **INVITED**

The molecular beam epitaxy (MBE) of ferromagnetic semiconductor heterostructures provides model systems for exploring fundamental issues in semiconductor spintronics. We provide an overview of heterostructures that combine the ferromagnetic semiconductor (Ga,Mn)As with conventional III-V and II-VI semiconductors, as well as with the metallic ferromagnet MnAs. After an introduction to the properties of MBE-grown (Ga,Mn)As, we discuss two classes of heterostructures: (a) hybrid ferromagnetic metal/semiconductor tunnel junctions that allow us to unambiguously probe spin injection into semiconductors using all-electrical techniques and (b) hybrid ferromagnetic/semiconductor photodiodes that serve as toy spintronic "devices" whose photo-response is magnetically controlled.

[1] This work is carried out in collaboration with S. H. Chun, K. C. Ku, S. J. Potashnik, and P. Schiffer, and is supported by grants from NSF, ONR and DARPA

11:00am **MI+EL+SC-TuM9 Epitaxial Growth of the Diluted Magnetic Semiconductor Cr_xGe_{1-x}**, ***G. Kioseoglou***, *A.T. Hanbicki,* Naval Research Laboratory, *Y.D. Park,* Seoul National University, Korea, *S.C. Erwin, B.T. Jonker,* Naval Research Laboratory

Ferromagnetic semiconductors (FMS) provide an opportunity to control spin-dependent behavior in semiconductor device heterostructures. Although much effort has focused on III-Mn-V materials such as GaMnAs , the mechanism of ferromagnetic order remains unclear; in particular the precise roles played by the dopant and the semiconductor host. We have explored this issue recently by developing a new Group-IV FMS, MnGe.[1] Here we report our work to develop an elemental FMS using a different dopant, Cr-doped Ge. This choice was motivated partly by our density-functional theory (DFT) calculations, which indicate that CrGe and MnGe should have comparable Curie temperatures. We report the epitaxial growth of Cr_xGe_{1-x} and describe the structural, magnetic and transport properties. The samples were grown on GaAs(001) substrates by molecular beam epitaxy at substrate temperatures of 40-500°C and the crystallinity was confirmed by the RHEED pattern. The Cr concentration used was 2-3% as determined from X-ray fluorescence. The RHEED pattern indicates single crystal growth for substrate temperatures above 200°C, with sharp 1x1 streaks. Growth at 40-70°C is initially single crystal, but the pattern becomes increasingly diffuse with film thickness. The samples are strongly p-type, and the hole density varies with the Cr concentration. SQUID measurements were performed on all samples to investigate the magnetic character of the Cr:Ge system. Samples grown at the higher growth temperatures exhibit only paramagnetic order. Co-doping with both Mn and Cr is also investigated. This work was supported by the DARPA SpinS program and ONR.

[1] Y.D. Park, et al., Science 295, 651 (2002).

11:20am **MI+EL+SC-TuM10 Cr-Doped III-V Ferromagnetic Semiconductors**, ***M.E. Overberg***, *G.T. Thaler, R.M. Frazier, C.R. Abernathy, S.J. Pearton, N.A. Theodoropoulou, A.F. Hebard,* University of Florida, *R.G. Wilson,* Private Consultant, *J.M. Zavada*, U.S. Army Research Office

Ferromagnetic semiconductors, consisting of a semiconductor host material doped with transition metal ions, are becoming increasingly prevalent in the literature as a candidate for incorporating the spin degree of freedom into device structures. To date, the vast majority of work in this area has centered on the incorporation of Mn into both II-VI and III-V materials by a variety of techniques. However, recent theoretical work has indicated that Cr may be a more suitable dopant for achieving room-temperature ferromagnetism within these materials.[1] In this paper, we will report on the preparation of GaCrN, GaCrP, and AlGaCrP by the direct implantation of Cr. The magnetic and magneto-transport (anomolous Hall Effect) properties of these films will be quantified both versus implantation dose (x=0.04, 0.06, 0.10) and versus post-implantation annealing, to identify an optimum combination of dose and annealing conditions. Analysis by SQUID magnetometry of the GaCrN with 6% Cr indicates the presence of a strong ferromagnetic phase with a Curie temperature above the 350 K limit of the magnetometer. High resolution x-ray diffraction (HRXRD) and transmission electron microscopy (TEM) results from the implanted films will also be presented to address the issue of the formation of second phases within these materials. HRXRD rocking curves of the implanted materials will also be used to trace the evolution of the implantation-induced lattice damage with annealing as well as strain-related effects due to the incorporation of Cr into substitutional lattice sites.

[1] K. Sato, and H. Katayama-Yoshida, Jap. J. Appl. Phys., Pt. 2, 40 (5B), p. L485 (2001).

11:40am **MI+EL+SC-TuM11 Suppression of Phase Segregation during MBE Growth of GaMnN Using Nitrogen-Hydrogen Plasma**, *Y. Cui,* ***L. Li***, University of Wisconsin-Milwaukee

Epitaxial growth of GaMnN by electron-cyclotron-resonance plasma-assisted molecular beam epitaxy using nitrogen-hydrogen plasma was studied by reflection high-energy electron diffraction, scanning electron microscopy, energy dispersive spectroscopy, and x-ray diffraction. The electron diffraction pattern changed from streaky to spotty when hydrogen was added to the nitrogen plasma, indicating that the effective N/Ga ratio was increased. Films grown with nitrogen plasma are phase segregated into GaN and manganese nitrides. In contrast, when nitrogen-hydrogen plasma was used, the films are single phase Ga1-xMnxN, with x can be as high as 0.06. These results indicate that phase segregation can be suppressed by adding hydrogen to the nitrogen plasma during growth.

Manufacturing Science and Technology
Room: C-109 - Session MS-TuM

Beyond Planar CMOS: Manufacturing Issues
Moderator: S Shankar, Intel Corp.

8:20am **MS-TuM1 A Systems Approach to Microelectronics**, ***J. Heath***, University of California, Los Angeles **INVITED**

In this talk I will present progress toward the fabrication of a molecular electronic computing machine, and I will discuss concepts related to machine architectures, including multiplexing and demultiplexing architectures for connecting the nano-dimensions of chemical assembly with the sub-micrometer dimensions of lithographic patterning. I will also discuss working devices and circuitry based on molecular mechanical switching complexes, as well as 3-terminal molecular electronic FETs for achieving gain. Finally, I will present patterning techniques for achieving bit densities in the range of 10^{11} to 10^{12}bits/cm^2.

9:00am **MS-TuM3 Integrated Circuit Technology Scaling: From Conventional CMOS to the Nanoscale Era**, ***P. Zeitzoff***, International SEMATECH **INVITED**

Integrated Circuit (IC) scaling per Moore's Law has been the cornerstone for IC industry growth for the last 35 years. Based on the projections in the International Technology Roadmap for Semiconductors (ITRS), we will examine the MOSFET scaling envisioned to sustain Moore's law for the next 15 years, during which the current MOSFET physical gate length of about 65 nm is expected to be scaled to about 9 nm. Issues discussed include the scaling of MOSFET performance, leakage, and power dissipation, as well as key innovations to enable the scaling. These include the potential utilization of high-k gate dielectrics, metal gate electrodes, and innovative source/drain (S/D) techniques such as raised S/D. Also, in the later stages of the ITRS, non-conventional, non-planar CMOS devices such as ultra-thin-body, fully depleted, double-gate MOSFETs may be utilized to overcome the limitations of conventional planar bulk CMOS transistors when the physical gate length is scaled to 25 nm or less.

9:40am **MS-TuM5 Nanoelectronics - Feast or Famine?**, ***J.A. Hutchby***, *V. Zhirnov*, *G. Bourianoff*, Semiconductor Research Corporation **INVITED**

Many concepts have been proposed to provide new means for information processing technologies as the industry standard CMOS MOSFET approaches its fundamental limits of scaling. Some concepts propose use of a particular nanotechnology to replicate the function of a silicon transistor albeit on a much smaller scale. Much of the known circuit and system architecture concepts may well be applicable in this new paradigm. Examples of this category include carbon nanotubes and molecular electronics. Other concepts(e.g. Quantum Computing and Quantum Cellular Automata) offer completely new paradigms for information processing, and will require new concepts and infrastructure to architect the desired systems functions. In this paper, the authors will discuss some of the more advanced candidates for new information processingparadigms and will show one concept for there possible relationship to silicon CMOS at the end of the current SIA Roadmap.

10:20am **MS-TuM7 Beyond Planar CMOS. A Reliability Perspective**, ***J. Maiz***, Intel **INVITED**

The aggressive scaling of the semiconductor technology continues relentlessly in order to satisfy the performance roadmap expectations created by "Moore's Law". The scaling of the planar CMOS transistor has been central to achieving past performance gains and remains as the main approach to realize the performance roadmap for at least the next decade. Concerns have been raised however, about the extendibility of this "evolutionary" approach because of the many integration, power and reliability challenges posed by the required use of exotic materials and extreme dimensional reductions. A number of companies and research institutions are looking into possible alternatives ranging from dual gate and FINFET transistors which still look & feel like CMOS devices, to more speculative and exotic solutions including quantum devices, molecular & organic transistors, novel non-volatile memory schemes, and carbon nanotube devices. Limited information exists on the reliability of such devices. This paper will discuss some of the key learnings reported, as well as speculate over the likely failure modes & mechanisms present for the more exotic configurations based on the extensive learning accumulated on the present planar CMOS devices and associated materials.

11:00am **MS-TuM9 Fabrication of Double-Gate Field Effect Transistors at the Limit of Device Scaling**, ***H.-S.P. Wong***, IBM T.J. Watson Research Center **INVITED**

As silicon CMOS devices scale into the nanometer regime, the material set and device structures employed by conventional field-effect transistors (FETs) are beginning to reach their limits. One way to extend the scaling of the FET towards smaller gate lengths (less than 20 nm) is to employ the double-gate device structure.[1] While the concept and the device physics of the double-gate FET has been explored for many years,[2] the fabrication of the double-gate FET remains difficult.[3] Self-alignment of the two gates with respect to each other and to the source and drain doping regions present a very difficult fabrication challenge. In addition, the thin silicon channel thickness required (5 to 10 nm) becomes a key manufacturing challenge as well as a unique opportunity to study fundamental device physics. This paper will review the history and state-of-the-art in double-gate device development, including the planar,[4,5] vertical(VRG),[6] and FinFET[7,8] device configurations. This paper will also review the device physics considerations which drive technology progress from SOI to the ultimate limit of FETs, highlighting the role that double-gate FETs will play in the future.

[1] H.-S. P. Wong, D. Frank, P. Solomon, H.J. Wann, J. Welser, Nanoscale CMOS, Proceedings of the IEEE, p. 259, 2001.

[2] T. Sekigawa et al., Calculated threshold voltage characteristics of an XMOS transistor having an additional bottom gate, Solid State Electronics, p. 827, 1984.

[3] H.-S. P. Wong, Beyond the Conventional Transistor, IBM J. Research and Development, p. 133, 2002.

[4] H.-S. P. Wong et al., International Electron Devices Meeting, p. 427, 1997.

[5] K. Guarini et al., International Electron Devices Meeting, p. 425, 2001.

[6] S.-H. Oh et al., International Electron Devices Meeting, p. 65, 2000.

[7] Y. Choi et al., International Electron Devices Meeting, p. 421, 2001.

[8] J. Kedzierski et al., International Electron Devices Meeting, p. 437, 2001.

Nanometer Structures
Room: C-207 - Session NS+SE+SS+MM-TuM

Nanotribology
Moderator: K.J. Wahl, Naval Research Laboratory

8:20am **NS+SE+SS+MM-TuM1 Ultralow Friction Coatings and Surfaces**, ***J.M. Martin***, Ecole Centrale de Lyon, France **INVITED**

From a technological point of view, very low friction in solid lubrication may be interesting in micromechanisms requiring neither friction noise nor instabilities, together with low power consumption. Theoretical approaches at the atomic scale coupled with experimental approaches using proximal probe techniques have been developed to study atomic scale friction behaviors and energy dissipation modes. The two limiting factors for friction reduction at the macro-scale are S0 (shear strength of the interface film) and a (pressure coefficient).[1] Approaching very low friction requires the reduction of both S0 and a below the MPa range. Thus lowering to zero friction would require the vanishing of both the adhesive and the external pressure. However these conditions are unlikely to be perfectly achieved in practice. Thus zero friction may not be possible. However, friction values in the 10-3 range or even less (near-frictionless sliding) have been experimentally reached in some practical situations. Here we examine ultralow friction by using a macro-scale sphere/plane contact configuration (maximum pressure of 1 GPa). Friction in the 0.001 range is associated with a shear strength of 1 MPa. We report experimental evidence of superlow friction with different coatings: pure molybdenum disulfide MoS2,[2] molybdenum dithiophosphate (Modtp) tribofilms and hydrogenated diamondlike carbon a-CH.[3]

[1] I. Singer, J. Vac. Sci. Technol., A12(5), (1994) 2605.

[2] J.M. Martin, C. Donnet, Th Le Mogne and Th Epicier, Physical Review B 48, No 14, (1993) 10583.

[3] C. Donnet et al, Surface and Coating Technology, 94, (1997) 456.

9:00am **NS+SE+SS+MM-TuM3 Frictional Properties of Small Model Lubricant Molecules Adsorbed on VC(100)**, ***L.C. Fernandez-Torres***, *S.S. Perry*, University of Houston, *B.-I. Kim*, Sandia National Laboratories

The frictional modification of the non polar (100) of vanadium carbide (VC) surface through small molecule adsorption at room temperature has been investigated from a fundamental perspective. These molecules represent the functionalities incorporated into lubricants and used to appropriately tailor the lubricant's properties and enhance its performance. Ultrahigh vacuum atomic force microscopy (AFM) has been employed to determine the changes in frictional response and interfacial adhesion. Scanning tunneling microscopy (STM) has been used to elucidate surface morphology. X-ray photoelectron spectroscopy (XPS) has been utilized to determine the composition of the species formed by the interaction of these adsorbates with the VC surface. This successful methodology has been developed during a recent investigation of ethanol, and in this study has been extended to other low molecular weight alcohols as well as an ester. The results will be rationalized in terms of chemical reactivity, adsorbate layer composition, extent of coverage, and changes in the interfacial shear strength and discussed in terms possible lubrication schemes.

9:20am **NS+SE+SS+MM-TuM4 Adhesion and Deformation in Nanoscale Contacts between W(110) and Au(110) in Ultra High Vacuum**, ***S.A. Smallwood***, *R.J. Lad*, *W.N. Unertl*, University of Maine

Tribological phenomena change as the contact area decreases from macroscopic to atomic dimensions, but these changes are not well understood. We report studies of the force versus deformation behavior of contacts with diameters up to about 50 nm using well-characterized metal surfaces in ultra-high vacuum. These contact sizes are intermediate between those previously studied. The contacting bodies were a Au(110) single crystal and sharp tips of W wires. The W probes were cleaned by field evaporation and their atomic structure determined using field ion microscopy (FIM). All were terminated by (110) planes and radii varied between 12 nm and 24 nm. The probes were mounted in double cross-hair force sensors. After cleaning by sputtering and annealing cycles, the Au was transferred to a piezoelectric tube scanner and moved into tunneling contact with the probe. Deflection of the force sensor and electrical current were measured as the Au crystal was brought into mechanical contact to a predetermined maximum displacement and then withdrawn. Prior to the first yielding event, the data is well described by elastic contact mechanics theory. The reduced modulus of 61 Â± 26 GPa agrees with the value calculated assuming bulk properties. The work of adhesion has an upper bound of about 0.3 J/m2. The first observable yielding events occur at a mean normal stress of 12 Â± 2 GPa, comparable to the values reported for larger probes, but half that reported for smaller contacts on Au(111). Hardness is about 6 GPa near the surface and decreases by about fifty percent at 8 nm indentation depth. Prior to first yield, contact conductance remains far below one quantum. Deformation is confined to the Au. FIM demonstrates that the W probe is not deformed for penetrations as deep as its radius. Scanning tunneling microscopy shows that the indentation holes are asymmetric and that pile-up extends about one indentation diameter beyond the indent.

9:40am **NS+SE+SS+MM-TuM5 Chemical Force Microscopy of Aluminium Oxide Surfaces**, ***T.T. Foster***, *M.R. Alexander*, UMIST, UK, *E. McAlpine*, Alcan International, UK, *G.J. Leggett*, University of Sheffield, UK

The combination of wettability, chemical force microscopy (CFM) and friction force microscopy (FFM) has been used to analyse changes at the oxide-covered surface of aluminium after magnetron sputter deposition. A model self-assembled monolayer (SAM) system was first developed to enable comparisons to be made with the more complex aluminium system. The monolayers were produced by self-assembly on Au (111) and Ag (111) substrates. The gold-coated AFM tips were modified with SAMs of alkanethiols terminated in a methyl or carboxylic acid group. Friction coefficients were measured for SAMs varying in chain length and terminal group chemistry. Using carboxylic acid modified tips; measurements were performed on the surface of aluminium. Adhesion forces were found to decrease with storage time in a desiccated environment, attributed to the adsorption of contaminant molecules from the atmosphere. In contrast the friction coefficient showed no significant change with storage time, presumably because the sliding tip, under loading, is able to displace contaminant molecules. Contact angle goniometry was used to study changes in surface wettability on the aluminium surface. The water contact angle increased linearly with the log of storage time, supporting the hypothesis that adsorption of hydrophobic contaminants modifies the aluminium surface. Contact mode characterisation of the aluminium oxide surface provided clear images of the oxide surface. A nitric acid-based cleaning procedure was developed that was capable of removing adventitious contamination and returning the aluminium oxide surface to condition that appears similar to the freshly deposited surface. This study clearly demonstrates the capability of CFM for characterising complex aluminium surfaces and studying changes in surface chemistry.

10:00am **NS+SE+SS+MM-TuM6 Nanotribology and Related Structural Changes During Wear of Diamond-like Carbon Films**, ***J. Goldsmith***, *E.A. Sutter*, *J. Moore*, *B Mishra*, Colorado School of Mines, *M. Crowder*, Maxtor Corporation

Diamond-like carbon (DLC) thin films are used for wear and corrosion protection of magnetic disks, micro-electro-mechanical systems (MEMS), and tool bits. Magnetic information storage density increases when the read-write head gets closer to the disk. The magnetic layers degrade very quickly without a good protective interface. The use of DLC thin films becomes increasingly popular as they can provide a protective surface due to their excellent tribological properties as low friction and high hardness. In both magnetic disks and MEMS applications, the DLC films are in the thickness range of 2 - 5 nm and in most cases are amorphous in structure. Characterizing the tribological and structural properties and identifying the wear mechanisms of DLC films on the nanoscale is a challenge. Here we present results on the nanotribology of the DLC films performed using both an atomic force microscope and a nanoindenter. We investigate the wear behavior of the DLC films and the role of transfer film. We find that the formation of transfer film plays an important role in providing low-friction. The nanotribological investigations are correlated with the structural changes that occur in the DLC film as well as in the transfer film detected using Raman spectroscopy and cross-sectional transmission electron microscopy.

10:20am **NS+SE+SS+MM-TuM7 Tribology and Surface Forces in MEMS**, ***J.S. Zabinski***, Air Force Research Laboratory, *S.T. Patton*, *K.C. Eapen*, UDRI, *S.A. Smallwood*, Systran, Inc. **INVITED**

Microelectromechanical systems (MEMS) offer the potential to provide new capabilities and products for commercial and military applications. Simple devices are already common in the marketplace, but friction, stiction, and wear prevent reliable operation of more sophisticated types of MEMS devices that have contacting surfaces in relative motion. These tribological problems are fundamentally difficult to solve and are magnified because MEMS are expected to operate in very harsh environments, such as at elevated temperature and in space. The performance and reliability of MEMS are strongly dependent on the environment in which they operate. For example, moisture can cause device failure by stiction or it can provide excellent lubrication, depending on the device and the relative concentration of water vapor (i.e., relative humidity). Operation in vacuum is particularly severe and the wear mechanisms are different than in dry or moist environments. Methods to control system tribology include lubricant coatings, monolayers, and new materials. The tribological mechanisms operating in moist air through vacuum will be discussed along with strategies to control friction, stiction, and wear that have significantly improved MEMS reliability. In addition, the effects of storage on device performance will be presented.

11:00am **NS+SE+SS+MM-TuM9 Tribological Measurement on MEMS Platforms[1]**, ***M.T. Dugger***, *S.V. Prasad*, Sandia National Laboratories **INVITED**

Microelectromechanical systems (MEMS) fabricated using surface micromachining (SMM) and other lithographic techniques such as LIGA have resulted in actuators, counter-meshing gears and other moving mechanisms having complex tribological interfaces that are rough on the nanometer scale and have unusual surface morphologies. Meaningful friction and wear measurements of microsystems must be made at loads and speeds relevant to MEMS operation. Since friction and wear are properties of systems, measurements must also involve interactions of surfaces having the morphology and chemistry present in real devices. Experimental techniques for acquiring friction data during sub-micron displacement and under nanoNewton forces are critical for the fundamental understanding of energy dissipation and wear mechanisms in MEMS. However, experimental investigation of surface interactions in MEMS under relevant contact conditions requires techniques beyond those that are currently available. MEMS friction measurement platforms which bring real MEMS surfaces into contact are needed to define the design space, to investigate aging and failure mechanisms, and to validate models of friction and wear derived from fundamental studies. We have therefore developed both SMM and LIGA devices containing isolated tribological contacts from which quantitative friction forces can be extracted. These structures are used to investigate interface performance, degradation and failure mechanisms. Methods of quantifying static and dynamic friction in SMM and LIGA micromachined contacts will be presented. Examples will be shown of how these structures are being used to investigate degradation of monolayer lubricants and hard coatings for SMM devices, as well as the tribological behavior of metallic contacts in LIGA.

[1] 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.

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-TuM

Nanotubes: Electronics and Field Emission
Moderator: B. Simard, National Research Council of Canada

8:20am **NT-TuM1 Room Temperature Coulomb Diamond Characteristics in Single Electron Transistor with Position Controlled Grown Carbon Nanotube Channel**, ***K. Matsumoto***, National Institute of Advanced Industrial Science & Technology, Japan, *T. Kamimura*, Tsukuba University, Japan, *M. Maeda*, *K. Sakamoto*, *K. Kurachi*, Meiji University, Japan

Even at room temperature, the clear Coulomb diamond structures were obtained in the single electron transistor which used the position controlled grown carbon nanotube as a channel, and Coulomb energy of the device is as high as 400meV. The position control of the carbon nanotube for the channel of the device was successfully achieved using the patterned chemical catalyst process without any difficulty, i.e., using the conventional photo-lithography process, 3 nm thick iron (Fe) catalyst was patterned for the source and drain structure on the SiO_2/Si substrate. Using the thermal CVD process, one carbon nanotube started to grow and bridged the gap between the source and drain patterned Fe catalysts. Ohmic metal was then deposited on to the source and drain regions and on the backside of the Si substrate for the gate. The electrical properties of the device were all measured at room temperature. The device showed the large Coulomb gap of 800mV at around zero gate bias and the Coulomb energy of the device is as high as 400meV that correspond to Coulomb temperature of 5000K. The Coulomb oscillation characteristics was also obtained and its modulation ratio is as high as 96~99% at the drain bias of around 20mV ~100mV even at room temperature. Five Coulomb diamond structures were obtained between the gate bias of @+ -@2V with the different structures sizes. This may come from the multi-islands formation by the residual chemical catalysts and/or the defects in the carbon nanotube. The corresponding island size is only 1nm diameter sphere. Using the position controlled grown carbon nanotube as a channel, ultra-high Coulomb energy of the single electron transistor is easily realized.

8:40am **NT-TuM2 Current Measurement with Tapping Mode AFM to Determine the Electrical Properties of Carbon Nanotubes**, ***M. Stadermann***, *J.J. Boland, M.R. Falvo, R. Superfine, S. Washburn*, University of North Carolina at Chapel Hill

Measurement of contact resistance and electronic transport properties of carbon nanotubes are typically performed with static contacts. Movable contacts provide many advantages over static contacts but difficulties arise from an inability to position the probe precisely on a nanotube, and to control the exact position of the electrical measurement due to thermal drift and piezoelectric hysteresis. The technique presented here allows characterization of the conductivity of different parts of a surface by applying a small voltage to a conductive AFM-tip and then scanning the surface in tapping mode. The resistance of the surface is determined from the current pulses flowing between tip and sample whenever the tip intermittently makes contact with the surface. The advantage of this technique is that electrical and topographical data are taken simultaneously and are therefore in registry. A further advantage is the high number and density of data points taken at constant contact force during a single scan. This method is applied to map out the contact resistance of carbon nanotubes on graphite and examine the coupling between charge transfer modes along and across the tube. It is found that the contact resistance of the nanotube varies with the contact angle.

9:00am **NT-TuM3 Modeling of Gate Bias Modulation in Carbon Nanotube Field-Effect Transistors**, ***T. Yamada***, NASA Ames Research Center

The threshold voltages of a carbon nanotube (CNT) field-effect transistor (FET) are derived and compared with those of the metal-oxide-semiconductor (MOS) FETs. The CNT channel is so thin that there is no voltage drop in a CNT diameter direction perpendicular to the gate electrode plane, and this makes the CNTFET characteristics different from those in MOSFETs. The relation between the voltage and the electrochemical potentials, and the mass action law for electrons and holes are examined in the context of CNTs, and it is shown that the familiar relations are still valid because of the macroscopic number of states available in the CNTs. This situation is significantly different from that of quantum dots. Using these relations, we derive an inversion threshold voltage V_{Ti} and an accumulation threshold voltage V_{Ta} as a function of the Fermi level E_F in the CNT channel, where E_F is a measure of doping. V_{Ti} of the CNTFETs has a much stronger dependence on E_F than that of MOSFETs, while V_{Ta}s of both CNTFETs and MOSFETs depend quite weakly on E_F with the same functional form. This means that the transition from normally-off mode to normally-on mode is much sharper in CNTFETs as E_F is modulated through doping, and this property has to be taken into account in circuit design.

9:20am **NT-TuM4 Charge Imaging and Manipulation Using Carbon Nanotube Probes**, *S.-D. Tzeng, C.-L. Wu, Y.-C. You, T.T. Chen,* ***S. Gwo***, National Tsing-Hua University, Taiwan, ROC, *H. Tokumoto*, AIST, Japan

Direct imaging and manipulation of electric and magnetic domain structures (spontaneously or artificially formed) on the nanoscale has become increasingly important because of the recent developments in high-areal-density storage devices using charge-trapping, ferroelectric, or ferromagnetic materials. Electrostatic force microscopy (EFM) and magnetic force microscopy (MFM), variations of scanning force microscopy (SFM) which utilize nano-sized conducting or magnetic probes to sense the distributions of long-range forces, are two of the most widely used techniques for this purpose. To date, the major difficulty related to the long-range force imaging is to decouple the short-range interactions without degrading the lateral resolution. This problem is especially severe with the conventional micromachined EFM and MFM probes, typically consisted of a cantilever and a tip of conical or pyramidal shape. Carbon nanotubes (CNTs) are novel nanostructures which have a great potential to be used as the probing tips for the scanning probe techniques. It has been shown that CNTs are electrically conducting, mechanically robust with unprecedented elastic properties, chemically stable, and having a perfect cylindrical geometry with very large aspect ratio for imaging long-range forces. Recently, several groups have reported experimental approaches to attach a single CNT to a conventional SFM-tip. Among them, scanning electron microscope (SEM) based technique is the preferred method for preparing CNT tips with controllable tube diameters, lengths, and desired orientations. In this work, we show that CNT is an ideal tip material for "true" local probing of long-range electrostatic forces with a lateral resolution better than 5 nm. Moreover, we demonstrate that CNT tip can be used to manipulate charges on the charge-trapping media (such as Si_3N_4 thin films and Si_3N_4/SiO_2 dielectric multi-layers) with an areal density greater than 60 Gbit/in ^{2}.

9:40am **NT-TuM5 Band Gap Engineering in Carbon Nanotubes**, ***J. Lee***, Seoul National University, *H. Kim, J. Ihm,* Seoul National University, Korea, *S.-J. Kahng,* Soongsil University, Korea, *H. Shinohara,* Nagoya University, Japan, *Y. Kuk*, Seoul National University, Korea

Carbon nanotubes have been successfully used for nanometer-sized devices such as diodes, transistors and random access memory cells. Despite these achievements, efforts to integrate these unit devices into functional systems have not yet succeeded. We report a method for constructing self-assembled, multiple quantum dots in a semiconducting carbon nanotube and demonstrate a spatial modulation of the band gap using a low-temperature scanning tunneling microscope.[1] When we imaged topographies of the semiconducting SWNTs at bias voltages of -0.8V to +1.0V, parts of the nanotubes appeared brighter than other areas, suggesting that the diameter may be greater there than at other areas or that the local electronic structure is modified by the inserted fullerene. In the dI/dV spectra, strong VHS peaks corresponding to conduction and valence band edges are clearly observed. The original band gap of about 0.5 eV is narrowed down to about 0.2 eV where the fullerene is expected to be located. There are two possible senarios to explain the observation: 1) Elastic strain can change the band gap significantly. For example, a strain of 4% in the tube axis direction can induce a gap reduction of 60% for the (15,1) tube. 2) Charge transfer from the nanotube to the metallofullerenes or the Au(111) substrate may also induce a change in the electronic structure. We have demonstrated that we can synthesize this band gap-engineered system by self-assembly instead of epitaxial growth.

[1] J. Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z.W. Wang, T. Okazaki, H. Shinohara, & Y. Kuk, Nature, 415, 1005 (2002).

10:00am **NT-TuM6 Modifying and Probing the Electrical Properties of Carbon Nanotube Devices using an Atomic Force Microscope**, ***J.-Y. Park***, *Y. Yaish, S. Rosenblatt, M. Brink, P.L. McEuen*, Cornell University

An atomic force microscope (AFM) is used to probe and modify electrical properties of nanotube devices. In one set of experiments, a metalized AFM tip in electrical contact with the nanotube is utilized as a local voltage probe. These measurements reveal the voltage distribution along a nanotube as well as the contact resistance between the nanotube and the metal electrodes. For semiconducting nanotube field effect transistors, these measurements give important information about the bending of the semiconducting bands along the length of the tube. In other experiments, electrical pulses applied to the AFM tip are used to permanently modify the electrical properties of nanotube devices. By controlling the height and duration of the pulses, electrical breaks ("cuts") or tunneling barriers ("nicks") can be created at any point along the tube. The application of these modification techniques in combination with mechanical manipulation for the creation of more advanced device geometries will also be discussed.

10:20am **NT-TuM7 Electrostatically Focused Microfabricated Field Emission Electron Sources with Single Vertically Aligned Carbon Nanofiber Cathodes**, ***M.A. Guillorn***, Oak Ridge National Lab, *A.V. Melechko, M.D. Hale,* Univ. of Tennessee, Knoxville, *R.J. Kasica, V.I. Merkulov,* Oak Ridge National Lab, *E.D. Ellis,* Univ. of Tennessee, Knoxville, *D.K. Hensley, M.L. Simpson, L.R. Baylor, J.H. Whealton, D.H. Lowndes*, Oak Ridge National Lab

Electron beam lithography using a single beam cannot achieve acceptable throughput levels to become a viable manufacturing technology. The digital electrostatic e-beam array lithography (DEAL) concept under development at the Oak Ridge National Laboratory proposes circumventing this problem by writing simultaneously with millions of e-beams from a massively parallel and digitally programmable array of microfabricated electron sources. Such a system will require a robust field emission (FE) source of electrons capable of operation in moderate vacuum. In previous work we have shown that microfabricated FE sources using a single vertically aligned carbon nanofiber (VACNF) cathode are well suited for this application.[1] The ability to synthesize individual VACNF deterministically and incorporate them into conventional device fabrication processes distinguishes this material from other nanostructured graphitic carbon-based FE cathodes. By extending the fabrication process presented in our earlier work we have realized multi-electrode FE devices using this technology. Here we present the design, fabrication and characterization of prototype electrostatically focused FE electron sources intended for use in the DEAL system. The dc operating characteristics of these devices were investigated and fit well to the Fowler-Nordheim model of FE. The divergence of the emitted electron beam from unfocussed devices was evaluated using a microchannel plate system and found to be between 10 and 15 degrees. The effect of the focusing electrodes was analyzed using this system and shown to dramatically improve the focus of the beam. A discussion of these results along with modeling of the device behavior will be presented.

[1] M.A. Guillorn, A.V. Melechko, L.R. Baylor, E.D. Ellis, et al, Appl. Phys. Lett. 79, 3506 (2001).

10:40am **NT-TuM8 Fabrication and Electrical Characterization of Multiwalled Carbon Nanotube Field Emission Devices with Integrated Focusing Electrodes**, ***M.D. Hale***, University of Tennessee, *M.A. Guillorn, M.L. Simpson*, Oak Ridge National Laboratory and University of Tennessee, *C.L. Britton, G. Eres*, Oak Ridge National Laboratory

We report on the fabrication of field emission devices with integrated focusing electrodes that use dense films of multiwalled carbon nanotubes for the emitter material. The fabrication process used to realize these devices is completely compatible with large-scale integrated device production techniques. The current vs. voltage characteristics of these devices were examined and displayed a low turn-on voltage for initiation of electron emission. The effects of the focusing electrode on the field emission characteristics were explored along with the gain, frequency response, and output impedance of these devices. Details on the fabrication process and aspects of device performance will be discussed.

11:00am **NT-TuM9 Field Emission Properties of Nanostructures Based on Molybdenum Ternary Compounds**, ***V. Nemanic***, *M. Zumer, B. Zajec*, Institute of Surface Engineering and Optoelectronics, Slovenia, *M. Remskar, A. Mrzel, D. Mihailovic*, Jozef Stefan Institute, Slovenia

We have investigated the field emission (FE) properties of quasi one-dimensional molybdenum ternary compounds synthesized by a catalytic transport reaction. The self-assembly of tip-shaped nanofibres leads to the growth of a thin foil composed of mutually oriented bundles, below 500 nm in diameter and up to 20 micrometers in length. All FE measurements were performed in a dynamically pumped UHV system at 10^{-9} mbar base pressure. The samples were mounted on the top of metal pins positioned some mm from the aluminized luminescent screen biased as the anode. Current - voltage (I-V) measurements were performed under continuous bias conditions up to 4.5 kV where the resulting macroscopic field reached approx. 0.9 V μm^{-1}. The I-V behavior follows predominately the Fowler-Nordheim equation over the measured range. The emission current from a few sites reached a value of some ten micro amps and the emission spots of various shapes were observed. The current initially dropped, but became relatively stable even on the time scale of few hundred hours.

Plasma Science
Room: C-105 - Session PS+MS-TuM

Plasma Diagnostics and Sensors
Moderator: R.J. Shul, Sandia National Laboratories

8:40am **PS+MS-TuM2 High-energy EEDF Tail Detection in High-frequency Discharges**, ***J. Kudela***, *K Suzuki, Y. Nakagawa, Y. Numasawa*, ANELVA Corporation, Japan, *T. Beppu*, RITE, Japan

It is well-known that the enhanced high-frequency (HF) fields in the oscillating plasma sheaths can lead to generation of high-energy electrons. At sufficiently low gas pressures, this phenomenon is crucial for the discharge maintenance. However, the phenomenon may also cause the discharge instabilities. The detection of the high-energy tail in the electron energy distribution function (EEDF) in HF discharges is, therefore, of a particular interest from the scientific point of view. It is also important from the technological point of view. The high-energy electrons are determining factor in processing plasmas affecting the discharge chemistry in the plasma volume, and on the processing surface as well. Moreover, on the processing surface, the high-energy electrons may also be responsible for undesired physical processes like charge damage. In our work, we illustrate the detection of high-energy electrons by electrostatic probes in HF discharges at two different frequencies, 2.45GHz and 60MHz. In the microwave band (2.45GHz), the detection of the high-energy electrons is rather simple and it requires only direction-sensitive probes.[1] Similar technique is applied to the VHF band (60 MHz) discharges. In these discharges, however, a proper probe compensation is necessary. The conventional compensation methods, which are based on sensing floating potential fluctuations around the probe tip, lose information about the EEDF tail. We propose a method that can lead to detection of high-energy electrons, as well as to the diagnostics of the VHF discharges. This work is supported by NEDO.

[1] J. Kudela, T. Terebessy, and M. Kando: Hot electrons and EEDF-anisotropy in large-area surface-wave discharges; Proc. IV Int. Workshop Microwave Discharges: Fundamentals and Applications, Sept. 18-22, 2000, Zvenigorod, Russia; ed. Yu.A. Lebedev (Yanus-K, Moscow, 2001), p.63.

9:00am **PS+MS-TuM3 Coupled Diagnostic Studies of Plasma Etch Byproducts**, ***M.T. Radtke***, *D.B. Graves, J.W. Coburn*, University of California Berkeley

Plasmas used for etching invariably include species that originate at surfaces. Etch byproducts commonly play a major role in plasma composition, in addition to influencing etch rate, anisotropy, critical dimension control, and selectivity. Etch byproducts often deposit on chamber walls, altering wall chemistry such as radical recombination reactions, and leading to the formation of particles. Chamber wall cleaning and conditioning protocols can play an important role in etch tool cost-of-ownership. For new high-k and low-k dielectrics and metal gate electrode materials, the etch characteristics and etch byproducts are usually not known. In addition to posing a challenge for feature critical dimension control and other etch objectives, the unknown etch byproducts may pose environmental, health and safety hazards. We reports studies using an inductively coupled plasma reactor equipped with a cooled, rf-biased chuck, a downstream FTIR spectrometer, a quartz crystal microbalance, a Langmuir probe, an ion flux wall probe, an ion mass spectrometer, a separate threshold ionization mass spectrometer for neutral radical detection, and optical emission spectroscopy. We have employed this system to measure etch byproducts and etch byproduct transport for a range of new high-k and low-k dielectric materials as well as candidates for metal gate electrodes. We illustrate the use of coupled plasma diagnostics for ZrO_2/Cl_2, SiO_2/CF_4, RuO_2/O_2, HfO_2/Cl_2, and $Si/Cl_2/O_2$. In particular, detection and identification of low volatility byproducts can be challenging, and often require combining information from the ion mass spectrometer, the neutral mass spectrometer, film composition measurements on the quartz microbalance, optical emission spectroscopy, and the downstream gas composition.

9:20am **PS+MS-TuM4 Two-Dimensional Ion Flux Distributions on the Wafer Surface in Inductively Coupled Plasma Reactors**, ***E.S. Aydil***, *T.W. Kim*, University of California, Santa Barbara

A two-dimensional array of planar Langmuir probes manufactured on a 200 mm diameter silicon wafer was used to measure the radial and azimuthal variation of ion flux impinging on the wafer surface in various mixtures of electropositive and electronegative gases maintained in an inductively coupled plasma etching reactor. The spatial variation of ion flux in a pure Ar discharge is radially symmetric and peaks at the center of the wafer for pressures between 10 and 60 mTorr. Addition of small amounts of electronegative gases to an Ar discharge flattens the radial and azimuthal ion flux distribution and accentuates azimuthal variation due to subtle asymmetries in the reactor geometry such as pumping ports. At fixed power, pressure, and flow rate, the spatially averaged ion current density decreases with increasing mole fraction of the electronegative gases in the feed gas. In conjunction with experimental data, we developed a simple theoretical framework within which the spatial variation of ion flux in gas mixtures can be understood. Ion Flux uniformity in various binary mixtures of Cl2, He, Ar, HBr, O2, and SF6 will be discussed. Spatiotemporal variation of ion flux in presence of instabilities in SF6 discharges will be presented.

9:40am **PS+MS-TuM5 Surface Dependent Effects at the Plasma-Surface Interface**, ***G.A. Hebner***, Sandia National Laboratories **INVITED**

In a typical etching application, a number of different materials from the common silicon, and silicon oxide to more exotic nitrides and low-k materials can be located in very close proximity to each other. The interaction of these different materials through changes in the plasma chemistry, non-equilibrium surface layers and local electric field is of fundamental interest since the local chemistry and plasma properties determine the characteristics of the resulting etch profile. A number of techniques have been used to characterize etching plasmas as a function of the surface material. Plasma species such as CFx, SIFx and BCl radials have been measured as functions of the surface material and radial position using laser induced fluorescence. Those measurements show significant changes in radical species concentration for silicon, silicon oxide and ceramic surfaces. Measurements of the electron and negative ion density using a microwave interferometer and laser photodetachment also show surface dependent changes in the bulk plasma chemistry. In addition to the plasma chemistry, the sheath electric field is of interest since it's magnitude and vector guide the ion species. Of particular interest is the measurement of the material dependent surface charging, a task that is challenging considering the required spatial, temporal and electric field sensitivity. An atomic beam system combined with pulsed laser spectroscopy has been used to directly calibrate the electric field induced Stark shift of high lying energy levels. Measurements of the electric field within an inductively driven argon discharge will be discussed. The possibility of using this system to calibrate energy level shifts in other gases of technological interest to the microelectronics and lighting industry will be discussed. This work was supported by the United States Department of Energy (DE-AC04-94AL85000).

10:20am **PS+MS-TuM7 Monitoring Sheath Voltages and Ion Energies in High-Density Plasmas using Radio-Frequency Current and Voltage Measurements**, ***M.A. Sobolewski***, National Institute of Standards and Technology

The bombardment of substrate surfaces by energetic ions plays an important role in plasma etching and other plasma processing applications. To obtain optimal results, ion kinetic energies must be carefully controlled. However, measuring ion energy distributions in situ, at a wafer surface during plasma processing, is difficult or impossible. A method for indirectly monitoring ion bombardment energies would thus be useful, both as a source of information to guide process development and as a tool for process monitoring and control in manufacturing. Accurate ion energy distributions can be calculated by models of plasma sheaths if one knows the sheath voltage, the electron temperature, and the total ion flux. These parameters are in turn related to radio-frequency (rf) current and voltage signals that can be measured outside a plasma reactor, without perturbing the plasma or the process. Indeed, several different model-based methods have been proposed for using rf current and voltage measurements to determine sheath voltages and ion energies. In this study, three such methods were tested. Tests were performed in argon and CF_4 discharges at 10 mTorr, in an inductively coupled, high-density plasma reactor. All the methods were able to successfully detect changes in sheath voltages and total ion flux, and to infer the effect of these changes on ion energy distributions. However, the rf measurements are relatively insensitive to changes in the electron temperature. To obtain the most accurate sheath voltages and ion energies from rf measurements, the electron temperature should be known ahead of time, or monitored by some independent measurement technique.

10:40am **PS+MS-TuM8 Gas Temperature Effects on CF_x Kinetics in a CF_4 Inductively Coupled Plasma**, *H. Abada*, ***J.P. Booth***, *P. Chabert*, Ecole Polytechnique, France

We have used Laser Induced Fluorescence to determine CF and CF_2 radical concentrations in steady state and pulse-modulated inductively-coupled plasmas in CF_4 at 5 and 33 mTorr. The rotationally-resolved LIF excitation spectra of the CF radical were used to determine the space and time resolved gas temperature. Strong temperature gradients were observed, with the temperature reaching 800 K in the reactor center at 33 mTorr, 250 W RF power. These measurements were used to correct the LIF measurements for the dependence of the partition function on the gas temperature, providing the first reliable measurements of CF and CF_2 kinetics in this system. The concentration profiles can be used to deduce the net flux of these species from or to the reactor walls, using Fick's law but also allowing for thermo-diffusion. The steady-state CF_2 profiles showed that this species is produced predominantly at the reactor walls by CF_x^+ ion bombardment. Surprisingly, in the post-discharge the CF_2 density increases markedly for several milliseconds, before decaying slowly. We will explore the possible origins of this phenomenon, which include convection induced by gas cooling, vibrational relaxation and conversion of CF to CF_2 by chemical reaction. In contrast, the CF radical appears to be both produced and destroyed in the gas phase, and it's concentration decays monotonically and rapidly in the post-discharge.

11:00am **PS+MS-TuM9 Electron Energy Distribution in C_2F_4/CF_3I Ultrahigh-Frequency and Inductively Coupled Plasmas**, ***T. Nakano***, National Defense Academy, Japan, *S. Samukawa*, Tohoku University, Japan **INVITED**

The electron energy distribution function (eedf) is an important factor in determining radical compositions in plasmas for nanometer-scale device fabrication. In this presentation, the electron energy distribution in plasma through a C_2F_4/CF_3I mixture, which is a novel chemistry proposed for low-damaged, fine structure etching of SiO_2, is studied by trace rare gas optical emission spectroscopy (TRG-OES) and probe measurements. The integrated eedf above 13.5 eV (S_{eedf}) is evaluated from the Ar emission at 750.4 nm. The S_{eedf} exhibits a weaker dependence on the gas composition for the C_2F_4/CF_3I mixture than for the C_4F_8/Ar mixture which is conventional chemistry for SiO_2 etching. For practical etching conditions, the S_{eedf} for the C_2F_4/CF_3I mixture becomes smaller than 1/3 of that for the C_4F_8/Ar mixture in both ultrahigh-frequency (UHF) plasmas and inductively coupled plasmas (ICP). Thus, using the C_2F_4/CF_3I chemistry, low charging damage in SiO_2 etching is expected. The probe-measured electron temperature (T_e), which indicates the degree of the exponential eedf decay in the low energy, is 2.5 eV in UHF plasma through the C_2F_4/CF_3I mixture and 4.1 eV in the ICP, while S_{eedf} is twice as large in the UHF plasma as in the ICP. This suggests an eedf enhancement in the middle energy region (5-10 eV) for the ICP, which prompts the dissociation of the feedstock gases. A quantitative estimation of the eedf using a bi-Maxwellian-like function, which is crucial to understanding the relationship between the eedf and feedstock gas dissociation, is in progress. The preliminary results also support the eedf enhancement in the middle energy region for the ICP.

11:40am **PS+MS-TuM11 Dependence of Radical Densities on Fluorocarbon Feed Gases in a Dielectric Etch Plasma**, ***E.A. Hudson***, *J. Luque*, Lam Research Corp., *N. Bulcourt*, *J.P. Booth*, Ecole Polytechnique, France

Unsaturated fluorocarbon gases are increasingly important for critical dielectric etch applications. Under typical plasma etch conditions, these feed gases promote the deposition of fluorocarbon polymer films. Using process parameters to tune the polymer deposition characteristics, one can control the critical dimension and profile of the etched feature, and minimize the loss of the photoresist mask. Different unsaturated fluorocarbon gases produce different process results, for reasons which are poorly understood. In an effort to better understand these differences, the plasma radical composition has been analyzed for a range of feed gases including the unsaturated fluorocarbons octofluorocyclobutane(C_4F_8) and octafluorocyclopentene (C_5F_8), and also a saturated compound, perfluoroethane (C_2F_6). Optical emission spectroscopy (OES) and broad-band UV absorption spectroscopy (UVAS) have been used to measure radical densities in a dual-frequency, capacitively-coupled, dielectric etch reactor. Species detected include CF, CF_2, and F. Notable variations in radical densities were observed for a series of processes based on Ar, O_2, and one of the fluorocarbon feed gases. CF_2 density, in particular, showed a strong dependence on fluorocarbon feed gas. The F/CF2 density ratio increased by more than a factor of 2 when C_2F_6 was substituted for C_5F_8. For each fluorocarbon feed gas, the sensitivity to changes in the O_2 flow has been evaluated. Results suggest that the role of oxygen in controlling polymer film thickness in and around etched features is related to polymer formation as well as polymer removal.

Plasma Science
Room: C-103 - Session PS-TuM

Atmospheric Pressure and Other Emerging Plasma Applications
Moderator: R. Blumenthal, Auburn University

8:20am **PS-TuM1 Instabilities in a Dielectric Barrier Discharge at Atmospheric Pressure**, *M.C.M. Van de Sanden*, ***E. Aldea***, Eindhoven University of Technology, The Netherlands, *C.P.G. Schrauwen*, TNO TPD, The Netherlands

Due to their enormous potential for cost-efficient industrial applications, atmospheric low temperature (300-500 K) plasmas at atmospheric pressure received large attention in recent years. From the points of view of power density and plasma stability the most efficient solution was proved to be the dielectric barrier configuration in which the electrodes are covered with a insulator. The procedure used to generate plasma is simple but the physical mechanism underlying the plasma generation is still unclear. The generation of homogeneous plasma at atmospheric pressure is assumed to be related to the gas pre-breakdown pre-ionisation by metastable-metastable collisions,[1] but there are not yet unambiguous experimental evidences of a significant pre-ionization due to this mechanism. In this paper the work was focussed on the investigation of the role of metastables in the excitation or ionisation processes in a plasma generated in Ar , nitrogen and air between two electrodes (electrode gap 0.3-5 mm) covered by a dielectric mounted in a gas tight cabinet. A study of dependence of plasma stability and filamentation on the electrode gap, surface temperature, voltage pulse frequency or shape was also performed and the optimum conditions range was defined. The importance of metastables is evaluated on basis of the plasma rovibrational and excitation temperatures derived from the optical emission spectroscopic data, and on the study of the correlation between temporal dependence of the plasma emission and of the current pulse. It is demonstrated that metastable-metastable collisions cannot be responsible for a significant pre-ionization. Therefore other factors must play a role in plasma stability.

[1] N. Gherardi, G. Gouda, E. Gat, A. Ricard, F. Massines , Plasma Sources Sci. Technol. 9 (2000), 340.

8:40am **PS-TuM2 Atmospheric Pressure Plasma Processing**, ***R.F. Hicks***, *G.R. Nowling*, *M. Moravej*, *X. Yang*, University of California, Los Angeles, *G. Ding*, Applied Materials, *S.E. Babayan*, Surfx Technologies LLC **INVITED**

Atmospheric pressure plasma discharges have emerged as exciting new tools for materials processing. There are many different sources to choose from depending on the application, including dielectric barrier discharges, microwave plasmas, transferred arcs and inert-gas-stabilized capacitive discharges. At UCLA, we have developed a novel low-temperature plasma source, in which reagent gases are mixed with helium or argon and passed through two closely spaced, perforated electrodes. By applying radio frequency power at 13.56 to 100.0 MHz to one of the electrodes, the gas becomes ionized with the dissociation of about 1% of the reagent molecules into atoms and radicals. This source exhibits a charged particle density of about 10^11 cm^-3 and an electron temperature from 2 to 4 eV. By contrast, the neutral temperature ranges from 300 to 450 K, depending on the process conditions. Many different gas mixtures may be fed through the source, including oxygen, nitrogen, hydrogen, carbon tetrafluoride, ammonia, etc. The concentration of ground-state atoms, e.g., O or N, varies from about 1.0 to 10.0 x10^15 cm^-3. These species may be used to drive a variety of downstream surface treatment processes, including polymer activation, organic residue removal, glass or metal etching, and chemical vapor deposition. At the meeting, I will briefly review atmospheric pressure plasma sources, and then describe our work on the physics and chemistry of these systems.

9:20am **PS-TuM4 Atmospheric Pressure Plasma Treatment of Polypropylene**[1], ***R. Dorai***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Atmospheric pressure plasmas, corona and dielectric discharges in particular, are used to modify polymer films to improve their wetting and adhesion properties. Production of O and OH radicals in humid air discharges produce surface oxidation of the polymer and result in the formation of Low-Molecular Weight Oxidized Material (LMWOM). Although a widely used industrial process, the fundamental plasma surface interactions which produce LMWOM and modify surface properties are not well understood. In this paper, results from a computational investigation of corona treatment of polypropylene will be discussed with the goal of determining the reaction mechanism which produce LMWOM. The investigation was performed using a global plasma chemistry model linked with a surface site balance model for the plasma-surface interactions. The surface reaction mechanism distinguishes between processes which produce hydrophilic and hydrophobic groups. Comparisons can then be made with experimental data for corona treated polypropylene based on wettability (contact angle), densities of different surface groups and erosion rates. With the validated reaction mechanism, parameterizations of the important variables affecting the adhesion properties namely, energy deposition and relative humidity will be performed.

[1] Work supported by 3M, Inc. and the National Science Foundation.

9:40am **PS-TuM5 Simulation of the Plasma Dynamics and Chemical Phenomena in Dielectric-barrier Controlled Atmospheric-pressure Glow Discharges**, ***X. Yuan***, *L. Raja*, University of Texas at Austin

Large-volume atmospheric-pressure glow (APG) discharges are emerging as an important new class of glow discharges with several potential applications in materials processing. These discharges operate in a previously inaccessible regime of plasma parameter space and have properties that resemble classical low-pressure glow discharges, but at atmospheric or near-atmospheric pressures. Important classes of APG discharges include a high-frequency capacitively coupled configuration with closely spaced parallel electrodes and a low-frequency dielectric-barrier configuration with parallel plates and an intermediate dielectric layer. In this talk, we will present detailed one-dimensional simulation results for a dielectric-barrier APG discharge for varying discharge parameters such as gap length, dielectric capacitance, and frequency. The mechanism of pulsed glow formation and extinction will be discussed for a noble gas (helium) and a molecular gas (nitrogen) APG plasma. Ion impact energy characteristics at the surfaces will be analyzed and its implications for in situ material processing will be reported. Simulation results will be verified with experimental data where available.

Supported by NSF-CAREER grant.

10:00am **PS-TuM6 Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon at Atmospheric Pressure**, ***M. Moravej***, *S. Babayan, G.R. Nowling, X. Yang, R.F. Hicks*, University of California, Los Angeles

The plasma enhanced chemical vapor deposition (PECVD) of hydrogenated amorphous (a-Si:H) and hydrogenated microcrystalline (uc-Si:H) silicon has been examined at ambient pressure. A hydrogen and helium gas mixture flowed through two electrodes supplied with 50 W RF power at 13.56 MHz. Silane was added downstream from this plasma, and the reactive mixture directed onto a heated glass substrate. After growth the thickness of the films was determined using a profilometer. The deposition rate increased with the H2 and SiH4 partial pressures and saturates at approximately 70 Å/min for both parameters. The deposition rate also increased with substrate temperature following an Arrhenius relation with an activation energy of 3.44 kJ/mol. However the growth rate decreased from 92 Å/min to 13 Å/min as the electrode-to-substrate distance increased from 10.5 mm to 5 mm. Fourier-transform infrared spectroscopy, Rutherford backscattering spectroscopy, and Raman spectroscopy were used to determine the structure and chemical composition of the films. The effect of the process conditions on the hydrogen content and degree of crystallinity of the films will be discussed at the meeting.

10:20am **PS-TuM7 Low Energy Electron Enhanced Etching (LE4) for Reduced Process Damage in Compound Semiconductor Devices**, ***H.P. Gillis***, *S.H. Lee*, University of California, Los Angeles, *D.I. Margolese, S.J. Anz*, Systine, Inc. **INVITED**

Dry etching for defining device features is a key process in manufacturing integrated circuits because it controls critical dimensions much more tightly than does wet etching. Indeed, the ability to etch transistor features at dimensions progressively smaller than 0.25 ?m has been a mainstay of the computer industry, and is one of the foundations of Moore's Law. As a side effect, the conventional dry etch methods inflict "etch process damage" caused by the surface ion bombardment needed for high resolution feature definition. Consequently, the need arises for developing alternative dry etch processes and for characterizing "etch process damage" in material terms to guide its control and elimination. We will describe an alternative dry etch method in which electrons with energies below about 15 eV stimulate high-resolution etching of features as small as 0.020 ?m with no apparent damage. Along with high-resolution feature definition, this method gives mirror-smooth etched surfaces and maintains stoichiometry of compound materials. We will relate these results to plasma conditions including the electron temperature and energy distribution. The discussion will emphasize compound semiconductor materials and applications for optical and wireless communications.

11:00am **PS-TuM9 Coulomb Crystals in Plasma Processing Reactors**[1], ***V. Vyas***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Many plasma deposition systems operate in regimes whereby large densities of small particles are nucleated in the gas phase. Given sufficient densities of these particles, they can exhibit collective behavior and form Coulomb solids. These structures typically form at moderate gas pressures, small particle sizes and lower powers in capacitively coupled, radio frequency discharges. Lattices having different radial structure functions [g(r)], non-ideality factors and geometrical shapes can be formed given somewhat subtle changes in discharge properties. Having scaling laws for their behavior would be desirable to minimize unwanted feedback to the plasma or film properites. To address these phenomena, a 3-dimensional dust transport simulation has been developed and incorporated into a plasma equipment model. The forces included in the dust transport model are electrostatic, ion-drag, thermophoretic, fluid-drag by neutrals, gravity and particle-particle Coulomb interactions. We will discuss formation of plasma crystals as function of operating conditions in rf discharges and, in particular, the formation of voids in the plasma crystal at high substrate biases. The negative ion fluxes in electronegative gas mixtures alter the ion drag force acting on the dust particle leading to qualitatively different crystal morphologies than those found in electropositive plasmas. For example, addition of electronegative gases such as Cl_2 and O_2 to Ar causes voids in the plasma crystals to close. The effect of ion streaming on dust particle motion will be discussed, as will the effect of surface topology on radial compression of the plasma crystal producing changes in interparticle spacing and g(r).

[1] Work was supported by Sandia National Laboratory and the National Science Foundation.

11:20am **PS-TuM10 Simplified Model for Calculating the Pressure Dependence of a DC Planar Magnetron Discharge and Experimental Verification**, _**G. Buyle**_*, *D. Depla, K. Eufinger*, Ghent University, Belgium, *W. De Bosscher*, Bekaert Advanced Coatings, Belgium, *J. Haemers, R. De Gryse*, Ghent University, Belgium

A simplified model for the DC planar sputter magnetron discharge allowing to simulate the pressure dependence over a wide range is presented. The model is based on the assumption that the discharge is built up by arch shaped regions which are determined by the orbits of the electrons emitted from the cathode by ion bombardment (secondary electrons). This assumption, combined with relatively simple schemes for the ionization, target erosion and secondary electron production, forms the core of the simplified model. Although the presented model has not the same accuracy as more advanced models based on the Monte-Carlo method, it has the major advantage of being much less computing intensive. This allows for quickly assessing the influence of a variety of discharge parameters and has proven to be well sufficient to explain our experimental results. We observed that at high gas pressures (above approximately 0.5Pa) there is a very weak pressure dependence of the observed discharge parameters, but for lower pressures an increase in the discharge voltage, cathode sheath thickness and erosion profile width is observed. Our modeling revealed the

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***** PSTD Coburn-Winters Student Award Finalist

necessity to integrate recapture of secondary electrons by the cathode to explain the observed pressure dependence. To our knowledge, recapture in planar magnetron discharges has not been acknowledged yet. This is because the small initial energy of the secondary electrons, which enables recapture, is neglected in recently published simulations. Given the good agreement between experiment and simulation in this study, it appears that recapture is essential for accurately modeling the planar magnetron discharge at low pressures and that the presented model, in spite of its simplifications, is a valuable tool for this.

11:40am **PS-TuM11 Conformal and Anisotorpic Deposition of Cu Films using H-assisted Plasma CVD**, ***M. Shiratani***, *K. Takenaka, M. Onishi, K. Koga, Y. Watanabe,* Kyushu University, Japan, *T. Shingen*, Asahi Denka Kogyo K.K., Japan

We have developed H-assisted plasma CVD (HAPCVD),[1,2] which realizes conformal and anisotropic deposition of Cu films in trenches for Cu interconnects of small width below 100 nm. Conformal deposition is aimed at creating thin Cu seed layer for Cu electroplating, while anisotropic deposition is aimed at filling trenches completely. We have obtained the results 1-4) using fluorine(F)-free complex, Cu(EDMDD)$_2$ and the result 5) using Cu(HFAC)$_2$. The following conclusions are obtained in this study. 1) H irradiation is effective in removing impurities from the surface and inside of Cu films for a substrate temperature above 170°C. 2) Initial nucleation densities of Cu on TiN, TaN, and SiO$_2$ layers are above $5x10^{15}$ m^{-2} which is quite high compared to those for thermal CVD. The high nucleation density is favorable to realizing smooth thin Cu films and their strong adhesion to under-layer. 3) Deposition of Cu films of a low resistivity, 1.85 μΩcm and a strong adhesion above 10 MPa to TiN diffusion barrier layer has been demonstrated. Concentrations of C and O in the Cu film are much less than 0.1%, while those values at the interface between Cu and TiN are 1 and 0.2%, respectively. 4) Conformal deposition of smooth Cu films of 20 nm in thickness in trenches 0.5 µm wide and 2.73 µm deep has been demonstrated. 5) Anisotropy, which is defined as a ratio of film thickness at bottom of trench to that at its side wall, increases from 100% to 550% with increasing energy of irradiating ions from 20 V to 220 V, while H-irradiation reduces anisotropy. Promising anisotropic filling of trenches 3.5 µm wide, 2.73 µm deep has been demonstrated.

[1] M. Shiratani, et al., Sci. and Technol. of Adv. Mater. , 2, 505 (2001).

[2] K. Takenaka, et al., Proc. of Int. Symp. of Dry Process, pp.169 (2001).

Surface Engineering
Room: C-111 - Session SE+NS-TuM

Nanocomposite and Nanolayered Coatings
Moderator: Y.-W. Chung, Northwestern University

8:20am **SE+NS-TuM1 The Effect of Columnar Growth in the Hardness of TiN/NbN Superlattices**, ***J.M. Molina-Aldareguia***, *T. Joelsson, M. Oden,* Linkoping University, Sweden, *W.J. Clegg,* Cambridge University, UK, *L. Hultman*, Linkoping University, Sweden

Nitride superlattices can be much harder than the individual component materials of which they are made, for a comparable defect and residual stress state. However, there appears to be considerable variation in the observed magnitude of this effect. The aim of this work was to investigate the origin of this variation by comparing two series of epitaxial TiN/NbN superlattices grown by reactive magnetron sputtering on MgO(001) single crystals: one that displayed superlattice hardening and another that did not. According to X-Ray Diffraction and X-Ray Reflectivity studies, the composition modulation was strong and the composition change at the interfaces abrupt in both series, indicating that the hardening is strongly influenced by some other microstructural parameter besides the layering. To investigate this, the deformation mechanisms were studied using a focused ion beam workstation to prepare cross-sectional transmission electron microscopy specimens under nanoindentations. These studies show that the superlattices with no hardening possess a columnar structure with voided boundaries, which act as preferential sites for shear to take place. This implies that the incorporation of porosity at the columnar boundaries, which is dependent on the growth conditions, is responsible for the variation observed in the magnitude of the hardening effect in TiN/NbN superlattices.

8:40am **SE+NS-TuM2 Optical Behavior of Zirconia-Titania Nanolaminate Films**, ***C.R. Aita***, University of Wisconsin-Milwaukee, *J.D. DeLoach*, Texas Instruments

Nanolaminate films of wide band gap semiconductors have bilayer periodicity much less than the wavelength of optical photons. These films are excellent candidates for high refractive index coatings througout the visible spectrum, coupled with optical band gap tailorability in the near-ultraviolet region. Here, we demonstrate this concept using ZrO$_2$-TiO$_2$ nanolaminates. Multilayer films were grown at room temperature by sequential reactive sputter deposition from metal targets using O$_2$-bearing discharges. Bilayer periodicity ranged from several to tens of nanometers. Total film thickness was in the 200 to 500 nm range. Optical transmission and reflection measurements were carried out in the 190 to 1100 nm wavelength range. Optical parameters were determined from these measurements. The results show that the refractive index throughout the region of high transmission was constant, equal to 2.2, and independent of nanolaminate architecture. On the other hand, the onset of fundamental optical absorption was strongly dependent upon bilayer architecture. A blue shift of the optical absorption edge was observed as the bilayer ZrO$_2$ increased. Optical band gap values spanned a range of 2 eV, from appproximately 3 eV for TiO$_2$ to 5 eV for ZrO$_2$, giving the system tailorability. The results are discussed in terms of the primacy of the coordination of a central cation (Zr or Ti) with its nearest neignbor O atoms in determining the features of the fundamental optical absorption edge. We show that the model developed to explain the results for the ZrO$_2$-TiO$_2$ system can be applied to other nanolaminates or nanocomposites in which the spatial extent of the wavefunctions describing near edge optical transitions is comparable to the short-range order in the film.

9:00am **SE+NS-TuM3 Nanocomposite and Nanolayered Hard Coatings**, ***J. Patscheider***, *T. Zehnder, J.C. Cancio*, EMPA, Switzerland **INVITED**

Nanostructuring of hard coatings, which is achieved by combining two phases with atomically sharp interfaces, opens up new possibilities to improve conventional coatings with respect to their hardness, limited temperature stability and their frictional behavior. The best known combinations of well-separated phases for increased hardness are multilayered superlattices as well as nanocomposite coatings. Nanocomposite coatings proved successful in promoting hardness, oxidation resistance, improved wear behavior and other properties relevant for protective coatings. Such coatings are composed of nano-crystalline grains of transition metal nitrides or carbides, which are surrounded by amorphous hard matrices. Most nanocomposite hard coatings show typically a maximum of the hardness, which can range from 30 GPa to reported values above 60 GPa, as the composition is changed from the pure crystalline phase (no amorphous component) to compositions dominated by the amorphous phase. At the hardness maximum the domain size of the nanocrystalline phase is below 10 nm and the amorphous layer separating the nanocrystals, is only a few atomic bond lengths thin. A comparison to hadness-enhanced superlattices show that the critical dimensions necessary to obtain this effect are of the same order, i.e. the domain size in hard nanocomposites and the single layer thickness in superlattices are both below 10 nm. Due to the absence of dislocation activity, deformation of nanocomposites will be only due to grain boundary sliding. This process requires more energy than deformation by dislocation movement, which is synonymous to increased hardness. In some cases the amorphous phase can act as a solid lubricant (a-C or a-C:H) or as diffusion barriers (Si$_3$N$_4$) for improved thermal stability. The amorphous phases in nanocomposites thus cause, apart from the enhanced hardness, additional effects that are beneficial for the performance of these new wear-protective coatings.

9:40am **SE+NS-TuM5 Characterization of TiCrN Nanocomposite Protective Coatings for Biomedical Applications**, ***S.M. Aouadi***, Southern Illinois University, *K.-C. Wong, K.A.R. Mitchell,* University of British Columbia, Canada, *F. Namavar, E. Tobin,* Spire Corp., *D.M. Mihut, S.L. Rohde*, University of Nebraska, Lincoln

The structural, chemical, optical, and mechanical properties of TiCrN nanocrystalline multiphase films deposited by ion beam assisted deposition (IBAD) were studied by means of X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and nanoindentation. The primary phases in the films, their volume fractions, and the elemental compositions were determined from XRD and XPS measurements. The TiCrN films consisted of two phases, namely Ti-N and Cr, for nitrogen concentrations lower than titanium concentrations. For larger nitrogen concentrations, an additional phase (Cr2N) was identified. The topography of the various films was measured using AFM. The optical constants were measured using spectroscopic ellipsometry. A correlation between the elemental/phase composition and optical constants was established. The usefulness and limitations of effective medium theories (EMA) to model the optical constants of these nanocrystalline composite materials will be discussed. The mechanical properties of the coatings were evaluated using nanohardness testing. The hardness and elastic modulii were found to depend on the constituting phases and were measured to be 22-32 GPa and 180-260 GPa, respectively.

10:00am **SE+NS-TuM6 Preparation and Characterization of Chemically Bonded Si_3N_4 and TiN Nanocomposites Prepared by Mechanical Alloying and Sintering**, ***S.W. Deore***, *M. Kesmez, M.A. Hossain,* Lamar University, *J.R. Parga,* Instituto Technologico de Saltillo, Mexico, *D.L. Cocke*, Lamar University

Mechanical alloying using high-energy ball milling is a promising materials processing technique to synthesize nanocomposites for superior mechanical and chemical properties. However, the need to sinter, the application of heat to a powder or a powder body, to increase interparticle bonding, and usually density, tends to result in the destruction of the nanosized components. We have been examining the use of chemical binders that can be pyrolyzed to ceramic binding components at lower temperatures. The heating regime for the sintering process has been determined from the DSC analysis of the binders. Silicon nitride and titanium nitride nanocomposite powders have been prepared using high energy SPEX milling in a nitrogen atmosphere. The composites have been characterized using XRD, XPS, FTIR and SEM. Although both solid phase and liquid phase binders have been examined for their binding properties and hence, the properties of the obtained nanocomposites. The preferred characteristics of the binder precursors will be discussed and a major problem of wetting of the binder to the nanoparticles encountered will be delineated.

10:20am **SE+NS-TuM7 Comparison Studies of Titanium Silicon Carbide Hard Coatings Deposited by Pulsed Laser Deposition and Magentron Sputtering Assisted Pulsed Laser Deposition**, ***A.R.P. Ayalasomayajula***, *J.E.R. Krzanowski*, University of New Hampshire

Titanium silicon carbide films have been grown by Pulsed Laser Deposition (PLD) as well as Magnetron Sputtering Assisted Pulsed Laser Deposition (MSAPLD) on Si (111) and 440C steel substrates at different substrate temperatures and at different substrate bias at 400°C. Experiments are also conducted with different laser powers for C ablation and sputtering powers for $TiSi_2$ content in the deposited films to investigate the effect of C and $TiSi_2$ mechanical and tribological properties. X-ray Diffraction has been employed to find the crystal structure and orientation of the deposited films. Film morphology and roughness are measured by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques, respectively. The film hardness was measured by nano-indentation, while x-ray photoelectron spectroscopy (XPS) was used to estimate the film composition using depth profiling. The residual stress of the deposited was measured by 2D-area General Area Detector Diffraction System. TiSiC films deposited by PLD have shown reasonably high hardness values (37GPa) compared to $TiSi_2C$ films by MSAPLD which have shown hardness values 30GPa at 400°C. The hardness is correlated with residual stress of the deposited films, where we have observed high tensile stress for MSAPLD films leading to decrease in hardness values. Tribological studies have also been conducted to evaluate the friction and wear properties of these films. The mechanisms of hardness enhancement and its relation to tribological properties has also been explained.

10:40am **SE+NS-TuM8 Response of Nanocrystalline Materials to Ion and Neutron Irradiation**, *A. Kubota,* ***M.-J. Caturla***, *T. Diaz de la Rubia, B.D. Wirth,* Lawrence Livermore National Laboratory

Plasma-facing materials are generally exposed to a harsh radiation environment. Radio-frequency excited plasmas under biased conditions produce energetic ion radiation which can lead to material damage and erosion at the surface. In fusion plasma applications however, materials face significant bulk defect production and damage due to deeply penetrating 14 MeV neutrons and Helium nuclear reaction products, leading to embrittlement and void swelling. We discuss results of computational simulations to assess the feasibility of high grain-boundary-density nanocrystalline materials in fusion environments. The performance of the nanocrystalline metals is discussed in terms of defect migration to and annihilation at the grain boundaries, as well as Helium migration along the grain boundary network.

11:00am **SE+NS-TuM9 Novel Properties and Potential Applications of CrBN Films Produced via Unbalanced Magnetron Sputtering**, ***D.M. Mihut***, *T.Z. Gorishnyy, D.M. Schultze,* University of Nebraska, *S.M. Aouadi,* Southern Illinois University, *S.L. Rohde,* University of Nebraska

CrBN nanocrystalline and amorphous materials produced using ion-assisted unbalanced magnetron sputtering were deposited on to a variety of substrates, to investigate the potential of these coating in several applications ranging from coatings on AFM tips to very smooth films for tribological coatings. Coatings were deposited over a range of temperatures from ambient (<200°C) to nearly 900°C, and their thermal stability investigated. Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, providing a valuable resource for work in these new, but complex multi-phase materials. In addition, these films were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), transmission electron microscopy (TEM), nanoindentation, and microwear. XPS, AES, and IR-SE were used in tandem to reveal the crystal structure of the BN phase in these ternary compounds. The amorphous to nanocrystalline nature of the coatings were deduced using AFM and TEM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness/microwear analyses. Several interesting applications, are currently under investigation as CrBN films have been found to provide a unique combination of very low roughness (rms < 0.2 nm) and high surface hardness (> 22 GPa) under certain growth conditions.

11:20am **SE+NS-TuM10 Preparation, Structure, and Properties of Composite Fullerene-Like CNx Films Produced by Pulsed Laser Ablation**, ***A.A. Voevodin***, *J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory, *Zs. Czigany, L. Hultman*, Linkoping University, Sweden

Production of composite CNx films made of fullerene-like structures in an amorphous matrix using laser ablation of graphite in nitrogen is reported. Deposition was optimized based on investigations of chemistry, excitation stage, kinetic energy, temperature, and spatial distributions of molecular (CN and C2) and atomic (C and N) species, using element specific imaging, time-of-flight experiments, fluorescence spectroscopy, and molecular vibration sequence analyses. Studies showed the importance of plume / substrate interaction in generating excited CN and C2 molecules with high vibrational energy at the condenasation surface for low deposition pressures. Films were characterized with x-ray photoelectron spectroscopy, Raman spectroscopy, high-resolution transmission electron microscopy, nanoindentation, and stress analyses. Nitrogen content directly depended on the concentration of CN radicals at the condensation surface. Formation of fullerene-like structures required a high vibrational temperature of these radicals, which was maximized at about 4 eV for depositions at 10 mTorr N2 and laser fluences of ~7 J/cm2. The presence of C2 had only a minor effect on film composition and structure. Optimization of plasma characteristics and a substrate temperature of 300 C helped to produce about 1000 nm thick solid films of CNx (N/C ratio 0.2 - 0.3) and pure carbon consisting of fullerene-like fragments and packages. Films exhibited elastic recovery of about 80%, elastic modulus of 160-250 GPa and hardness of up to 30 GPa, which was twice that of fullerene-like carbon films. The unusual combination of high elasticity and hardness was explained by cross-linking of fullerene fragments induced by the incorporated nitrogen. Correlations between plasma composition, film structure and properties are established. Results of film mechanical testing demonstrate benefits of the film application as a hard protective coating to resist brittle fracture at high contact loads.

11:40am **SE+NS-TuM11 Tribological Analysis of Nano-composite Diamond-like Carbon Films Deposited by Unbalanced Magnetron Sputtering**, ***D.-Y. Wang***, Mingdao University, Taiwan, *Y.-Y. Chang*, National Chung-Hsing University, Taiwan

Ti contained nano-composite DLC coatings have been developed with improved tribological characteristics. These coatings were synthesized using an unbalanced magnetron sputtering (UBMS) process with a combination of graphite and metal targets. A 100 kHz pulsed d.c. power supply was applied to the substrates to control the substrate arcing and radical excitation during the DLC formation. The microstructure of the nano-composite DLC film was investigated by using cross-section TEM/SAD, x-ray diffraction, Raman and XPS. Tribological properties such as wear mechanism, transfer phenomenon, friction coefficient, and wear life were evaluated and compared with commercial Ti-C:H DLC coatings by using pin-on-disk wear test analyses. The optimized Ti/C multi-layered DLC coatings give satisfied friction performance in the pin-on-disk test with lower wear rate of $1\text{-}3 \times 10^{-17}$ m^3/Nm and lower friction coefficient of 0.09-0.1 sliding against 100Cr6 and WC materials. The easily transferred oxide- free graphite-like sp^2 phases form a lubricious layer, which posses low shear strengths under applied stresses. The low friction coefficients and wear rates during the tribological action are anticipated.

Surface Science
Room: C-108 - Session SS1-TuM

Hydrocarbon Catalysis
Moderator: J.L. Gland, University of Michigan

8:20am **SS1-TuM1 The Role of Defects in Surface Resistivity: The Unusual Case of Sulfur on Cu(100)**, ***R.G. Tobin***, Tufts University

Adsorbate-induced surface resistivity – the change in electrical resistivity of a metal film when a gas adsorbs on its surface – provides a simple but powerful probe of the dynamical interaction between conduction electrons and adsorbates.[1] The dominant mechanism is generally diffuse scattering of the electrons from the adsorbate, and the scattering cross section per adsorbate is usually nearly independent of adsorbate coverage. For sulfur on Cu(100), however, the resistivity increases rapidly with coverage up to a threshold, and then remains constant as the coverage increases further. This effect was first observed by Xu and Hirschmugl using infrared reflectance and a single crystal sample.[2] They attributed the rapid increase at low coverage to a large scattering cross section for S adsorbed on defect sites, with a near-zero cross section for S on terrace sites. In the present study the same behavior is seen in both the dc resistivity and the infrared reflectance of epitaxial Cu(100) thin films. The transition between the two scattering regimes, however, occurs at a higher coverage (~0.2 ML) than in the single-crystal measurements (0.04 ML). The role of defects is investigated by quantitatively estimating the defect density from CO adsorption measurements, and by sputtering the surface before adsorption to increase the defect density.

[1] R.G. Tobin, Surf. Sci., in press.

[2] X.F. Xu and C.J. Hirschmugl, Surf. Sci. 490 (2001) 69.

8:40am **SS1-TuM2 Chemistry of One-dimensional Metallic Edge States in MoS_2 Nanoclusters**, ***J.V. Lauritsen***, University of Aarhus, Denmark, *B.S. Clausen, H. Topsoe,* Haldor Topsoe A/S, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

We report on interesting chemistry of MoS_2 nanoclusters, which we show to be able to hydrogenate and break up thiophene (C_4H_4S) molecules at unusual sites on the cluster edges. We associate this behavior with one-dimensional metallic electron states located at the perimeter of the otherwise insulating nanoclusters. Since MoS_2 nanoclusters constitute the basis of hydrotreating catalysts used to remove sulfur from oil products through the hydrodesulfurization (HDS) process, the kind of chemistry identified in this work has significant implications. Our approach exploits recent progress in the synthesis of a relevant catalyst model system, i.e. we can synthesize MoS_2 nanoclusters image them on the atomic-scale with STM.[1] With STM prominent electronic features are observed near the edges of triangular MoS_2 clusters, which are associated with 1D metallic edge states.[2] By adsorbing hydrogen and thiophene, we pin-point, in the STM studies, active sites on these metallic edge states and reveal signatures of thiophene reaction intermediates adsorbed onto the metallic edge state. At the cluster edges, we find that S-H groups form, which are involved in a hydrogenation reaction and subsequent C-S cleavage of thiophene. In an interplay with density functional theory we elucidate the reaction pathway and classify the adsorbed species as ring-opened thiolates. We have thus identified a new route for activating a relatively inert, sulfur containing molecule like thiophene. Unexpectedly, this process does not take place through direct interaction with the Mo atoms. Instead, metallic states on the fully sulfided edges have the ability to donate and accept electrons and thus act as catalytic sites just like ordinary metal surfaces.

[1] S. Helveg, J. V. Lauritsen et al. Phys. Rev. Lett. 84, 951 (2000).

[2] M. Bollinger, J. V. Lauritsen et al., Phys. Rev. Lett. 87, 196803 (2001).

9:00am **SS1-TuM3 Electron-Induced Dissociation and Reactions of Methyl Groups Adsorbed on Cu(110)**, *Y.L. Chan, P. Chuang,* National Taiwan University, Republic of China, *R. Klauser,* Synchrotron Radiation Research Center, Taiwan, Republic of China, *S.-H. Chien,* ***T.J. Chuang***, National Taiwan University, Republic of China

Methylene was suggested in some prior studies to be the key species responsible for the propagation of long chain hydrocarbons from methyl groups on catalyst surfaces. So far, direct evidence to show the presence of such reaction intermediate remains elusive, particularly under UHV condition. With the combination of HREELS vibrational spectroscopy, TPD and LEED techniques, we have observed that CH_3(ads) groups adsorbed on Cu(110) can be dissociated by low energy electrons to form CH_2(ads). In subsequent thermal process, CH_2(ads) can react with coadsorbed CH_3(ads) to produce C_2H_4, C_3H_6 and C_4H_8 molecules desorbed from surface. The desorption peaks for the various alkenes center at the same temperature independent of the CH_2(ads) average surface concentration and exhibiting the first-order reaction kinetics. Furthermore, the product ratio of C_3H_6/C_2H_4 is found to be linearly proportional to the ratio of CH_2(ads)/CH_3(ads) concentrations. The results show that aggregation of the adsorbates and close proximity of the reactants in the form of two-dimensional islands may be essential for the chain propagation reactions. In this study, the e-beam irradiation effects on molecular dissociation and desorption are investigated in the electron energy range of 5-70 eV. Preliminary report of these effects was given recently,[1] and a detailed account will be presented in this paper.

[1] P. Chuang, Y.L. Chan, S.-H. Chien, R. Klauser and T.J. Chuang, Chem. Phys. Lett. 354,179 (2002).

9:20am **SS1-TuM4 Oxidative Coupling of Methane to Higher Hydrocarbons Using Li_2O/MgO Catalysts**, *J. Langohr, R. Heinisch,* ***F. Behrendt***, Technische Universität Berlin, Germany

Oxidative coupling of methane represents an important pathway to produce higher hydrocarbons especially those with two carbon atoms, i. e, ethane and ethane, representing a key component for chemical industry. The reaction scheme - which still is not completely understood -involves a number of steps with the heterogeneous formation of methyl radicals and the homogeneous recombination of methyl radicals to ethane as key parts. The second of these reactions is in competition with reactions leading to the total oxidation products carbon dioxide and water - a pathway occurring both homogeneously and heterogeneously. With respect to the concentration of methyl radicals the reaction order is one for the total oxidation but two for the formation of ethane. An increase of the concentration of methyl radicals should promote an increased production of the C_2 hydrocarbons. For the example of a set of Li_2O/MgO catalysts it is shown that an increase of the BET surface area - resulting in a higher number of active sites at the catalyst^{1}s surface - results in an increased yield of C_2 hydrocarbons. By variation of the preparation technique (aqueous mixtures of various Li and Mg salts are dried and then calcinated at different temperatures and periods of time) catalysts are produced which indeed show an increase in methane turn-over - without losing selectivity for C_2 hydrocarbons - with increasing surface area. The BET surface area is varied between 0.3 and 4.2 m^2/g. Ongoing experiments aim at further increasing this surface area. Modifications of the preparation technique will include calcination under low-pressure conditions and on carrier materials having high surface areas themselves, e. g., polyurethane foams or activated carbon.

9:40am **SS1-TuM5 The Dynamics of Alkane Adsorption on Pt(111), Pd(111) and Ni(111): Prediction from One Metal to Another?**, *C.-L. Kao,* Stanford University, *J.F. Weaver,* University of Florida, ***R.J. Madix***, Stanford University **INVITED**

The adsorption and reaction of alkanes on metal surfaces is fundamental to hydrocarbon catalysis. In order to adsorb the kinetic energy of the incident molecule must be dissipated in the gas-surface collision. To develop a predictive capability for the adsorption probabilities of alkanes on surfaces we have combined molecular beam methods with molecular dynamics simulations. The objective is to determine simple empirical potential parameters that govern the alkane-metal interaction from experimental measurements for a single alkane-surface combination and to use these parameters to predict trapping probabilities for other alkanes on other surfaces. A single set of potential parameters, determined from measurements of the trapping probabilities of ethane on Pt(111) can be used to predict the trapping probabilities of C3-C5 alkanes on Pt(111) and ethane and propane on Pt(110). More recently, these predictions have been extended to C1 - C5 alkane trapping on Pd(111). Palladium and platinum have similar lattice constants and Debye temperatures, differing primarily in their atomic mass, and thereby offer a good first order test of the predictive capability of the molecular dynamics simulations. Indeed, the trapping probabilities for Pd(111) are accurately predicted. Generally, the trapping probabilities for a given alkane are higher on Pd(111) due to the lower mass of the palladium atoms. The simulations show the importance of both the excitation of lattice vibrations and cartwheel rotational motion in affecting trapping. Predictions for Ni(111) are potentially more challenging, since the Ni-Ni force constants are much higher and both the mass and lattice parameter differ significantly from those of platinum. The theory correctly predicts that the adsorption probabilities on Ni(111) are lower than those for both Pt(111) and Pd(111). In general trapping probabilities are predicted to within about 50%.

10:20am **SS1-TuM7 Molecular Mechanisms of Propylene Adsorption and Oxidation on the Stepped Pt(411) Surface**, ***H.D. Lewis***, *D.J. Burnett, A.M. Gabelnick,* University of Michigan, *D.A. Fischer*, National Institute of Standards and Technology, *J.L. Gland*, University of Michigan

The influence of surface defects on the chemistry of propylene adsorption and oxidation was investigated using temperature-programmed reaction spectroscopy (TPRS) and in-situ fluorescence yield soft x-ray techniques on the stepped Pt(411) surface. Mass spectrometer based TPRS studies show that propylene adsorbed on Pt(411) at 100 K undergoes disproportionation and decomposition to propylene, propane, hydrogen and surface carbon. Reacting coadsorbed propylene with excess oxygen, complete oxidation occurs with oxydehyrdogenation to water preceding skeletal oxidation to carbon dioxide. Based on the qualitative mechanistic understanding from TPRS, in-situ oxidation experiments were performed in oxygen pressures up to 0.02 Torr. The mechanism is the same in flowing oxygen, and preadsorbed propylene is completely oxidized by 475 K. The 280 K initiation temperature for oxydehydrogenation is independent of oxygen pressure, while the initiation temperature for skeletal oxidation is oxygen pressure dependent beginning at 370 K in 1 x 10^{-5} Torr oxygen and decreasing to 300 K in 0.02 Torr oxygen. A stable intermediate is observed after oxydehydrogenation is complete. The molecular mechanism for propylene oxidation on Pt(411) with both propylene and oxygen in the gas phase was also studied. With increasing oxygen pressure less propylene is adsorbed and the onset temperature for deep oxidation decreases. Taken together, results indicate that the inhibition of oxygen adsorption is important in limiting this complex oxidation reaction. Results for propylene oxidation on this stepped surface are compared to studies on Pt(111) to delineate the role of surface defects in this interesting surface reaction network.

10:40am **SS1-TuM8 Catalytic Arene Oxidation on Supported Platinum Nanoparticles**, ***A.L. Marsh***, University of Michigan, *G.E. Mitchell*, The Dow Chemical Company, *D.A. Fischer*, National Institute of Standards and Technology, *J.L. Gland*, University of Michigan

The cleanup of volatile organic compounds from industrial emissions is a current environmental issue that requires knowledge of molecular-level mechanisms for catalytic processes. Aromatics such as benzene, toluene, and chlorobenzene are often present in emissions because of their stability. However, these molecules can be removed by oxidation over nanoparticulate-supported catalysts. In order to better understand the mechanisms of catalytic oxidation, the reactions of benzene, toluene, and chlorobenzene on a commercial alumina-supported platinum catalyst have been characterized both in vacuum and in the presence of oxygen. Molecular-level mechanisms for both decomposition and oxidation have been determined using Temperature-Programmed Reaction Spectroscopy. The structures of intermediates present during oxidation or decomposition have been identified using Fluorescence Yield Near-Edge Spectroscopy. Comparisons will be made to the chemistry on the Pt(111) surface in an effort to show the effects of particle size and of the support. Substantial substituent effects on the chemistry of the aromatic ring are also observed. This molecular-level understanding of these reactions will aid in tailoring catalysts for the efficient cleanup of industrial emissions.

11:00am **SS1-TuM9 In situ XPS Investigation of the Methanol Oxidation Over Copper**, ***H. Bluhm***, *M. Hävecker, A. Knop-Gericke*, Fritz Haber Institute of the Max Planck Society, Germany, *V.I. Bukhtiyarov*, Boreskov Institute of Catalysis, Russia, *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory, *R. Schlögl*, Fritz Haber Institute of the Max Planck Society, Germany

We have used in situ X-ray photoelectron spectroscopy (XPS)[1] in combination with mass spectrometry to investigate the partial oxidation of methanol to formaldehyde over a polycrystalline copper sample. The experiments were performed at a methanol to oxygen flow ratio of 3:1 (total pressure 0.4 torr) in the temperature range from 300 K to 750 K. The correlation of in-situ XPS spectra of the copper surface and the simultaneously obtained mass spectrometer data (which show the catalytic activity) allow us to draw conclusions about the electronic state of the catalyst under reaction conditions. Valence band and Oxygen 1s spectra show that after the onset of the catalytic reaction at T>550 K the copper surface has a metallic character. The Oxygen 1s spectra reveal that at least two different oxygen species with binding energies (BE) of 529.7 eV and 531.4 eV, respectively, are present at the catalytically active Cu surface. The O 1s peak at 529.7 eV is assigned to chemisorbed oxygen at the Cu surface. The integrated intensity of the chemisorbed oxygen peak is proportional to the amount of formaldehyde that is produced in the catalytic reaction. The peak at 531.4 eV is assigned to subsurface oxygen. The formaldehyde yield increases linearly with the integrated intensity of the subsurface oxygen peak, up to a concentration of the equivalent of about one monolayer of subsurface oxygen. A further increase of the amount of subsurface oxygen does not lead to an increase of the formaldehyde yield.

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[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, submitted to Rev. Sci. Instrum.

11:20am **SS1-TuM10 Determination of the Adsorption Site of a Polyatomic Adsorbate Using Vibrational Spectroscopy and ab initio Calculations: Methoxy and Ethoxy on Cu(100)**, ***P. Uvdal***, *M.P. Andersson*, Lund University, Sweden

Using infrared vibrational spectroscopy and ab initio electronic structure calculations of small metal cluster models we have determined the adsorption site of methoxy and ethoxy on Cu(100). The experimental intramolecular vibrational frequencies are very well reproduced by the model cluster representing the four-fold hollow adsorption site. In contrast calculated frequencies for intermolecular modes modeled by clusters representing bridge and on-top adsorption is not not reproduce as well.

11:40am **SS1-TuM11 A Model Catalyst with Selectivity Controllable Functions: The Effects of Frequency in Thickness Extension Mode Resonance Oscillation on Ethanol Decomposition Over a Thin Ag Film Deposited on a Ferroelectric z-cut $LiNbO_3$ Single Crystal**, ***N. Saito***, *Y. Yukawa, H. Nishiyama, Y. Inoue*, Nagaoka University of Technology, Japan

The resonance oscillation of acoustic waves is generated on a poled ferroelectric crystal by a piezoelectric effect. We have shown that the thickness extension mode resonance oscillation (TERO) has the ability to remarkably change the reaction selectivity over thin metal catalysts deposited on a z-cut $LiNbO_3$ (z-LN) crystal.[1] The TERO has a series of resonance frequencies (the first, the second, the third and so on) determined by the crystal constants. A z-LN crystal shows 3.5(first), 10.8 (second) and 17.9 (third) MHz. It is interesting to see the frequency effects on TERO-induced selectivity changes. In the present work, the TERO of 10.8 and 17.9MHz were employed for ethanol decomposition on a thin Ag film catalyst deposited, and the results were compared with those reported previously for 3.5MHz. The TERO of 10.8 and 17.9 MHz at 1.5W caused the enhancement of ethylene production without significant changes in acetaldehyde production. The selectivity for ethylene production, S_e, increased from 62% without the TERO to 96% for 3.5MHz, 85% for 10.8MHz and 75% for 17.9MHz. The selectivity increases became small with increasing resonance frequency. Laser Doppler measurements showed that the TERO generated randomly distributed standing waves vertical to the surface. With increasing frequency, the magnitude of the waves, corresponding to lattice displacement, decreased (98 nm for 3.5 MHz, 28 nm for 10.8 MHz and 15 nm for 17.9MHz at 1W), whereas the number of the standing waves per unit area increased remarkably. In photoelectron emission spectroscopy, the TERO shifted the threshold energy of photoelectron emission from Ag surface by 0.08-0.25eV. The present results indicate that the magnitude and the density of standing waves strongly related to activity enhancement and selectivity changes. A mechanism of the frequency-dependent TERO effects is discussed.

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[1] N.Saito and Y.Inoue, J.Chem. Phys. 133,469(2000).

Surface Science
Room: C-110 - Session SS2-TuM

Diffusion & Growth on Metal Surfaces
Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

8:20am **SS2-TuM1 Long Jumps in the Surface Diffusion of Large Molecules**, *M. Schunack*, ***T.R. Linderoth***, *F. Rosei, E. Laegsgaard, I. Stensgaard, F. Besenbacher*, University of Aarhus, Denmark

While the surface mobility of atomic adsorbates has been studied extensively, similar investigations of large organic molecules are very scarce. Here, we report a detailed variable-temperature Scanning Tunneling Microscopy investigation of the one-dimensional diffusion of two largish molecules, decacyclene (DC) and hexa-tert-butyl-decacyclene (HtBDC), on a Cu(110) surface. The molecular diffusion was studied by acquiring series of STM-images at substrate temperatures of 172-200 K and 218-251 K for HtBDC/DC, respectively. Surprisingly, we find that long jumps, i.e. adsorbate transitions spanning multiple lattice sites, play a dominating role for the diffusion of DC and HtBDC. The root mean-squared (RMS) jump lengths are as large as 3.9 and 6.8 Cu lattice spacings, respectively. The presence of long jumps is revealed by a new and simple method of analysis, which we have tested quantitatively by kinetic Monte Carlo simulations. The dominating role played by long jumps is in strong contrast to previously investigated adsorbate systems where diffusion typically occurs by jumps between nearest neighbor sites. Our results furthermore demonstrate the possibility of tailoring molecular diffusion properties: DC and HtBDC both have the same aromatic plane, which interacts strongly with the surface. In the case of HtBDC, however, the plane is raised away from the surface by spacer groups, resulting in an approximately four orders of magnitude higher diffusion constant compared to DC. The higher diffusivity results both from the larger RMS jump length and from a reduction of the activation barrier for diffusion from 0.73 to 0.59 eV.

8:40am **SS2-TuM2 Observation of the Motion of Individual Lead-oxide Molecules on Reconstructed Au(111) Using Scanning Tunneling Microscopy**, *M.C. Robinson, **A.J. Slavin***, Trent University, Canada

Ultra-thin metal oxides are of great technological importance, so it is necessary to understand how these films grow, beginning at the molecular level. In this study we have used scanning tunneling microscopy (STM) to observe the room-temperature diffusion of lead-oxide molecules, most probably PbO, on the reconstructed Au(111) surface at coverages below 0.06 monolayers (ML). To our knowledge, this is the first direct observation of the diffusion of metal-oxide molecules. The existence of mobile molecules suggests that, at least in some cases, oxide layer formation may be driven by the same processes governing metal-on-metal growth. If the motion is not tip-induced, then an upper limit for the molecule diffusion energy is 0.7 eV, based on the motion of the molecules between successive STM images. Atomic resolution is lost above 0.06 ML, probably because the Au reconstruction is lifted allowing a large increase in the rate of adatom diffusion.

9:00am **SS2-TuM3 Initial Stages of Transition-Metal-Assisted Carbon Nanotube Growth: A First-principles Study***, ***Z. Zhang***, Oak Ridge National Laboratory, *Q. Zhang,* The University of Texas at Arlington, *J.C. Wells,* Oak Ridge National Laboratory, *X. Gong*, Fudan University, China **INVITED**

The initial stages of catalytic growth of single-wall carbon nanotubes (SWNT) on transition metal clusters and surfaces are investigated using the first-principles molecular dynamics method. Selected nickel surfaces and magic-sized nickel clusters have been used as a paradigm for this type of catalyst. The method is based on density-functional theory using the local-density approximation with gradient corrections (GGA). The computation scheme is based on the expansion of valance electrons in a plane wave basis. The ultra soft pseudopotentials for nickel (Ni) and carbon (C) are employed to describe their interaction with ionic cores. The energetics involved in the elemental processes of SWNT growth, such as adsorption, diffusion, and nucleation of carbon atoms on the elemental facets of Ni magic clusters as well as on the different Ni surfaces, is investigated and compared, with the objective of identifying the precise role of catalytic clusters. We also investigate the energeticc involved in the possibility of a concerted motion in the atom supply and growth of a baby nanotube on a given surface.

* Research sponsored by the Material Sciences and Engineering Division Program of the Department of Energy (DOE) Office of Science and by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the US DOE under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC, and the National Science Foundation (NSF).

9:40am **SS2-TuM5 Water Diffusion and Clustering on Pd(111)**, ***T. Mitsui,*** Lawrence Berkeley National Laboratory, *M.K. Rose, E. Fomin,* University of California, *F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

The adsorption, diffusion and the formation of clusters of water molecules on Pd(111) has been studied by scanning tunneling microscopy. Water adsorbs in the form of isolated molecules at 40 K. With the help of STM movies of the molecular random walk and of atom-tracking techniques we studied the process of diffusion and cluster formation. When two water molecules meet they form a dimer, then a trimer and so on. The mobility of dimers and trimers was found to be nearly three orders of magnitude larger than that of single molecules. Pentamers and larger clusters are immobile at 40 K, although changes in their conformation were observed. Hexamers with a cyclic configuration are particularly stable. They grow with further coverage forming a commensurate hexagonal honeycomb with $(\sqrt{3}x\sqrt{3})R30°$ structure relative to the Pd(111) substrate.

10:00am **SS2-TuM6 A New Mechanism of Mo Growth on Au (111) by Chemical Vapor Deposition from a $Mo(CO)_6$ Precursor**, ***Z. Song***, *T. Cai, Z. Chang, G. Liu, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

Chemical vapor deposition (CVD) of metal carbonyls has been attractive for decades in both making supported metal catalysts and fabricating electronic devices. In most of the previous morphology studies of metal deposition on Au (111), the physical vapor deposition (PVD) method was used to prepare the samples. So far, it is not clear what to expect for the growth of metals from CVD of metal carbonyls. In this study, a Mo submonolayer has been grown by CVD of $Mo(CO)_6$ on a reconstructed Au (111) at a substrate temperature of 500 K and studied by STM. The $Mo(CO)_6$ molecules decompose on the Au(111) surface at elevated temperatures and form Mo nano-scale clusters. The Mo clusters grow on both upper and lower steps and at elbows of the Au (111) herringbone structure at low coverages. New clusters are formed with increasing Mo coverage and found preferentially within the fcc troughs and randomly at elbows. In contrast to the Mo-PVD, where Mo clusters form well-ordered arrays by decorating all elbows of Au template, the Mo-CVD clusters aggregate without coalescing and develop ramified islands of clusters. An auto-catalyzed carbonyl decomposition is proposed to explain a facile formation of Mo clusters before they anchor on the surface. The Mo growth at upper steps can be attributed to the presence of CO, that modifies locally the surface potential of Mo. This research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

10:20am **SS2-TuM7 Vacancy-Mediated and Exchange Diffusion in the Pb/Cu(111) Surface Alloy**, ***B.S. Swartzentruber,*** *M.L. Anderson, M.J. D'Amato, P.J. Feibelman*, Sandia National Laboratories

To understand the formation and stability of surface alloy systems, it is important to know the fundamental atomic-intermixing and mass-transport processes. Using STM measurements and first-principles DFT calculations we have explored them for the formation and evolution of the Pb/Cu(111) surface alloy. When Pb atoms are deposited on Cu(111), they place exchange with surface Cu atoms forming a 2-d surface alloy phase. At low coverage, thermodynamics favors a random distribution of Pb atoms in the surface layer. However, upon deposition, the Pb atoms take the easy path, forming metastable stripes of high Pb concentration embedded near steps. Over time, equilibrium is reached through the much slower decay of this initially non-uniform concentration profile. We measure the kinetics of mass transport, using STM, by following the motion of individual embedded Pb atoms and also the time evolution of the concentration profile. By analyzing the statistics of the local motion we find the most likely process to be one in which diffusion of the embedded Pb atoms occurs via exchange with thermal surface vacancies. There is also a minority process - occurring much less often - wherein an embedded Pb atom exchanges with a thermal Cu adatom and travels over long distance before re-embedding into the surface layer. Although this minority process rarely occurs, the long length scale over which it transports Pb atoms makes it a crucial ingredient of the overall mass transport process as measured in the decay of the concentration profile. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

10:40am **SS2-TuM8 Ultrathin Transition Metal Films on W Surfaces - Conditions for Surface Alloy Formation**, *J. Block, E. Schroder,* Chalmers University of Technology and Gothenburg University, Sweden, *J.J. Kolodziej,* Rutgers, The State University of New Jersey, *J.W. Keister, J.E. Rowe,* North Carolina State University, ***T.E. Madey***, Rutgers, The State University of New Jersey

We report theory and experiment for the formation of alloy layers in the growth of transition metal films on W surfaces. When W(111) is covered by monolayer films of certain metals (Pt, Pd, Ir, Rh, Au), followed by annealing to T>750 K, the surface becomes covered with three-sided pyramids of nanometer-scale dimensions, having {211} planes as facet sides. High resolution soft x-ray photoelectron spectroscopy using synchrotron radiation is employed to study metal films (Pt, Pd, Ir, Rh) on W(111) and W(211). Surface core level shifts of $4f_{7/2}$ photoemission peaks indicate that single physical monolayers of these metals are stable against thermal rearrangement. In contrast, when multilayer films of Pd, Pt, Ir, Rh are annealed above 700-1000 K, tungsten atoms diffuse into the overlayer to form alloy films. We also characterize ultrathin Pd and Pt films on W(211) by first-principles density-functional theory (DFT) methods. Both to confirm the formation of alloy from theory and to help characterize the alloy, we present studies of Pd and Pt films with included W atoms. The DFT methods allow us to suggest the energetically preferred structures. We studied both pseudomorphically-grown alloy films and alloy films with the atomic positions locally optimized by minimizing the Hellmann-Feynman forces. The DFT calculations are consistent with the experimental observations.

11:00am **SS2-TuM9 Metastable Pb Microcrystals on Ru(0001) Formed by Oxygen Segregation***, ***D.B. Dougherty,*** *K. Thuermer, J. Reutt-Robey, E.D. Williams,* University of Maryland

Microcrystals formed after dewetting a continuous Pb film grown on Ru(0001) have provided a convenient model system for understanding a variety of surface mass transport issues.[1,2] In particular, the relaxation of crystallites toward thermodynamic equilibrium has been studied in detail. Here we report the formation of an unusual metastable crystallite shape and its STM tip induced rapid decay. Combined AES and STM investigations show that this new behavior is the result of minute amounts of oxygen that segregates from the substrate into the Pb. AES is used to observe the segregation of oxygen from the Pb/Ru interface to the surface of the continuous Pb film upon post-deposition annealing. This effect, when combined with the absence of any other detectable contamination explains the presence of nearly spherical crystallites on a surface for which the overwhelming majority have long since decayed to a steady, facetted shape. The decay of the unusual crystallites is induced by repeated scanning of an STM tip, suggesting the removal of a low-mobility oxygen species. This interpretation is consistent with previous observations of the effect of oxygen on single crystal Pb(111) surfaces[3] and our Auger analysis. The highly nonequilibrium tip-induced decay is compared with the previously studied decay of Pb microcrystals. * Work supported by UMD-NSF-MRSEC.

[1] K. Thuermer et al., Step Dynamics in 3D Crystal Shape Relaxation. Phys. Rev. Lett 87 186102 (2001)

[2] A. Emundts et al., Experimental Absolute Step and Kink Formation Energies on Pb(111) Vicinal Surfaces. Surf. Sci. 496 L35-42 (2002)

[3] L. Kuipers et al., Jump to Contact and Neck Formation Between Pb Surfaces and a STM tip. Surf. Sci. 340 231-244 (1995).

11:20am **SS2-TuM10 Selforganized Nanostructures at Vicinal Surfaces**, *N. Nöel, T. Maroutian, L. Douillard,* ***H.-J. Ernst***, CEA Saclay, France

The use of intrinsic instabilities in epitaxial growth is currently actively explored as a promising pathway for lateral nanostructuring of surfaces as a cost-effective alternative to lithography based schemes. The origin of these instabilities is traced back to the presence of an excess energy barrier for adatom diffusion over descending steps, the Ehrlich-Schwoebel barrier. Upon growth of Cu on vicinal Cu templates a step-meandering instability develops, resulting in an in-plane patterning of the surfaces at the nanometer scale with a temperature- and flux-dependent characteristic wavelength.[1] The step width increases with time (coverage) according to a power law with exponent 1/3. This experimental finding is at variance with currently existing theories.[2]

[1] T. Maroutian et al., Phys. Rev. Lett. 83, 4353, (1999); idem, Phys. Rev. B 64, 165401 (2001)

[2] M. Rusanen et al., Phys. Rev. B 65, 41404 (2002).

11:40am **SS2-TuM11 Azimuth Dependent Nanogroove Creation by Grazing Ar^+ Bombardment on Cu(001)**, ***H. Wormeester****, M.M. Ovsyanko, A.A. Mewe, G. Stoian, B. Poelsema*, University of Twente, The Netherlands

Grazing incidence 800 eV Ar^+ sputtering on a Cu(001) surface leads to the formation of nanogrooves in which only 3 layers are involved.[1] We found with high resolution LEED (SPA LEED) that the distance between the nanogrooves L depends on the azimuthal orientation of the incident ions, with a larger distance L for incidence along <100> than <110>. Extrapolation to zero time shows that initially no azimuthal dependence of L is noticable. The time dependent behaviour, however, shows a much larger separation speed for [100] oriented nanogrooves. The creation and azimuth dependent development of these nanogrooves will be discussed.

[1] Phys. Rev. Lett. 86, 4608 (2001).

Surface Science
Room: C-112 - Session SS3-TuM

Metals, Adsorbates, and Defects on TiO_2
Moderator: R.L. Kurtz, Louisiana State University

8:20am **SS3-TuM1 Effects of Cluster Size and Deposition Energy on Adsorption and Sintering Behavior of Metal Nanoclusters on Oxide Supports**, *M. Aizawa, S. Lee,* University of Utah, *J. Lee,* Seoul National University, Korea, ***S.L. Anderson***, University of Utah **INVITED**

Size-selected metal nanoclusters on oxide supports are prepared by deposition of pre-formed, mass-selected cluster ions, allowing impact energy to be varied over a wide range. The samples thus prepared, are probed by a combination of XPS, AES, ISS, and TPD, providing insight into changes in oxidation state, morphology, and chemical behavior, induced by varying deposition conditions, thermal processing, and exposure to adsorbates. Results will be presented for Ni_n and Ir_n on TiO_2. In both cases, the clusters appear to be stable with respect to breakup or sintering for a range of deposition energies on room temperature substrates. Significant morphology changes are observed following exposure to adsorbates. Both the adsorbate interation strengths and morphology changes are strongly size dependent.

9:00am **SS3-TuM3 Bonding of Gold Nano-Clusters to Vacancies on Rutile TiO_2(110)**, ***E. Wahlström****, R. Schaub,* University of Aarhus, Denmark, *N. Lopez,* Technical University of Denmark, *A. Ronnau,* University of Aarhus, Denmark, *J.K. Norskov,* Technical University of Denmark, *F. Besenbacher,* University of Aarhus, Denmark

We have studied the early stages of Au cluster nucleation on defective rutile TiO_2(110) using scanning tunneling microscopy (STM). STM images and STM movies show a diffusion controlled growth mechanism. Room temperature STM movies show that the smallest stable clusters have a radius > 0.6 nm, while at 140 K not even single gold atoms seem to diffuse on the surface. It is also shown that a correlation exists between a decrease in density of bridging oxygen vacancies and growth of Au clusters at all investigated temperatures. This is direct evidence of a strong interaction between Au atoms and single atomic oxygen vacancies. Density functional theory calculations support these findings.

9:20am **SS3-TuM4 The Chemical and Catalytic Activity of Au/TiO_2(110) towards Sulfur Dioxide**, ***Z. Chang****, J.A. Rodriguez, G. Liu, T. Jirsak, J. Hrbek, J. Dvorak,* Brookhaven National Laboratory, *A. Maiti*, Accelrys Inc.

Bulk metallic gold typically exhibits a very low chemical and catalytic activity. Recently gold has become the subject of a lot of attention due to its unusual catalytic properties when dispersed on some oxide supports. Gold particles supported on titania are active catalyst for the low temperature oxidation of CO, the selective oxidation of propene, and photocatalytic oxidations used for environmental cleanup. We used synchrotron-based high-resolution photoemission and first-principles density-functional slab calculations to study the interaction of gold with titania and the chemistry of SO_2 on Au/TiO_2(110) surfaces. Au/TiO_2 is much more chemically active than metallic gold or stoichiometric titania. On Au(111) and rough polycrystalline surfaces of gold, SO_2 bonds weakly and desorbs intact at temperatures below 200 K. For the adsorption of SO_2 on TiO_2(110) at 300 K, SO_4 is the only product. In contract, Au/TiO_2(110) surfaces fully dissociate the SO_2 molecule under identical reaction conditions. Interactions with titania electronically perturb gold, making it more chemically active. Furthermore, our experimental and theoretical results show quite clearly that not only gold is perturbed when gold and titania interact. The adsorbed gold, on its part, enhances the reactivity of titania by facilitating the migration of O vacancies from the bulk to the surface of the oxide. In general, the complex coupling of these phenomena must be taken into consideration when trying to explain the unusual chemical and catalytic activity of Au/TiO_2. The research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

9:40am **SS3-TuM5 STM Studies of Titanium Oxide Adlayers on a Pt(100) Surface**, ***T. Matsumoto***, University of Southern California, *M. Batzill,* Tulane University, *S. Hsieh, B.E. Koel,* University of Southern California

Pt supported on titanium oxide catalysts exhibit effects termed SMSI (strong metal support interaction). In order to probe aspects of this chemistry, thin films of titanium oxide on Pt single crystal surfaces have been observed by using surface science techniques, but most studies focused on titanium oxide films that fully covered the surface. In this study, submonolayer coverages and ultrathin films of titanium oxide on Pt(100) were observed by STM, LEED and XPS, and we report several new, ordered structures. These titanium oxide structures were produced by annealing to 800-1300 K after the deposition of Ti in an oxygen atmosphere or additional oxidation with NO_2 and O_3 after Ti deposition. A (3×5) structure of Ti_2O_3 was found after annealing above 800 K. This structure could also be produced by O_3 oxidation of the Pt_3Ti surface alloy produced on Pt(100). Our proposed structural model suggests that the thin film of titanium oxide with the (3×5) structure covers the Pt(100) surface fully. Several other locally ordered structures were found by annealing below 1000 K after additional oxidation of the (3×5) structure with NO_2 and O_3. These were more oxidized than Ti_2O_3, and were changed to the (3×5) structure after annealing to 1000 K.

10:00am **SS3-TuM6 Oxygen Vacancies on TiO_2(110) : An STM Study of Adsorbate Mediated Diffusion**, ***R. Schaub****, E. Wahlström, A. Ronnau, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

Time resolved fast Scanning Tunneling Microscopy (STM) experiments reveal a spatially correlated diffusion of oxygen vacancies present on the rutile TiO_2(110) surface. The diffusion is observed to occur exclusively perpendicular to the oxygen bridging rows of the (1x1) reconstructed surface. This unexpected behavior is unambiguously assigned to trace amounts of adsorbates present on the surface which mediate the oxygen vacancy diffusion. Based on high resolution STM movies, a novel atomistic diffusion mechanism is proposed.

10:20am **SS3-TuM7 Oxygen Vacancies as Active Sites for Water Dissociation on Rutile TiO$_2$(110)**, ***P. Thostrup***, *R. Schaub,* University of Aarhus, Denmark, *N. Lopez,* Technical University of Denmark, *E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark, *J.K. Norskov,* Technical University of Denmark, *F. Besenbacher,* University of Aarhus, Denmark

Water dissociation on TiO$_2$ is of fundamental interest as an example of a simple surface chemical process with significant applications. In addition, TiO$_2$ is the material of choice for photochemical hydrogen production from water and for biocompatible implants. Earlier experimental studies report a minor degree of water dissociation on TiO$_2$(110) while theoretical studies predict the dissociated state, or mixed dissociated-molecular states, to be most energetically favorable. Thus, even for this simple process we do not have a clear picture of the dissociation energetics and the active site for dissociation. Through an interplay between scanning tunneling microscopy experiments and density functional theory calculations, we determine unambiguously the active surface site responsible for the dissociation of water molecules adsorbed on rutile TiO$_2$(110). Oxygen vacancies in the surface layer are shown to dissociate H$_2$O through the transfer of one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy. The amount of water dissociation is limited by the density of oxygen vacancies present on the clean surface exclusively. The dissociation process sets in as soon as molecular water is able to diffuse to the active site.[1]

[1] R. Schaub, P. Thostrup et al., Phys. Rev. Lett. 87, 266104 (2001).

10:40am **SS3-TuM8 The Influence of Subsurface, Charged Impurities on the Adsorption of Chlorine at TiO$_2$(110)**, ***M. Batzill***, *B. Katsiev,* Tulane University, *E.L.D. Hebenstreit,* Lawrence Berkeley National Laboratory, *W. Hebenstreit,* Optical Coating Laboratory, Inc., *U. Diebold*, Tulane University

A fundamental surface science study on the influence of single, subsurface dopants on the chemical surface properties is presented. In particular the adsorption of chlorine atoms on TiO$_2$(110) samples modified by low concentrations of impurities were investigated. Subsurface impurity atoms were identified by scanning tunneling microscopy and spectroscopy. This analysis established that positively charged impurity atoms, most likely substitutional vanadium atoms, are present in some samples. Areas of about 2 nm in diameter around these impurities are imaged as protrusions in empty state STM images. This is consistent with a downward band bending induced by positively charge impurity atoms. Adsorption studies of Cl at room temperature on these samples showed that Cl atoms avoid chemisorption in the vicinity of these impurity atoms. Cl is an acceptor-like adsorbate that is negatively charged at the surface. The suppressed adsorption is explained by an increased local electron affinity due to the only partially screened positively charged impurities. This lowers the energy gain for adsorption of Cl at the surface and thus renders adsorption sites close to impurities as energetically disfavored compared to unaltered surface areas.

11:00am **SS3-TuM9 Lower 3-fold Hollow Site of K on TiO$_2$(110)1x1**, ***G. Thornton***, *C.L. Pang, C.A. Muryn,* Manchester University, UK, *V.R. Dhanak,* Daresbury Laboratory, UK

Recent calculations by San Miguel et al (J. Phys. Chem. B 105 (2001) 1794) and Bredow et al (Surf. Sci. 418 (1998) 150) both predict that the low coverage bond site of K on TiO2(110) is the so called lower three fold hollow site. This involves two bridging O atoms and an in-plane O. In our work we have tested this prediction at a K coverage of 0.15 ML using a combination of surface extended X-ray absorption fine structure (SEXAFS), scanning tunneling microscopy (STM), and non-contact atomic force microscopy (NC-AFM). The polarisation dependence of the SEXAFS data rules out the atop, bridge and upper three fold hollow sites, and are consistent with the lower three fold hollow predicted by theory, with a K-O distance of 2.63 Å±0.03 Å. In addition to elements of the clean surface STM image, images of the K dosed surface contain wide dark rows running along the [001] direction. These are about 3 nm in length and centered along the dark bridging oxygen rows such that the two adjacent 5-fold coordinated Ti rows are not imaged. These presumably arise from K-induced blocking of the tunneling current, either by charge transfer to Ti 3d states, or because there are no empty states of K near EF. The clustering of alkali metal sites is consistent with molecular dynamics simulations. In the absence of useful topographic information in STM, we turn to NC-AFM images of TiO2(110)1x1, where the [001] direction bright rows arise from bridging O atoms. In addition to straight rows characteristic of the clean surface, zigzag rows are observed on the K-dosed surface, presumably arising from K atoms alternately occupying sites on either side of a bridging O row, as predicted by theory.

11:20am **SS3-TuM10 Electronic and Geometric Structure of Anatase TiO$_2$(101) and (001) Single Crystals**, *A.R. Kumarasinghe, W.R. Flavell, A.G. Thomas, A.K. Mallick, D. Tsoutsou, G.C. Smith,* UMIST, UK, ***R.L. Stockbauer***, Louisiana State University, *M. Grätzel, R. Hengerer,* Swiss Federal Institute of Technology

Scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and resonant photoemission studies on single crystal anatase TiO$_2$ (101) 1x1 and (001) 1x4 surfaces are reported. The (101) surface exhibits triangular shaped large terraces/steps leading to a saw tooth like structure. The steps are monatomic and are ~ 4Å high. Atomically resolved STM images show that the (101) surface has a bulk (1x1) termination and is unreconstructed. Defect states which are clearly observed in atomically resolved images can be created on clean (101) surfaces following sputter anneal cycles. Bright features are seen on atomic rows are most likely due to adsorbed molecules.[1] A defect peak is observed near 1 eV BE in UPS and is thought to arise from the loss of surface oxygen. This state is investigated using I/V measurements from scanning tunnelling spectroscopy (STS). Ti 3p-3d resonant photoemission of the surfaces are compared with earlier work from rutile TiO$_2$ (110) and features in the valence band at around 6 and 8 eV BE are assigned regions of weak and strong Ti-O hybridisation respectively. The defect peak is observed at around 1 eV BE for both surfaces following surface defect creation and is thought to arise from Ti^{3+}. This peak can be removed by gentle heating in oxygen.[2] Constant initial state spectroscopy reveals differences in cation-anion hybridisation between the two surfaces, while repeated sputtering shows the (001) surface to be more resistant to the creation of O vacancies than the (101) face.

[1] W. Hebenstreit, N. Ruzycki, G. S. Herman, Y. Gao, and U. Diebold, Phys Rev B, 62, 24, (2000).

[2] A.G. Thomas, W.R. Flavell, A.R. Kumarasinghe. A.K. Mallick. D. Tsoutsou, G.C. Smith, R. L. Stockbauer, M. Grätzel and R. Hengerer (in preparation).

11:40am **SS3-TuM11 Interactions of Oxygenated Hydrocarbons with Stoichiometric and Defective SrTiO$_3$(100) Surfaces: Role of Surface Structures and Defects**, ***L.-Q. Wang***, *S. Azad, K.F. Ferris, M.H. Engelhard*, Pacific Northwest National Laboratory

Molecular interactions on metal oxide surfaces are influenced by the surface structures and by the presence of surface defets. Adsorption and reactivity of oxygenated hydrocarbons on metal oxide surfaces have recently received considerable attention due to the environmental concerns. In this study, we examined the interactions of a series of oxygenated hydrocarbons with stoichiometric and defective SrTiO$_3$(100) surfaces using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. The goal of this study is to have a fundamental understanding of the role of surface structures and defects on the adsorption and reactivity of these oxygenated hydrocarbons on metal oxide surfaces. SrTiO$_3$(100) was chosen as our model surface not only because of its heterogeneous and photo-catalytic activities but also because investigation of oxygenated hydrocarbons on single crystal oxide surfaces is very rare. This presentation compares the interaction of acetaldehyde with that of methanol, ethanol and formic acid on the same surface. Since aldehydes are weaker than carboxylic acids and stronger than alcohols, the comparison of their reactivity on the surface is very interesting. It was found that methanol, ethanol and acetaldehyde adsorb molecularly whereas formic acid goes through dissociative adsorption on stoichiometric SrTiO$_3$(100) surface. As comparable with studies on other oxides such as TiO$_2$, adsorption and protonation of weaker acids such as methanol, ethanol and acetaldehyde are found to depend more on the surface structures than stronger acids such as formic acid and these results are in good agreement with our theoretical calculations. However, decomposition and redox reactions of methanol, ethanol, and acetaldehyde take place when surface defects are created by Ar$^+$ sputtering. In addition, such surface defects change the reaction pathway for formic acid.

Thin Films
Room: C-101 - Session TF-TuM

Mechanical Properties of Thin Films
Moderator: L. Hultman, Linkoping University, Sweden

8:20am **TF-TuM1 Mechanical Properties of TiN and Ti$_{1-x}$Si$_x$N$_y$ Coatings using Surface Acoustic Wave Techniques**, ***D.C. Hurley***, National Institute of Standards and Technology, *A.J. Richards,* CSIRO, Australia, *V.K. Tewary,* National Institute of Standards and Technology, *A. Bendavid, P.J. Martin,* CSIRO, Australia

Surface acoustic wave (SAW) spectroscopy is a nondestructive, noncontacting technique to determine thin-film mechanical behavior. In some cases, it may be more suitable than other, more conventional methods. The approach involves optical generation and detection of SAWs over a bandwidth of several hundred megahertz. Measurements of the SAW displacement versus propagation distance allow the frequency dependence of the phase velocity (dispersion relation) to be determined. Quantitative values for properties like Young's modulus E and film thickness d are obtained by comparing the dispersion data to analytical models. Our model allows analysis for anisotropic film properties and uses an elastodynamic Green's function method. We illustrate our techniques with results on TiN and $Ti_{1-x}Si_xN_y$ coatings for enhanced wear resistance. In TiN films prepared with filtered-arc physical vapor deposition techniques, E increased from 368 to 453 GPa with increasing d and decreasing compressive residual stress. SAW results were in good agreement with those from two destructive methods: instrumented indentation techniques (IIT) for E and scanning electron microscopy for d. $Ti_{1-x}Si_xN_y$ films with a nanocomposite structure were prepared by concurrent reactive deposition of Ti by a cathodic arc source and Si by a magnetron sputter source. Values greater than 40 GPa for the microhardness H were measured by IIT. SAW and IIT values for E were in good agreement and ranged from 325 to 417 GPa. Both H and E were observed to depend on the magnetron power or atomic per cent of Si in the films. From these results the ratio H/E, an indicator of wear resistance, was found to be relatively high.

8:40am **TF-TuM2 Mechanical Testing of Thin Films: Experiments and Analysis**, ***O. Kraft***, Forschungszentrum Karlsruhe, Germany, *R. Schwaiger*, Massachusetts Institute of Technology **INVITED**

Several specialized testing techniques have been developed to study the mechanical behavior of thin films, including thermal cycling experiments, micro-tensile testing, bulge testing, nanoindentation, and microbeam deflection. They are specifically aimed at determining material properties such as Young's modulus, yield strength, strain hardening rate, ultimate tensile or fracture strength of thin film materials. For these techniques, however, the required sample geometry, loading and straining conditions can be quite different, and as a result, comparisons between the different techniques are not straightforward. This is illustrated in this paper by studying the deformation behavior of sputter-deposited Cu films with thicknesses between 200 and 1500 nm by considering results from several techniques. In particular, nanoindentation and microbeam deflection experiments on identical samples will be compared which were both analyzed by using finite element modeling. The main difference between the two techniques is that the plastic strain is less than 1 % during a bending experiment while it is about 8 % during indentation. It will be shown that it is not possible to describe the stress-strain behavior of the films over this wide range of plastic strains by the use of a simple bi-linear material law. Nevertheless, both techniques show that during deformation of thin metal films strong strain hardening effects are present.

9:20am **TF-TuM4 Copper Gallium Thin Film as the Stress-release Coating for Optical Fiber Metallization**, ***M.X. Ouyang***, *L.D. Kinney*, Corning Inc.

It is well known that the strength of optical fiber can be degraded dramatically during fiber stripping and UV irradiation.[1] The existence of defects which has been created both on the surface and inside optical fibers during the fiber fabrication process is the reason for their mechanical degradation.[2] Flaws on the surface of glass fibers have a significant effect on the fiber strength. However, little is reported on optical fiber mechanical strength change due to fiber surface treatment and metallization. The report discusses mechanical properties of metallized optical fibers (strength, adhesion, stress, solderability) and the impact on optical properties such as PMD spectra. The fiber strength of polymer removed optical fibers with different surface and coatings is studied. Using a thin Cu:Ga film (80 nm)[3] to replace Cr or Cr2O3 film as the adhesion enhancement layer between Pt film (1 µm) and single mode fiber (SMF), the average fiber pulling strength increased 5-6 times. Polarization mode dispersion (PMD) spectra shows that only 0.1 nm blue shift is observed comparing with 0.3-0.4 nm shifting using Cr or Cr2O3 as under layer or only Pt film without underlayer. Cu:Ga film has excellent wetting properties to Pb:Sn (1:1) solder. Cu:Ga films on glass and Si substrates are solderable.

[1] Varelas, D., et al: "UV-induced mechanical degradation of optical fibers", Electron. Lett., 1997, 33, (9).pp.804-806

[2] R. Olshansky and D.R. Maurer: "Tensile strength and fatigue of optical fibers": J. Appl. Phys, 1976, 47, (10), pp4497-4499

[3] Mike X. Ouyang, et al: US patent : US6347175 B1

10:00am **TF-TuM6 Role of Interface Free Energy in Hardness Enhancement in PTFE/Al, PTFE/Cu, and PTFE/Ti Nanomultilayered Thin Films**, ***E. Kusano***, *N. Kikuchi, I. Yoshimura, A. Kinbara, H. Nanto*, Kanazawa Institute of Technology, Japan

In nanostructured materials, interface or surface affects their mechanical properties strongly. In this study internal stress and hardness in polytetrafluoroethylene (PTFE)/Al, PTFE/Cu, and PTFE/Ti nanomultilayered thin films have been investigated as a function of modulation period, i.e., the number of interfaces in the films. PTFE, which has a low surface energy of 17 mJ/m^2 was used to introduce a large interface energy in thin films. The designed value of interface energy accumulated in thin films is up to 80 J/m^2. PTFE thin film was deposited by rf magnetron sputtering using the target of a PTFE sheet. Al, Cu, and Ti were deposited by dc magnetron sputtering. Multilayers were fabricated sequentially without breaking vacuum on aluminosilicate glass. The total thickness of films was about 200 nm for all samples. Modulation period was changed from 10 nm to 200 nm. Internal stress in metal layers was evaluated from strain obtained by X-ray diffraction measurements. Hardness was measured by nanoindentation. The surface energy of a monolithic PTFE film deposited by sputtering was about 18 mJ/m^2. The compressive internal stress evaluated by XRD increases with decreasing the modulation period. Hardness enhancements were also investigated for films with a short modulation period. Further it was shown that the hardness has a linear relationship to internal stress. A large compressive stress introduced in thin films increases the energy needed to drive cracks made by a nanoindentation deep into the film, resulting in the increase in hardness. The results emphasize an important role of interfaces in mechanical properties of nanomultilayered thin films.

10:20am **TF-TuM7 Pulsed Laser Ablated MoS_2-Al Films Characterized for Friction and Wear in Humid Conditions**, ***J.J. Nainaparampil***, AFRL/MLBT, *A.R. Phani, J.E. Kraznowski*, University of New Hampshire, *J.S. Zabinski*, AFRL/MLBT

Molybdenum disulphide films are well known solid lubes in dry environmental conditions. However, even a slightest increase in humidity can adversely affect the performance of these films. Different authors tried various additives to strengthen the system and to change microstructure in such a way that wear life could be increased even in dry conditions compared to pure MoS_2 films.[1,2,3] Some of those work addressed the problem of humidity by adding metals and oxides of metals. However, the complete explanation of the phenomenon has not been discovered and an approach that focuses on both tribochemical reactions and microstructure is required. The work reported here deals with addition of Al metal as an additive to resist the degradation of MoS_2 coatings in humid conditions. Since aluminum shows very high affinity for (OH) radicals to form $Al(OH)_3$, it is suggested that aluminum likely reacts with H_2O in humid conditions. $Al(OH)_3$ is relatively soft and may enhance lubrication and reduce friction and wear. The microstructure of Al-containing films and their mechanical properties may also contribute to tribological performance. Films for this study were prepared by pulsed laser ablation of MoS_2 targets along with magnetron sputtering of aluminum to form aluminum alloyed MoS_2 films. Data from pin on disc tribotests showed long wear life and a friction coefficient between 0.1 and 0.2 even at high relative humidity (i.e., 50%). The microstructure and stoichiometry of these films are under further study to control mechanical properties such as hardness, adhesion and toughness. Micro-Raman and high-resolution SEM pictures of wear tracks will be presented.

[1] Stupp B. C. Thin Solid Films, 84, 1981, 257

[2] J. S. Zabinski, M. S. Donley, and S. D. Walck, Tribol. Trans. 38(4) 1995, 894

[3] E. Pfluger, J. D. Holbery, A. Savan, Y. Gerbig, Q. Luo, D. B. Lewis, W. D. Munz, Proceedings of II World Tribology Congress, Vienna, 2001, 313.

10:40am **TF-TuM8 Thin Films of TiSiC MAX Phase - Growth, Characterisation and Properties**, ***J. Emmerlich***, Linköping University Sweden, *J.-P. Palmquist*, Uppsala University, Sweden, *T. Seppänen, J. Molina*, Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden, *J. Birch*, Linköping University, Sweden, *P. Isberg*, ABB Group Service Center AB, Sweden, *L. Hultman*, LinköpingUniversity, Sweden

Ti_3SiC_2 a so-called MAX-Phase (M: early transition metal; A: element of A-group III, IV (V); X: C or N) with a chemical composition of $M_{n+1}AX_n$ belongs to a new class of ternary carbides. The unique compilation of properties like high electrical and thermal conductivity, ductility, low friction additional to high oxidation and thermal shock resistance make for highly interesting materials. The Ti_3SiC_2 is readily machinable as well as damage tolerant. Polycrystalline Ti_3SiC_2 in bulk form has been investigated and well-characterised since late 1960s. Single crystal Ti_3SiC_2 thin films were recently reported by Palmquist et al. Magnetron sputtering was employed as deposition technique using either Ti and Si targets with a C_{60} evaporation source or deposition from a stoichiometric Ti_3SiC_2 target. This presentation describes a third and new method of employing three single-element-targets: Ti, Si and C. We could establish epitaxial and single-crystalline growth of Ti_3SiC_2 above 700°C. Best results were achieved with -30 V bias and using TiC as nucleation layer. Two epitaxial orientations were deposited on MgO: Ti_3SiC_2(0001)//TiC(111)//MgO(111) and Ti_3SiC_2(104)//TIC(100)//MgO(100). Deviations in Si content led to a mixture of Ti_3SiC_2 and the new Ti_4SiC_3 MAX-phase. Friction measurements carried out with a Hysitron system gave values of µ lower than 0.1. The E-modulus was 325GPa. A conductivity of $4x10^6$ $(\Omega m)^{-1}$ was reported. Nano indentations and nano-tribology experiments in situ AFM and ex situ TEM were made to investigate the deformation behaviour and revealed delaminations, pile-up and kink formation around the indent.

11:00am **TF-TuM9 Carbon Incorporation in Boron Suboxide Thin Films**, ***D. Music***, *V.M. Kugler, Zs. Czigány, A. Flink, O. Werner,* Linköping University, Sweden, *J.M. Schneider,* RWTH-Aachen, Germany, *L. Hultman, U. Helmersson*, Linköping University, Sweden

Boron suboxide thin films, with controlled carbon incorporation, were grown by RF dual magnetron sputtering of boron powder and sintered carbon targets in an argon-oxygen atmosphere. Film composition, structure, mechanical, and electrical properties were evaluated by x-ray photoelectron spectroscopy, x-ray diffraction, transmission electron microscopy (TEM), nanoindentation, and high-frequency capacitance-voltage measurements, respectively. B-O-C films (O/B=0.02, carbon concentration <2.0 at.%), albeit x-ray amorphous, showed an increase in density from 2.0 to 2.4 g/cm^3 as the carbon concentration was increased and the film with the highest density had nanocrystalline inclusions, as observed by TEM. All measured material properties were found to depend strongly on film density. The elastic modulus increased from 188 to 281 GPa with increasing film density, while the relative dielectric constant decreased from 19.2 to 0.9. Hence, B-O-C films show a potential for protective coatings and even for application in electronic devices.

11:20am **TF-TuM10 Synthesis and Characterization of Nanolayered TiB$_2$/TiC Coatings for Possible Elevated Temperature Applications**, ***K.W. Lee***, *Y.-W. Chung, L. Keer, E. Ehmann*, Northwestern University

Multilayered coatings composed of 3 nm TiB$_2$ and various individual layer thicknesses of TiC were synthesized using non-reactive dual-cathode magnetron sputtering techniques with substrate rotation on silicon (001), M2 steel and WC cutting inserts. The two coating materials were chosen for their high hardnesses, melting temperatures, and immiscibility. The goal of the research is to synthesize hard and chemically stable coatings that provide wear protection at high contact pressures and temperatures. Under appropriate deposition conditions, we obtained coatings with TiB$_2$(001) preferred orientation. Room-temperature hardness of these coatings approaches 60 GPa, far exceeding the rule-of-mixture value. High-resolution transmission electron microscopy and low-angle x-ray diffraction studies confirmed that the layer structure of these coatings was preserved after one-hour annealing in argon at 1000C. Scanning electron microscopy shows that coatings were rapidly oxidized at 800C in 25% oxygen/argon environment. Wear and durability tests on coated M2 steels and C6 WC cutting inserts demonstrated the improved room temperature tribological performance of these coatings under unlubricated conditions compared with standard coatings such as TiN. Actual dry machining on coated C3 WC cutting inserts was performed. Scanning electron microscopy and white-light interferometry were used to evaluate durability of these coatings before and after machining. These results will be presented and discussed in terms of the coating's potential in dry machining and high-temperature tribological applications.

11:40am **TF-TuM11 Fluorinated Amorphous Carbon Thin Films: Analysis of the Role of the Plasma Excitation Mode on the Structural and Mechanical Properties**, *L. Valentini, M.C. Bellachioma,* University of Perugia, Italy, *S.I.-U. Ahmed, G. Bregliozzi, Y. Gerbig,* CSEM Centre Suisse d'Electronique et de Microtechnique, *H. Haefke,* CSEM Centre Suisse d'Electronique et de Microtechnique, Italy, ***J.M. Kenny***, University of Perugia, Italy

Fluorinated amorphous carbon (a-C:H:F) thin films were grown using a 13.56MHz radio frequency pulsed plasma source by varying the on-time plasma excitation from 1ms to 0.1s. The effect of the plasma excitation mode on the mechanical and tribological properties of the films was investigated by depth sensing indentation and microfriction tests using a reciprocating microtribometer. Nanoindentation measurements showed increased elasticity of the film, as well as increased hardness upon reduction of the plasma excitation time while a decrease of the friction force was also detected. The structural arrangement of the films investigated by means of thermal induced gas effusion shows that for a plasma excitation time of 1ms the material is relatively compact and the effusion of hydrogen related species (hydrogen molecules and hydrocarbons) dominate. For the highest on-time plasma excitation (0.1s) a strong change in the effusion characteristics indicates that an interconnected network of voids is present. Strong effusion of CF4 related species is found to be consistent with a surface desorption process and can only be observed when the void network dimensions are large enough, i. e., for films deposited with the highest on-time excitation. Raman spectroscopy is successfully applied to corroborate the effusion results indicating a structural transition from diamond-like to polymer-like film with increasing the plasma excitation time.

Vacuum Technology
Room: C-104 - Session VT-TuM

Novel Vacuum Materials and Pumps, Including Getters
Moderator: M.L. Ferris, SAES Getters USA

8:20am **VT-TuM1 Expanded Characteristics Evaluation for Low Vacuum Dry Pumps**, ***J.Y. Lim***, *S.H. Chung, W.S. Cheung, K.H. Chung, Y.H. Shin, S.S. Hong,* Korea Research Institute of Standards and Science, *W.G. Sim*, Hannam University, Korea

Since positive-displacement dry pumps were first launched into the semiconductor industry in 1984, issues concerning about characteristics evaluation on consistent bases have been continuously arisen from the mass production lines. Besides their clean and continuous pumping capability, occasional devastating malfunctions or characteristic degradations of such pumps during the manufacturing processes have been also reported in the Korea semiconductor industry. On behalf of these issues, the integrated characteristics evaluation system for dry vacuum pumps has been developed collaborating with several semiconductor and branch dry pump manufacturers in Korea. The evaluation system exploits the constant volume flowmeter to measure the mass flow rate in standards level, and facilitates the evaluation of spatially averaged sound power levels using a reverberation chamber.[1] New and overhauled roots, claw, classical screw, and scroll type pumps supplied from the manufacturers have been evaluated using the evaluation system in terms of ultimate pressure, pumping speed, vibration, and sound power. The correlation analyzed among those results shows clear signs of pump degradation related each other. We selected the mass flow measuring method with a constant chamber volume of 874 L because of its direct monitoring capability not allowing blind mass flow rate measurement, and proved the method allows us to measure five decades of mass flow rates from 0.01 to 10^3 mbar-l/s with an uncertainty of ±3% which is within the internationally accepted standards limit. In this work the integrated characteristics evaluation method has been significant because of pump degradation or malfunction symptom to be further understood and predicted.

[1] W.S. Cheung, J.Y. Lim, K.H. Chung, Experimental study on noise characteristics of dry pumps, The 2002 International Congress and Exposition on Noise Control Engineering, Inter-noise 2002, Dearborn, MI, USA.

8:40am **VT-TuM2 High Throughput Continuous Cryopump, with Gas Dynamic Compression of the Helium Minority Stream, for Pumping Fusion Reactors**, ***C.A. Foster,*** Cryogenic Applications F, Inc., *S. Willms, S. Letzring,* Los Alamos National Laboratory, *D. Schechter,* Cryogenic Applications F, Inc.

An analysis of the flow of gases in a large cryopumping system designed to pump a magnetic plasma fusion reactor is presented. The pumping system for a 3gigawatt thermal reactor must handle a throughput of 2 Pa-m3/s of He and 200Pa-m3/s of D/T and maintain a pressure in the diverter at about 0.5Pa. A cryopump which removes the cryo-ice during operation with a regenerating head or "snail" is capable of pumping the D/T stream. A set of twelve 500mm bore pumps would each pump 16.7 Pa-m3/s of the D/T stream with the He being pumped by a set of turbo pumps downstream to the cryopumps. In designing the entrance baffle and analyzing the gas flow in the pump, it was determined that whereas the gases were close to free molecular flow conditions in a room temperature design, at 30K they would be in the viscous flow regime. The viscous flow conductance of the entrance duct at room temperature was not drastically different from that calculated using the free molecular flow equations. However, Poiseuille flow has a strong temperature dependance, so that the pressure drop across a pipe in viscous flow at 30 K is dramatically lower than at 300K. Since a cold baffle is typically used to precool the gases entering a cryopump, it was decided to replace it and the room temperature ducts with a refrigerated duct operating in the viscous flow regime. An analysis of long cold ducts replacing the conventional vacuum pipes between the reactor diverter chamber and the cryopumps allowed the pipe size to be reduced by a factor of four in area. This is especially advantageous in a reactor since the vacuum ducts have to pass between the coils and through the neutron shielding blankets. An analysis of the fluid flow of the D/T and He in the cold ducts showed a gas dynamic drag compression of the He minority species(10X to 30X) by the D/T stream as was utilized in the Gaede diffusion pump. This pre-compression allows conventional turbo-molecular pumps to be used as the compound helium pumps.

9:00am **VT-TuM3 Vacuum System Design and Simulation Program for PCs**, ***R.A. Langley***, *L.R. Baylor, P. LaMarche*, Oak Ridge Scientific Consultants

A new integrated software package for Windows has been developed to design vacuum systems and to simulate existing vacuum systems. The package is modeled after earlier DOS based programs by Santeler.[1,2] The initial setup of the design calculation allows the choice of up to five parallel pumping modules on the vacuum chamber with the choice of up to six different gas types. At this stage, the primary pump for each module is chosen. Each pumping module is then separately addressed to choose the optimum secondary pump or pumps for that pumping module. Both circular and rectangular cross section tubing is allowed. Pumping speed data for many types of pumps and many sizes of pumps is maintained within the program and additional pumping speed data can also be input for use by the program. The calculation is based on a precision set of gas flow equations for all pressure conditions, i.e. molecular, transition, and viscous, and provides pumpdown and steady state data. True gas fractionation is calculated and gas flow for tubes of varying lengths, i.e. from an orifice to a long tube, can be calculated. Various examples of the use of the program will be presented.

[1] Donald J. Santeler, Vacuum System Design, Donald J. Santeler Assoc.

[2] Donald J. Santeler, VSD-II Vacuum System Design, Donald J. Santeler Assoc.

9:20am **VT-TuM4 Design Fabrication and Processing of Vacuum Chambers for High Energy Accelerators at Brookhaven***, ***H.C. Hseuh***, *M. Mapes, D. Weiss*, Brookhaven National Laboratory **INVITED**

There are several distinct accelerators and storage rings at Brookhaven ranging in length from tens of meters for the Tandem to several kilometers for the Relativistic Heavy Ion Collider. The vacuum systems of these facilities must provide a suitable environment for the circulating beams while also being subjected to the intense bombardment of various energetic particles. The unique physics requirements and material selection criterions for the vacuum chambers will be described. The fabrication, cleaning and conditioning of the vacuum chambers will be reviewed. The treatment, sealing techniques and performance of non-conventional materials such as ceramic and ferrites in an ultrahigh vacuum and high radiation environment will also be presented. *Work performed under the auspices of the U.S. Department of Energy.

10:00am **VT-TuM6 Advanced Materials and Fabrication Techniques for the Next Generation Light Source**, ***J.R. Noonan***, *G.A. Goeppner, J. Gagliano, R.A. Rosenberg,* Argonne National Laboratory, *D.R. Walters*, Veeco International **INVITED**

The next generation of light source will probably be based on electron linear accelerators using a laser driven photocathode gun. The accelerator requirement will be very stringent: very short pulses (< 100 fs, >1,000 amp peak current, and large electric accelerating gradients > 30 MeV/m). These specifications will impose new, significant requirements on the vacuum systems. For example, the cathode material in the photocathode gun not only must have high photo-electron yields, but also must withstand high laser power and high RF electric gradients. The beam tube must be fabricated to new tolerances with respect to surface finish, surface resistance, and change of cross section. The new accelerator requirements are leading the need for new materials and manufacturing technology. The talk will review research at several Free Electron Laser accelerators, and how the technology assisted the success in VUV photon emission from free electron lasers.

10:40am **VT-TuM8 Investigations of Novel Getter Materials**, ***W. Knapp***, *D. Schleussner,* Otto-von-Guericke-Universität Magdeburg, Germany, *T. Stenitzer*, Konstantin Technologies GmbH, Austria, *K. Chuntonov*, Alkali Metals Ltd., Israel

The novel chemisorbents on the basis of alkali, alkali-earth and rare-earth metals have recently emerged as one of the most promising getter materials. The novel getters are based on an A-B alloy system, where A is a chemically active metal and B is a fusible non-volatile metal. Metal B is creating a protective shell on the whole surface of the novel getter material, which is impermeable during handling and storing and permeable when activated. The main advantages of the novel getters compared to the standard getter materials in use are: - Much higher kinetic and capacity sorption, - Significant lower activation temperatures, - Very small size and flexible design possible, - Easy handling of very active materials, e.g. Li, Na, Cs etc. In quantitatively proof of advantages and for basic getter investigations an ultra-high vacuum (UHV) experimental setup with a high measurement standard was developed. Getter temperatures and gas flow rates are regulated for different operations. On the basis of precise total and partial vacuum pressure measurements the getter sorption capacities are valued and compared in dependence on vacuum pressure range and kind of gases. For this with our experimental setup different measurement methods are possible, like pressure rise, throughput and difference method. We investigated sorption capacities of standard and novel getters using the pressure rise method. In our presentation comparative results of our investigations are presented and discussed.

11:00am **VT-TuM9 Modern Types of Getters for Novel Applications**, ***L. Rosai***, Saes Getters, Italy

Modern applications of gettering aimed to remove unwanted impurities and contaminants in vacuum and gas filled environments encompass new types of evacuated or gas filled devices, each requiring a tailor made solution in terms of gettering materials, geometry, process integration. In addition to the traditional types of getters in form of rings, porous pellets and coated strips, nowadays new configurations are available to meet the specific requirements of new applications: the getters can be prepared in form of very porous thin films sheets, coated in-situ as sputtered films, patterned on a semiconductor substrate, made in form of thin permeable bags filled with different materials each devoted to a specific gettering task, filling small capsules equipped with special mounting features. In these modern getters the so called activation process is no longer necessary thanks to special features of getter packaging and/or a natural activation occurring during device manufacturing. New types of getter pumps, not requiring substitution for many months or years are also available, for different applications in portable instruments, semiconductor, LCD and magnetic recording media manufacturing In some of these applications these new getter types are necessary not only for ensuring a long life to the device but also as a process aid during the manufacturing of the device itself .The vacuum and purity requirements of the most recent applications of getters will be illustrated. These will include: Vacuum Insulated Panels, Vacuum Pipes, Flywheels, Plasma Display Panels , Field Emission Displays, OLEDs, MEMS, Opto-electronic devices, Magnetic recording devices, Semiconductor and LCD production tools.

11:20am **VT-TuM10 Gaede Langmuir Award Address: The Impact of Non-evaporable Getters on the Evolution of UHV/XHV Technology**, ***C. Benvenuti****, CERN, Switzerland **INVITED**

Non-Evaporable Getters (NEG) entered the field of UHV technology with the advent of powder-coated gettering strips. Coated strips are particularly well suited to provide large, linear pumping for the conductance limited vacuum chambers of particle accelerators. An example of this application is the pumping system of the Large Electron Positron collider (LEP) at CERN. The development of alloys of lower activation temperature (about 400 °C) may be seen as another major break-through in the NEG technology. In this case the activation may be achieved "passively" during the bakeout of a stainless steel vacuum system, resulting not only in a simplified solution (no need of electrical insulation, feedthroughs and power supply), but also in improved vacuum performance (larger pumping speed and capacity, lower ultimate pressure). The final stage of the NEG technology evolution has been reached with the recent development of thin getter films coated on the inner surfaces of a vacuum chamber. These films offer an even lower temperature of activation (180 °C), a feature which renders them applicable also to copper and aluminum structures. In addition, they provide large and evenly distributed pumping, suppress the thermal degassing of the underlying material and strongly reduce, after activation, both the degassing and the secondary electron yield induced by the surface bombardment. The impact of NEGs on the evolution of vacuum technology will be illustrated and the new possibilities offered by the thin film coatings will be reviewed with the help of some examples.

***** Gaede Langmuir Award Winner

Applied Surface Science
Room: C-106 - Session AS-TuA

Imaging in Surface Analysis
Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:00pm **AS-TuA1 Using Gold Liquid Metal Ion Sources for Imaging ToF-SIMS**, *A.V. Walker*, ***N. Winograd***, Pennsylvania State University

Molecule-specific imaging TOF-SIMS experiments require the highest possible sensitivity in order to achieve the spatial resolution normally associated with the ion probe. For example, Ga+ ion beams can be focused to less than 100 nm in diameter. However since there are only ~104 molecules per layer and Ga+ ions have a low ionization efficiency, the maximum possible count rate per pixel is extremely small. Previous studies have suggested that sources other than Ga+ produce molecular ions and fragments with higher efficiency, e.g. In+. Gold has also been shown to be an effective source, particularly since it is possible to generate Au++, Au+ and Au2+ beams. Yield enhancements of several orders of magnitude have been reported, although the source was not used in an imaging modality.[1] Here, we examine the prospects for routine use of Au LMIG sources for TOF-SIMS imaging. We employ Au-Si or Au-Ge eutectics to allow the metal to be melted around the tip at a temperature low enough to prevent gold evaporation. Currently, the tips have a lifetime in excess of 1500 amp-hours. Mass selection is achieved using a double blanking system which allows pulsing and mass selection. The probe size for each of the three gold species is < 300 nm. The performance of this tip will be compared against In and Ga sources for a number of standard materials including Irganox, phenylalanine and several long chain alkanethiols adsorbed on gold. In general, we find the yield of Au is enhanced by up to an order of magnitude over Ga. Of special interest is the fact that Au++ ions exhibit the largest enhancement in many cases, and that Au2+ ions do not yield significant advantage over Au+ ions.

[1] H. H. Anderson, A. Brunelle, S. Della-Negra, J. Depauw, D. Jacquet, Y. LeBeyec, J. Chaumont, H. Bernas, Phys. Rev. Letts., 80 (1998) 5433; B. Hagenhoff, R. Kersing, D. Rading, S. Kayser, and E. Niehuis, SIMS XII, (1999) 833.

2:20pm **AS-TuA2 Molecular Imaging Using Atomic and Molecular Primary Ions**, ***F. Kollmer***, *R. Moellers*, *D. Rading*, ION-TOF GmbH, Germany, *R. Kersting*, TASCON GmbH, Germany, *E. Niehuis*, ION-TOF GmbH, Germany

The secondary ion yield Y of organic materials increases considerably with the mass of the primary ion. A further yield enhancement can be achieved when changing from atomic to polyatomic primary ions. As the corresponding increase in damage cross section σ is much smaller, the ion formation efficiency E:= Y/σ also increases significantly. The efficiency E not only determines the achievable detection limits in surface spectrometry but also influences the useful lateral resolution Δl in organic imaging via Δl ~ $(1/E)^{\text{Â½}}$. In order to investigate the influence of the primary ion bombardment conditions in imaging of real world samples we applied both monoatomic as well as polyatomic primary ions including Ga^+, In^+, $Au_1{}^+$, $Au_2{}^+$ and $Au_3{}^+$. The application of a Au LMIS combines capabilities such as high brightness and high lateral resolution with the advantages of molecular primary ion bombardment. The investigated samples consisted of various thick organic materials with analyte molecules in the mass range > 500 u. The results confirm the dependence of the useful lateral resolution on E and show that imaging of organic materials can best be performed with polyatomic primary ion bombardment. If monoatomic bombardment is used high mass ions are preferable compared to low mass ions. Enhancement factors (E compared to E_{Ga}) for polyatomic primary ions reach several orders of magnitude whereas at maximum an enhancement factor of 10 can be achieved with monoatomic primary ions.

2:40pm **AS-TuA3 Topographic Effects in SIMS Imaging**, ***S. Rangarajan***, *B.J. Tyler*, University of Utah

One of the most notable of these challenges in TOF-SIMS imaging is differentiating between chemical and topographical effects. The intensity of ion signals depends not only on the surface composition but also upon the surface height and inclination (topography) and the material beneath the surface (matrix). In many cases, the intensity variations due to the structure of the sample can obscure features associated with surface chemistry. Images of surfaces with strong topographic features, including fibers and spherical particles have been presented. Topographic effects include the influences of the height of topographic features, the incident angle between the beam and the surface and variations in the electric field associated with topographic features. We have explored the influence of these topographic features on the absolute and relative ion intensities on conducting and insulating surfaces. Data from both TRIFT and reflectron systems will be presented. When images are generated by rastering the ion beam, topography can cause severe distortions in the image. Additional, particles can create field lines that result in repressed ion emission causing a halo surrounding the particles. Typically, researchers have assumed that topography effects only the absolute intensity of ions but will not significantly alter the relative intensity of peaks in the spectrum. Our results suggest that this assumption is incorrect in many cases. Several data processing methods have been used to compensate for topographic effects in images and there effectiveness will be discussed. Multivariate statistics can help reduce some but not all of these effects on the images. Results will be presented using principle components analysis and mixture models to process images with confounding chemical and topographical features.

3:00pm **AS-TuA4 Towards Quantitative Chemical State XPS Imaging**, ***C.J. Blomfield***, *S. Page*, *A.J. Roberts*, *S.J. Hutton*, Kratos Analytical Ltd, UK

XPS imaging is an established method for determining the qulitative lateral distribution of chemical species across a sample surface. Early methodologies for this technique involved acquiring XPS maps, where a virtual probe or X-ray spot was scanned across a sample surface and an image built up pixel by pixel as the analysis point was moved across the sample. Other methods involved the paralell detection over a predefined field of view in one specific binding energy range. Improvements in detector and instrument design in general have lead to the development of truly quantitative pulse counting methods which can give high lateral resolution XPS images with quantitative intensities. This paper describes the issues which must be adressed and the applications which could benefit from a quantitative chemical state imaging technique.

3:20pm **AS-TuA5 Analysis Area and Sample Area Viewed by the Analyzer in a Scanning Auger Microscope**, ***C.J. Powell***, *S.A. Wight*, *J.T. Armstrong*, National Institute of Standards and Technology

The lateral resolution, δr, is a critical parameter in a scanning Auger microscope (SAM) since it is a measure of the distinguishability of small objects. For quantitative interpretations of measured Auger signals, however, it is necessary to consider also the analysis area (the area from which all or a defined percentage of the detected signal originates). We report results of model calculations (based on the work of Cazaux[1]) that show how the analysis area depends on material parameters associated with backscattered electrons in a SAM. These results are compared with measurements of signal changes as the incident beam in a commercial SAM is scanned across a chemical edge consisting of Cr/CrO_2 on indium-tin-oxide. As the beam voltage is increased from 5 kV to 20 kV, the effects of backscattering on the analysis area become more pronounced, in general agreement with the calculations. These results indicate that the analysis area can be much greater than $\pi(\delta r)^2$. In addition, we report on measurements of the sample area viewed by the analyzer in the SAM for different electron energies and different analyzer operating conditions. Changes in the sample area viewed by the analyzer as a function of electron energy need to be carefully considered in SAM measurements with different rastered areas.

[1] J. Cazaux, Surf. Interface Anal. 14, 354 (1989).

3:40pm **AS-TuA6 Materials Characterization using High Spatial Resolution XPS: Multi-technique, Multi-variate, Multi-collaborator Analyses**, ***J.E. Fulghum***, University of New Mexico **INVITED**

Recent instrumentation developments have improved spatial resolution and decreased acquisition times in x-ray photoelectron spectroscopy (XPS). 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. The combination of high spatial and high energy resolution XPS enhances analysis of heterogeneous samples ranging from microelectronic materials to fossils. This enhanced chemical characterization of heterogeneous samples comes at the cost of increasing complexity in the XPS data sets acquired. Spectra-from-images data sets, and imaging series, can produce complex data structures that are not readily interpreted by visual inspection alone. A variety of multi-variate analysis methods can be utilized to facilitate analysis of multi-dimensional data sets, and several examples will be shown. Conclusions based on visual inspection versus principal components analysis will be discussed. New opportunities for multi-technique correlations also arise from the improved spatial resolution and decreased acquisition times. A variety of techniques, including FTIR, AFM and confocal microscopy have fields-of-view which are comparable to imaging XPS, making correlative analyses possible. Data from multi-component polymer samples will be used to demonstrate the direct correlation of XPS images with other imaging methods. This work has been partially supported by NSF ALCOM (DMR89-20147) and NSF CHE-0113724.

4:20pm **AS-TuA8 Nano-XAS and Nano-XPS: Energy-discriminating Imaging Utilizing a PEEM Lens Combined with Retarding or Dispersive Electron Energy Filters**, ***M. Merkel***, *M. Escher, J. Settemeyer, M. Schicketanz, T. Unger,* FOCUS GmbH, Germany, *D. Funnemann, J. Westermann, B. Krömker,* OMICRON GmbH, Germany, *Ch. Ziethen, A. Oelsner, P. Bernhard, F. Wegelin, A. Krasyuk, G. Schönhense,* Johannes Gutenberg Universität, Germany

The strong gradient in the field of nanotechnology and materials research calls for surface imaging techniques with nanoscopic lateral resolution and intrinsic spectroscopic information. We will present our recent activities in this field. We have already reported on the combination of a laboratory X-ray source with an energy filtered bolt-on photoemission electron microscope (PEEM) optics.[1] Spectroscopic information with sub-micron lateral resolution was possible, however imaging at certain spectroscopic features failed due to the lack of excitation intensity. Recently, this development received strong impetus from novel technical achievements. For example, micro technology delivers new solutions in terms of electron optical components with critical dimensions. Highly brilliant synchrotron beamlines deliver the needed excitation intensity. Finally, state of the art ray tracing and a three dimensional computer aided design is capable of delivering optimised technical solutions. Two approaches with their actual results will be shown in comparison: PEEM imaging combined both with an energy dispersive analyser and with the most advanced RFA type imaging energy filter. The latest milestone results of dedicated research projects will be reported, showing the present limits of Nano-XAS (X-ray absorption spectroscopy) and Nano-XPS (X-ray photoelectron spectroscopy). Until now, we achieved about 20nm lateral resolution using the XAS imaging mode. Using XPS we got about 140 nm resolution. These methods also provide well differentiated spectra drawn from sample areas near the resolution limit. The best energy resolution of both methods is currently about 0.1 eV. Part of the work was funded by BMBF, Germany, through grants FKZ-No: 13N7864, 13N7887 and 13N7863.

[1] M.Merkel, M. Escher, J. Settemeyer, D. Funnemann, A. Oelsner, Ch. Ziethen, O. Schmidt, M. Klais und G. Schönhense, Surface Science 480 (2001), 196-202.

4:40pm **AS-TuA9 Imaging Thin Oxide-Covered Metal Lines with the Photoelectron Emission Microscope***, ***V.W. Ballarotto***, *K. Siegrist, M. Breban, E.D. Williams*, University of Maryland

The contrast mechanisms in photoelectron emission microscopy (PEEM) are significantly different than those in secondary electron microscopy (SEM), and thus PEEM may serve as a complementary tool to SEM in analytical applications to semiconductor device characterization. As part of an on-going study to quantify PEEM imaging response[1,2] we have investigated imaging of metal lines buried under thin layers of silicon dioxide, including the effect of an electrical bias applied to the lines. Numerical simulations show that the lateral field strength that is generated at the edge of a metal line is the same order of magnitude as the perpendicular accelerating field strength (~10^6 V/m) necessary for imaging. Therefore, electrons emitted near the edge can be displaced from the image collection volume and generate contrast. Several well-characterized samples have been used to test this contrast mechanism when imaging with and without oxide-covered metal structures. We will show images of the lateral width of the edge-contrast increasing as the bias voltage is increased from 0 to ±10 V. The magnitude of the edge effect observed for a metal line buried under 4.5 nm of SiO_2 is comparable to an uncovered metal line. Numerical studies suggest that the bias voltage necessary to minimize the edge-contrast increases about 2.5 mV per nanometer increase in height. Thus, image analysis of this effect may allow for height determination of structures. Moreover, this contrast mechanism could also be used in failure analysis by helping to identify breaks in metal lines. *Supported by LPS and in part by the NSF-MRSEC. .

[1] V.W. Ballarotto, K. Siegrist, R.J. Phanuef and E.D. Williams, J. Appl. Phys. 91, 469 (2002).
[2] V.W. Ballarotto, K. Siegrist, R.J. Phanuef and E.D. Williams, Appl. Phys. Lett. 78, 3547 (2001).

Advancing Toward Sustainability Topical Conference
Room: C-210 - Session AT-TuA

Benign Manufacturing, Climate Change, International Trade and World Economy, and Theological Considerations of Sustainable Development

Moderator: P. Maroulis, Air Products & Chemicals Inc.

2:00pm **AT-TuA1 A Framework and Practices for Advancing Toward Sustainability**, ***L.G. Heine***, Zero Waste Alliance/International Sustainable Development Foundation **INVITED**

There is currently a movement, gaining momentum worldwide, toward what is commonly called sustainability or sustainable development. A generally accepted definition of sustainability is that which meets the needs of the present without destroying the ability of future generations to meet their own needs. While few would disagree that this is an imperative, there is confusion as to how to achieve this goal. Green Chemistry is often held up as a tool for chemists, chemical engineers and others who design materials to help move society towards the goal of sustainability. Green chemistry is the design of products or processes that reduce or eliminate the use and/or generation of hazardous substances. The focus of green chemistry is on design because it is at the level of molecular design that decisions are made that impact how the material will be processed, used and managed at the end of its life. A framework for sustainability called The Natural Step (TNS) has emerged from Sweden as a mental model of what sustainability might look like at the global level. In The Natural Step, four System Conditions are defined that characterize how humans can engage with the natural world in a way that will not lead to progressive deterioration. This model is helpful in defining what sustainability is NOT, but it is not prescriptive for how sustainability can be achieved. This presentation looks at the System Conditions as defined in The Natural Step along with the principles and practices of Green Chemistry, and ideas taken from frameworks for ecologically sound manufacturing and product design such as "zero waste" to illustrate how some businesses are positioning their companies to become more economically competitive through sustainable business practices.

2:40pm **AT-TuA3 Chemical Plant Safety After 9/11: Reducing Risks Associated with the Use of Organo/chlorinated Solvents in Degreasing Operations**, ***C.A. LeBlanc***, Toxics Use Reduction Institute **INVITED**

The mission of the Surface Solutions Laboratory (SSL) is "to identify, develop and promote safer alternatives to hazardous materials such as chlorinated and other organic solvents." These materials are often used in industrial processes such as surface preparation, coating, cleaning, rinsing, drying and analysis in the production of manufactured goods. Located at the University of Massachusetts Lowell, SSL is a division of the Toxics Use Reduction Institute (TURI), established by the Commonwealth in 1989. Chemical advances are typically accompanied with advances in equipment, in this case, degreasing operations. This talk will focus on the lessons learned and the progress made in working with well over 100 companies in solvent-substitution projects during a five-year period. These firms range from high-tech (for example, semiconductor) to low-tech (for example, machine shop) enterprises. The events of September 11 may serve as a catalyst to improve plant safety, as local, state and federal agencies, as well as businesses contend with the prospect of deliberate chemical misuse. Attendees to this session will better understand how successful technical diffusion and technical transfer occurs. The role that 'disruptive technologies' play in these endeavors will be discussed as time allows.

3:20pm **AT-TuA5 Global Warming: How Much is Too Much?**, ***J.B. Smith***, Stratus Consulting Inc. **INVITED**

The Earth's climate warmed about one degree Fahrenheit during the 20th century. Most of the warming in the last half of the century was the result of greenhouse gas emissions from societal activities. Should emissions continue increasing without a concerted effort to control them, projections are that temperatures could increase about 3 to 10°F by 2100. Policy makers are struggling to control the growth of greenhouse gas emissions. While initial efforts such as the Kyoto Protocol will at best slow the rate of emissions growth, ultimately concentrations of greenhouse gases need to be stabilized. What is an appropriate target for stabilizing atmospheric concentrations of greenhouse gases? The United Nations Framework Convention on Climate Change, which the United States ratified, states that concentrations of greenhouse gases will eventually be stabilized at a level that is not dangerous. This talk, which is based on a recent report by the Intergovernmental Panel on Climate Change, addresses different ways in which policy makers may be able to determine what is a safe (i.e., not dangerous) level of climate change. Five "reasons for concern" about climate are addressed: 1) impacts on unique and threatened systems; 2) effects of change in extreme weather; 3) inequitable distributional effects of climate change; 4) total (aggregate) impacts of climate change; 5) risk of major changes in the climate system. The literature on climate change impacts was surveyed to determine what a dangerous level of climate change may be for each reason for concern.

4:00pm **AT-TuA7 The Garden, the Wilderness, and Covenant: Formulating a Theological Mandate for Sustainable Development**, ***S. Meyers***, Harvard Divinity School

The 20th Century witnessed a debate between paradigms of economic development, namely the State-led and Neo-liberal models. Each have gained ascendancy and "orthodoxy" at different points in time but neither have brought forth their promised fruits to many of the peoples who continue to dwell in abject poverty and both have contributed to worldwide environmental degradation. Yet these economic debates contain theological notions of humanity's relationship to creation which predate them be several millennia. The Hebrew Bible provides three symbols through which humans understand the earth. The first two symbols are found in the beginning of the book of Genesis and are those of the Garden of Eden and the chaos of the wilderness. The third is found later in Genesis as the covenant made between God and all of creation following Noah's flood and in the covenant that formed the People of Israel in the book of Exodus. The Garden of Eden symbol underpins neo-liberal theory which sees the earth as a gift from God to be exploited and, through human ingenuity and God's divine will, never to prove human consumption unsustainable. The wilderness imagery corresponds to state-led development which advocates authoritarian rule, central planning, and an underlying Malthusian belief that the earth can not sustain humanity unless nature can be carefully controlled and subjugated. Both symbols are anthropocentric and can never produce environmental ethics that are not fundamentally related to an understanding of the earth as the object of human dominion. Covenant, however, is a theocentric perspective that recognizes God as the Creator of both humans and all of nature, and denies a natural order that puts humans as the "lords of the earth." Building on Moltmann's Trinitarian process, basic moral axioms can be created that form the basis for reinterpreting humanity's relationship to nature and God and to create a theological underpinning for new paradigms of sustainable development.

4:20pm **AT-TuA8 Climate Change Science Economics and Politics**, ***W. Moomaw***, The Fletcher School **INVITED**

The science of climate change has been studied for over 100 years, but only in the past 15 years has it been a subject of policy and diplomacy. There is now a substantial body of scientific knowledge that demonstrates that certain atmospheric trace gases such as water vapor, carbon dioxide, methane, ozone and nitrous oxide trap heat that keeps the earth's average temperature around 60 deg. F. Human activities have increased each of these gases substantially: carbon dioxide by 30% and methane by over 100%. Temperature measurements on land and in the oceans demonstrate a clear rise in temperature of about 1 deg F during the past century. Measurements several miles above the earth's surface show a smaller increase. Since fossil fuels are associated with both carbon dioxide, methane and some nitrous oxide releases, attention has focused on the energy sector as the major target of mitigation efforts. Modeling of the climate system and the economy with and without climate change show a range of energy intensity have generated an intense debate over what to do. The U.S. has withdrawn from the Kyoto Protocol that would require emissions reductions 7% below 1990 levels by 2012, but remains committed to the Climate Convention that identifies climate change as a problem requiring action. The Kyoto Protocol could be ratified by enough countries to enter into force for a majority of industrial countries even if the U.S. that is responsible for about one-quarter of emissions does not participate. This has major implications for international trade and for industrial design. This presentation will attempt to untangle claims and counterclaims to reveal what is at stake and what are some possible outcomes for planetary systems and for the world and U.S. economy.

5:00pm **AT-TuA10 Invited Speakers Panel Discussion with Audience Participation. Title of the Panel Discussion and background information on the panelists will be posted openly at the Symposium.**

Biomaterials
Room: C-201 - Session BI+SS-TuA

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

2:00pm **BI+SS-TuA1 Medard W. Welch Award Address: The Biointerface Examined in Five Dimensions**, ***B.D. Ratner****, University of Washington **INVITED**

Twenty years ago, we had no such word as "biointerface." Now we use that word almost routinely to suggest surface-localized events between biological systems and solid surfaces (solids that vary in solidity from almost fluid to hard). To examine with a new perspective this burgeoning field, five facets of the biointerface will be explored. The five faces of the biointerface will be: temporally (and historically), spatially, molecularly, entrepreneurially and virtually (in computer space). Studies from our groups at the University of Washington and from others in the field will be presented. The talk will aim at defining the new field of the biointerface, relating it to "classical" surface science and highlighting opportunities.

2:40pm **BI+SS-TuA3 "Smart" Biomolecular Conjugates**, ***P.S. Stayton***, *A.S. Hoffman, N. Malmstadt, C. Hu, S. Kulkarni*, University of Washington

One of the hallmarks of biological systems is their ability to change important properties in response to environmental cues. We have been developing stimuli-responsive biomolecular materials for biosensors, diagnostics, affinity separations, microfluidic devices, and chip/array devices that exhibit responsiveness to specific environmental cues. For many of the diagnostic and sensor technologies that utilize biomolecular recognition properties, there is a continuing need for better control routes. Current environmental methods are relatively harsh and can lead to damage of biomolecules and cells. In addition, the environmental signals are typically large general solution changes and thus not targeted to selective recognition components. The stimuli-responsive biomolecular materials allow reversible control over protein recognition properties by utilizing small changes in environmental conditions or signals. The "smart" polymers reversibly cycle between an extended and hydrophilic random coil, and a collapsed, hydrophobic state that is reduced in average volume by ca. 3-fold. When the smart polymers are attached at defined protein side-chains, typically by genetically engineering cysteine or lysine residues, the polymers serve as sensors and actuators to control access of ligands or substrates to binding or catalytic sites. This general approach targets mild environmental signals to specific polymer-protein conjugates, and thus for example allows differential control of different antibodies in a device by using conjugated polymers that are sensitive to different signals (e.g. antibody 1 with pH, antibody 2 with temperature, antibody 3 with light). They can thus allow multiplexing control in complex mixtures, and are thus relevant to a number of different diagnostic and sensor formats.

3:00pm **BI+SS-TuA4 Molecular Recognition Mediated Fabrication of Protein Nanostructures by Dip-Pen Lithography**, *J. Hyun, S.J. Ahn, W. Lee*, ***S. Zauscher***, *A. Chilkoti*, Duke University

The spatially controlled immobilization of biomolecules on solid surfaces at the nanometer length-scale is driven by the possibility of fabricating new sensors and actuators that will enable detection and actuation at the single molecule level. This communication describes how dip-pen nanolithography (DPN) in combination with the high-affinity streptavidin-biotin, protein-ligand system provides a simple and versatile "bottom-up" approach to create nanoscale biomolecular architectures in a step-wise fashion. This method involves the fabrication of nanoscale features by patterning a self-assembled monolayer (SAM) of a COOH-terminated alkanethiol on a gold substrate by DPN, followed by covalent immobilization of a high-affinity small-molecule ligand (biotin) onto the nanopatterned SAM and subsequent molecular recognition of its protein binding partner (streptavidin) from solution. We fabricated streptavidin nanostructures with lateral feature sizes in the range of 10-400 nm by this method, and have shown that the streptavidin nanopatterns can be used as a template to pattern biotinylated molecules of interest from solution. Because the binding of the final, target molecule is mediated by a highly

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***** Medard W. Welch Award Winner

specific molecular recognition interaction that occurs solely in the patterned region against a non-fouling background, this approach should allow patterning a biomolecule of interest directly from complex mixtures such as cell lysate without purification, which is not possible with alternative DPN methods that involve physisorption or covalent conjugation.

3:20pm **BI+SS-TuA5 Threading DNA Through a Nanopore: Applications for Analyte Detection**, ***J.J. Kasianowicz***, *S.E. Henrickson, B. Robertson*, National Institute of Standards and Technology, *H.H. Weetall*, EPA, *M. Misakian*, National Institute of Standards and Technology **INVITED**

We recently demonstrated that single-stranded DNA (ssDNA) can be driven electrophoretically through a solitary Staphylococcus aureus alpha-hemolysin (alpha-HL) ion channel. In an effort to use this model system to understand DNA transport in biological systems, we show that the partitioning of ssDNA into the pore depends on the side to which the polymer is added and on the magnitude of the applied potential. Kramer's reaction rate theory was used to estimate both the height of the energy barrier for polymer translocation and the integral number of charges on ssDNA that interact with the barrier. In a related research effort, we illustrate three experimental results that suggest the interaction between polymers and a single nanopore can be used to quantitate analyte concentration and type. First, the probability that ssDNA enters the alpha-HL channel is proportional to the polymer concentration. Second, analyte binding to sites on ssDNA predictably alters the ability of the polymer to thread through the pore. Third, different ssDNA homopolymers induce current blockade patterns that are characteristic of the nucleotide type. We compare this method to other channel-based detection schemes. Finally, we show that modified polynucleotides might prove useful as "molecular rulers" for probing the structure of nanopores.

4:00pm **BI+SS-TuA7 Novel Immunosensor Interfaces based on Mixed Self-Assembled Monolayers of Thiols on Gold**, ***F. Frederix***, *M. Boesmans, K. Bonroy, W. Laureyn, A. Campitelli*, IMEC, Belgium, *M.A. Abramov, W. Dehaen, G. Maes*, KULeuven, Belgium

The two components that make up a biosensor are the biological recognition layer, which selectively binds the analyte, and the transducer which translates this recognition event into an electrical signal. The increasing miniaturization of biosensor transducers (and thus of their active areas) and the demand for sensitivity, require a fully evaluated and optimized covalent immobilization of antibodies. Our research is therefore not only focusing on the transducer but also on the biological interface. This biological recognition layer mainly determines the specificity, stability, reproducibility, and durability of the biosensor as a whole. Our strategy is to achieve the above-mentioned properties based on mixed Self-Assembled Monolayers on gold. The realization of a biological recognition interface encompasses various aspects. Cleanliness and structural properties of the gold surface are very important for perfect SAM formation and were therefore optimized. Novel thiols able to couple antibodies or to mitigate non-specific adsorption were synthesized and evaluated, along with new molecules for blocking. The mixed monolayer formation of these novel thiols was characterized using contact angle measurements, XPS, cyclic voltammetry, and GA-FTIR. The immobilization of proteins on mixed SAMs is the most important step in the realization of immunosensors because it determines the activity of the antibodies and therefore the sensitivity. Random and orientated immobilizations of (chemically modified) antibodies on mixed monolayers of thiols were compared using Surface Plasmon Resonance. The enhanced sensitivity (< 0,1 ng/mL) and selectivity (no non-specific adsorption) were compared to commercially available biological recognition layers. In summary, we will show the importance of the biological recognition layer for the global performance of a biosensor and how the sensitivity can be drastically enhanced by modifications on the biological interface of an immunosensor.

4:20pm **BI+SS-TuA8 Electrostatic and Fluorescence Sensing of DNA Hybridization at Electrode Surfaces**, ***R.M. Georgiadis***, *J. Wang, L.K. Wolf, A.W. Peterson*, Boston University

Current microarray technologies, based on specific probe-target hybridizations, often suffer from nonspecific surface interactions. In addition, for surface immobilized probes, thermodynamic equilibrium conditions may not be reached without excessively long incubation times and hybridization may be kinetically or sterically inaccessible for some probe sequences or for some surface probe densities. In previous work on perfectly matched duplexes, we have shown that probe density is a controlling factor for DNA hybridization at surfaces. Here, we expand our studies to investigate probe density effects for mismatched sequence or targets that access different binding locations on the immobilized probe. To improve mismatched hybrid discrimination we detect different dissociation profiles for matched and mismatched 25-mer targets from surface-immobilized probes in the presence of an applied repulsive electrostatic field and present denaturation profiles for surface-bound hybrids obtained by continuously varying the applied electrostatic surface field. Finally, we examine the immobilization and hybridization of covalently-bound molecular beacons on gold surfaces using surface plasmon resonance (SPR) spectroscopy and fluorescence spectroscopy.

4:40pm **BI+SS-TuA9 Characterization of DNA on Gold: A Quantitative Surface Science Approach**, ***D.Y. Petrovykh***, University of Maryland - College Park / NRL, *H. Kimura-Suda, M.J. Tarlov*, National Institute of Standards and Technology, *L.J. Whitman*, Naval Research Laboratory

Covalent attachment of thiolated DNA onto gold surfaces is one of the most common methods for immobilizing aqueous DNA onto solid substrates. The formation of the DNA film in this case is thought to closely resemble that of alkanethiol self-assembled monolayers (SAMs). DNA films in modern applications, e.g. DNA microarrays, are < 10 nm thick with submonolayer surface coverage, which means that the traditional surface characterization techniques can be employed to complement biochemical analysis. We are applying XPS, FTIR, and ellipsometry to systematically quantify the chemical structure and coverage of self-assembled single-stranded DNA (ssDNA) films. Thymine (T) has the simplest structure of the four nucleotide bases: a single ring with two N atoms. Moreover, the environment of the two N atoms is so similar that the resulting XPS peak is consistent with a single N1s state in a polymer-like material. Backbone P atoms produce a base-independent single P2p peak. N and P are not subject to significant contamination, so the peak intensities can be used to estimate the coverage of immobilized DNA. N1s chemical shifts together with the base-dependent N/P ratio can confirm the presence of specific polynucleotides on the surface. The coverage determined by XPS is linearly correlated with base-specific IR features and agrees with absolute values obtained from radiolabeling measurements. We will also discuss how the XPS and IR spectra of dT-polynucleotide films can provide information about other basic properties of ssDNA films, such as uniformity and orientation, as well as issues of damage, degradation and contamination.

5:00pm **BI+SS-TuA10 Antibacterial Coatings of Immobilised Furanones**, ***H.J. Griesser***, *S. Al-Bataineh*, University of South Australia, *B.W. Muir, H. Thissen, M. Willcox*, CRC for Eye Research and Technology, Australia

The formation of bacterial biofilms and subsequent infections can cause serious complications in the use of biomedical devices such as catheters, and broadly effective technology is lacking. Nature has, however, addressed very effectively the problem of microbial colonisation of surfaces. For instance, the red alga Delisea pulchra secretes brominated furanones that prevent its microbial colonisation. These compounds are thought to interfere with bacterial quorum sensing by their chemical similarity with homoserine lactone, an important bacterial regulator. We have immobilised various furanones onto synthetic surfaces and tested the efficiency of such coatings in bacterial colonisation assays. A broadly applicable covalent immobilisation strategy involves nitrene chemistry, with light-activated reaction between furanones and azido aniline coupled onto a surface hydrogel interlayer. This allows coupling of furanones without reactive substituents but is non-selective with regard to molecular orientation and location of attachment. Other strategies require functionalised furanones, for example reaction between a hydroxylated furanones and surface isocyanate groups; such furanones can be more difficult to synthesize. Work to date has produced substantial reductions in bacterial colonisation, but not to the high degree required in clinical applications. Investigations now focus on the interactive effects of furanone molecular composition, immobilisation chemistry and surface density. An interesting finding is that these compounds are effective when surface immobilised although the classical microbiological model of homoserine lactone action requires entry into the microbial interior. This dichotomy calls for detailed surface characterisation of furanone coatings, including study of whether the entire population of surface-bound molecules is indeed covalently linked and thus non-diffusible and acting via a different mechanism to stifle bacterial colonisation.

Electronic Materials and Devices
Room: C-107 - Session EL+SC-TuA

Semiconductor Characterization
Moderator: P.H. Holloway, University of Florida

2:00pm **EL+SC-TuA1 Active-Device Scanning Voltage Microscopy Studies on a Forward and Reverse Biased InP pn Junction Sample**, ***ST.J. Dixon-Warren***, *R. Dworschak, G. Este, AJ. SpringThorpe, J.K. White,* Nortel Networks, Canada, *D. Ban, E.H. Sargent*, University of Toronto, Canada

Active-Device Scanning Voltage Microscopy (SVM) is a new Scanning Probe Microscopy (SPM) technique in which a two-dimensional voltage map is obtained on the cross-section of a biased semiconductor sample. The voltage is measured using a very high impedance voltmeter that is connected to a conductive doped-diamond coated SPM tip. Recently obtained results on a molecular beam epitaxy (MBE) grown InP pn junction sample will be reported, under both forward and reverse bias conditions. The results are compared to those obtained with Scanning Spreading Resistance Microscopy (SSRM) measurements under zero bias on the same sample. The SVM and SSRM results will be discussed in terms of the semi-classical model of the pn junction. The physics of the SVM measurement process will also be discussed. Finally, the results obtained on the simple pn junction sample will be compared with those obtained on more complex samples, such as InP based ridge waveguide and buried heterostructure laser samples under forward bias.

2:20pm **EL+SC-TuA2 Scanning Tunneling Microscopy Imaging of Charged Defects on Clean Si(100)-(2x1)**, ***G.W. Brown***, *H. Grube, M.E. Hawley,* Los Alamos National Laboratory, *S.R. Schofield, N.J. Curson, M.Y. Simmons, R.G. Clark*, University of New South Wales, Australia

We have used scanning tunneling microscopy (STM) to image charged defects on the clean Si(100)-(2x1) surface. In the absence of "C"-type defects, band bending can occur during STM imaging, allowing near surface charge to influence the state density contributing to the tunnel current. As in the case of cleavage faces of III-V semiconductor crystals, the charge-induced band bending produces long range enhancements superimposed on the periodic surface lattice. We observe this in empty-state STM images taken on n-type Si(100). No band bending signature is seen in the filled-state images. This can be understood by considering the band structure at the surface, which has surface states within the gap. The charged defects observed in this work are of the types commonly observed in clean Si(100)-(2x1) STM studies, however, not all defects of a given type appear charged. This would indicate subtle differences in defect structure or the influence of impurities. This work demonstrates the ability to observe charged features on the clean Si(100) surface, which will be important for current and future research focussed on producing atomic scale electronic structures. Predictions for signatures on p-type material will also be made.

2:40pm **EL+SC-TuA3 The Surface Photovoltage and Photoelectron Spectroscopy**, ***J.P. Long***, Naval Research Laboratory **INVITED**

Frequently, the surface of a semiconductor in equilibrium exhibits "band bending," an electrostatic shift of the surface relative to the bulk that arises from the built-in electric field associated with a surface depletion layer. When such a surface is illuminated, photogenerated electrons and holes move to screen the built-in field, thereby reducing the band bending and shifting the surface energy levels, an effect known as the surface photovoltage (SPV). Because the energy levels measured by photoelectron spectroscopy shift with the electrostatic potential of the surface, the technique is sensitive both to equilibrium band bending, a fact often exploited to characterize Schottky barrier heights, and to the SPV, which makes photoemission a useful SPV detector. However, under certain conditions, the ultraviolet or x-ray photoemission source itself can induce a sizable SPV that seriously hampers the measurement of equilibrium energy levels. This talk will introduce the SPV at a tutorial level, and will discuss the interplay between photoelectron spectroscopy and the SPV. Illustrations of photoemission as a SPV detector include the use of synchrotron radiation to characterize SPV decays in laser-excited Si and to detect, via SPV-induced band-flattening, inhomogeneous band bending on GaAs caused by Ga islands. In addition, the problem of SPV's induced by photoemission sources themselves will be addressed. Usually encountered below room temperature where the SPV is enhanced, source-induced SPV's become an important issue at and above room temperature in wide band-gap materials, which are acutely prone to a SPV when large equilibrium band bending is present. A striking example of current relevance is p-type GaN, which exhibits source-induced SPV's at room temperature exceeding a volt when examined by ordinary UPS and XPS laboratory sources.

3:20pm **EL+SC-TuA5 Direct Measurement of the Electrical Potentials in GaInP$_2$ Solar Cells**, ***C.-S. Jiang***, *H.R. Moutinho, J.F. Geisz, D.J. Friedman, M.M. Al-Jassim,* National Renewable Energy Laboratory

We report the application of electrostatic force microscopy (EFM) to photovoltaic devices. The built-in electric field plays a major role in photovoltaic devices, because it collects photo-excited carriers and is a key factor in determining the open-circuit voltages of solar cells. However, the measurement of the built-in potential has been limited to indirect ways such as the characteristics of current-voltage and capacitance-voltage. In these measurements, it is hard to distinguish the contributions from the multi-junctions or interfaces of a modern solar cell device. In this presentation, we report a direct measurement of the electric potential on cross-sectional planes of a GaInP$_2$ device both quantitatively and spatial-resolvedly, by using the Kelvin probe force model of the EFM technique. Two features on the potential profile are assigned respectively to the p-n junction of GaInP$_2$ and the band offset between the GaInP$_2$ base and the GaAs substrate materials. With varying the light intensities irradiated at the sample, we found that, in addition to the flattening of the p-n junction, two changes in the potential profile happened in the locations of the front window or the back surface field (BSF) layers under the condition of a lower or a higher light intensities, respectively. The two potential changes, together with the flattening of the p-n junction, contribute positively to the open-circuit voltage of the device, indicating the importance of the window and the BSF layers in solar cell designs. Furthermore, the potential change at the window layers is understood in terms of the band offset between the AlInP$_2$ window and the GaInP$_2$ emitter layers, and the potential change at the BSF layer is understood in terms of the total effect of the photo-induced flattening of the band bending and the band offset at the interface between the base and the BSF, respectively.

3:40pm **EL+SC-TuA6 Deep Level Defect Characterization of InGaAsN Layers Grown by Molecular-Beam Epitaxy**, ***S.W. Johnston***, *R.K. Ahrenkiel, A.J. Ptak*, National Renewable Energy Laboratory

The quaternary alloy $In_xGa_{1-x}As_{1-y}N_y$ can be grown lattice-matched to GaAs and can potentially be used as the 1-eV bandgap material in a four-junction, high-efficiency solar cell. We have characterized a series of $In_xGa_{1-x}As_{1-y}N_y$ samples with varying N content by measuring deep level transient spectroscopy (DLTS). The samples were grown by rf plasma-assisted molecular-beam epitaxy and contain N concentrations $0 \leq y \leq 0.02$. Our data show that each as-grown sample contains a hole trap whose peak occurs near 350 K for the 0.2-ms rate window. Analysis of these peaks indicates activation energies of 0.62, 0.62, and 0.75 eV for samples with y = 0.003, 0.013, and 0.02, respectively. Electron traps were also detected, even though the DLTS measurements were performed with Schottky contacts deposited on p-type material. This is attributed to a large Schottky barrier. For the sample with y = 0.003, an electron trap with an activation energy of 0.50 eV was detected. As N-content increased, the detected electron-trap activation energies decreased to 0.22 and 0.27 eV for the y = 0.013 sample, and to 0.13 eV for the y = 0.02 sample. We also show DLTS data correlating to varying growth conditions and the effects of annealing processes.

4:20pm **EL+SC-TuA8 Thermal Quenching and High Temperature Cathodoluminescent Degradation of Sulfide-Based Powder Phosphors**, ***B.L. Abrams***, *L.C. Williams, J.-S. Bang, P.H. Holloway,* University of Florida

Temperature effects on cathodoluminescent (CL)intensity, spectrum and degradation of ZnS:Ag,Cl powder phosphor have been investigated. Thermal quenching was studied by increasing the phosphor temperature without exposure to a continuous electron beam and measuring the decreased CL intensity. A characteristic thermal quenching temperature of 150°C with an activation energy (E_a) of 0.87eV was observed for ZnS:Ag,Cl. Along with reduced CL intensity, the spectra shifted to longer wavelengths and changed shape at elevated temperature. The shift was dominated by band gap narrowing at high temperatures. Shape change was attributed to Cu contamination from the heater stage. The CL spectral distribution and intensity were 100% recoverable upon cooling back to room temperature when electron beam exposure was minimal (<1C/cm^2). With continuous electron beam exposure, CL intensity upon cooling to RT (after 24C/cm^2, 2keV primary beam energy) was <40% of the original intensity before heating. The loss of CL intensity at high temperatures was less than at RT for the same primary beam energy and coulombic dose. This is consistent with the Electron Stimulated Surface Chemical Reaction (ESSCR) Model of degradation which predicts that elevated temperatures will reduce the mean stay time of physisorbed gases, decreasing the rate of the surface reactions leading to CL degradation. Electron beam heating was calculated using a simple heat transfer model and was significant for powder samples. This is consistent with morphological erosion observed on the surface of the ZnS particles degraded at elevated temperatures or high power densities. It is speculated that at temperatures of about 300°C, surface chemical reactions in combination with heating leads to removal of S and evaporation of Zn. Work supported by DARPA Grant MDA 972-93-1-0030 through PTCOE.

4:40pm **EL+SC-TuA9 Analysis of Ion Implantation Damage in Silicon Wafers by a Contactless Microwave Diagnostic**, ***R.K. Ahrenkiel***, National Renewable Energy Laboratory, *B. Lojek*, Atmel Corporation

Rapid thermal annealing (RTA) of ion implantation damage is required to maintain the integrity of submicron integrated circuit devices. A quick, efficient, and contactless diagnostic of the implantation damage is highly desirable. The residual radiation damage drastically reduces the recombination lifetime in the implanted region. Here, we will demonstrate the use of resonance-coupled photoconductive decay (RCPCD) technique allows us to to probe this region in boron and arsenic-implanted silicon wafers. Using a tuneable optical excitation source, we excite electron-hole pairs in the implanted region only. We compare these recombination times with those of the non-implanted bulk of the crystal. The lifetime is independent of excitation wavelength for the as-grown, oxidized wafers with typical values larger than 50 ms in semiconductor-grade silicon. After ion implantation with either arsenic or boron, the near-surface (711 nm) lifetime drops more than two orders of magnitude because of recombination at implantation-produced defects. After an RTA process, the lifetimes increase and again approach the bulk lifetime. One first group of wafers was processed in a standard rapid thermal processing (RTP) system SHS 2000 with a Hotliner. A second set of wafers were exposed to constant wavelength irradiation with maximum photon energy of approximately 1.4 eV for about 5 seconds, which has been called a "spike anneal". Our studies showed that the latter process produces wafers of lower recombination center density that the standard process. We propose some possible models to explain the improved properties of the "spike-annealed" wafers.

5:00pm **EL+SC-TuA10 Gas-phase Nanoparticle Formation during AlGaN MOCVD**, ***J.R. Creighton***, *W.G. Breiland, M.E. Coltrin*, Sandia National Laboratories

The AlGaN MOCVD process is often plagued by parasitic chemical reactions that diminish the group-III deposition efficiency and make it difficult to control alloy composition. We have explored many possible mechanisms for the parasitic reactions using a variety of experimental techniques and complex reactive flow simulations. Results indicate that the 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^{8-9} cm^{-3}. At these densities a significant fraction (20% or more) of the input Al is converted into nanoparticles. Analysis of the polarization dependence of the scattering from GaN nanoparticles indicates that they are non-spherical. This makes determination of their size and density more difficult, but they are in the range observed for AlN nanoparticles. For GaN and AlN nanoparticles the balance of thermophoretic and viscous forces results in a sharp height distribution centered at ~6 mm above the surface, which is in good agreement with the theoretical prediction.[1]

[1] 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.

Molecular and Bio-Magnetism
Room: C-205 - Session MB+BI+OF-TuA

Molecular and Bio-Magnetism
Moderator: M. Grunze, Heidelberg Universität, Germany

2:00pm **MB+BI+OF-TuA1 Single-Molecule Magnets: A Molecular Approach to Nanoscale Magnetic Materials**, ***G. Christou***, *M. Soler, N. Aliaga-Alcalde, S. Bhaduri*, University of Florida, *W. Wernsdorfer*, Laboratoire Louis Neel - CNRS, France, *D.N. Hendrickson*, University of California at San Diego **INVITED**

Single-molecule magnets (SMMs) are molecules that function as single-domain magnetic particles which, below their blocking temperature, exhibit the classical macroscale property of a magnet, namely magnetization hysteresis.[1] SMMs owe their properties to a combination of a large ground state spin value and easy-axis-type anisotropy, which give a significant barrier to magnetization relaxation. SMMs thus represent a molecular (or bottom up) approach to new nanoscale magnetic materials, offering all the advantages of molecular chemistry (room temperature synthesis, purity, solubility in many solvents, a well defined periphery of organic groups, a crystalline ensemble of monodisperse units) as well as displaying the superparamagnetism of a mesoscale magnetic particle. They also display quantum tunneling of magnetization (QTM), emphasizing that they straddle the interface between the classical and quantum regimes. SMMs have many potential applications, but these require that their properties be both understood and controlled, particularly QTM. The Mn12 SMMs are the best understood. Various derivatives have been prepared differing in the organic groups, and it has been discovered that the magnetic properties (including QTM) can be significantly altered. This is also possible by adding additional electrons, and both the [Mn12]- (S = 19/2) and [Mn12]2- (S = 10) versions have been prepared. Mn4 SMMs with S = 9/2 have also been extensively studied. In some cases, two Mn4 SMMs occur as supramolecular dimers, [Mn4]2, and exchange interactions between them lead to interesting modifications of their QTM properties, establishing the feasibility of tuning the QTM in SMMs.[2]

[1] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, MRS Bulletin 25, 66 (2000).

[2] W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, and G. Christou, Nature 416, 406 (2002).

2:40pm **MB+BI+OF-TuA3 Density-Functional-Based Simulation of Molecular Magnets**, ***M.R. Pederson***, *N. Bernstein*, Naval Research Laboratory, *T. Baruah*, Georgetown University, *J. Kortus*, Max-Planck-Institute, Germany **INVITED**

Recently a class of transition-metal containing molecules have attracted significant experimental interest because they retain their magnetic orientation at relatively high temperatures and because they exhibit quantum tunneling of magnetism. These molecular magnets consist of approximately 70-200 atoms and are typically composed of 4-15 transition metal atoms which are held in place by organic ligands and anions. The fundamental figure of merit which governs these phenomena is the magnetic anisotropy which arises due to the spin-orbit interaction and other couplings between spin and spatial degrees of freedom. Recently, a quantum-mechanical method has been developed which allows for the density-functional-based determination of magnetic anisotropies in molecules and clusters.[1] We have used this method to calculate anisotropies in several molecular magnets which include: $Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4$, $Fe_8O_2(OH)_{12}(C_6N_3H_{15})_6$, $Co_4C_5NH_4CH_2O)_4(CH_3OH)_4Cl_4$, and $[Mn_{10}O_4(2,2'\text{-biphenoxide})_4Br_{12}]^{4-}$. Our calculations show that good agreement between experiment and theory can be obtained. While the reorientation barriers and magnetic resonant tunneling fields are primarily determined from the second-order anisotropy hamiltonian,[1] higher-order effects can change these quantities by about ten percent. Further, such effects determine tunnel splittings and play a significant role in tunneling dynamics. Currently the primary source of such splittings is an active area of investigation. We have recently suggested that vibrationally induced changes in the spin-orbit interaction will contribute to higher-order anisotropies.[2] Further, computational results on the 4th-order magnetic anisotropy show that this interaction may provide a dominant contribution to the higher-order barriers and that it partially contributes to tunnel splittings. We discuss these calculations and compare our results to the experimental infrared work of Sushkov et al which shows that certain vibrational intensities are strongly perturbed by applied magnetic fields in the Mn_{12}-Acetate system.[3] A very brief review of the computational method, NRLMOL, used in this work will be included in the talk.

[1] M.R. Pederson and S.N. Khanna, Phys. Rev. B 60, 9566 (1999).

[2] M.R. Pederson, N. Bernstein and J. Kortus, (Cond-mate/0201353).

[3] A.B. Sushkov, B. Jones, J.L. Musfeldt, et al, Phys. Rev B 65,(2002).

3:20pm **MB+BI+OF-TuA5 Measuring and Manipulating Single Molecules Inside Living Cells**, ***J.S. Kanger***, *A.H.B. de Vries, J. Greve*, University of Twente, The Netherlands, *B. Krenn, R. van Driel*, University of Amsterdam, The Netherlands **INVITED**

For manipulating single molecules, techniques like AFM or optical tweezers are typically used. However, the actual actuators of these systems are relatively large, and therefore we are not able to manipulate single molecules that are situated deep inside the cell (for example inside the nucleus), without causing massive damage to the cell itself. We describe a conceptual simple arrangement for manipulating ultra small magnetic beads inside living cells using magnetic forces. By using magnetic forces to manipulate the bead, and a low yield HeNe laser to measure its position, we are able to generate a relatively high force, without damaging the cell. The setup is designed to measure the movement of a bead with nanometer precision, and apply picoNewton forces on it. Experimental results combined with model calculations show that a force of 15 pN is feasible for a ferrite bead of 50 nm diameter. If a bead is attached to a functioning protein the movement of this protein in the cell can be monitored and manipulated. We plan to apply this technique to the study of chromatin structure function relations inside the living cell. The magnetic force on a bead is proportional to the magnetization of the bead, and the gradient of the magnetic field. To produce a magnetic field that gives a gradient that is controllable both in direction and strength we constructed a four pole configuration. The tips of these poles (5 µm width and height) are placed 20 µm from each other, which leaves enough space to place a cell, with a magnetic bead in the nucleus, between the poles. The magnetic field is guided from external coils to the poletip that becomes magnetically saturated (1.8 Tesla). The pole tips are produced in the cleanroom facilities of our university. Bead position detection is done by back focal plane interferomtery. A low-yield HeNe laser will is focused on the bead. The combination of the laserbeam and, and the forward scattered light gives a interference pattern on a quadrant detector, which is depended on the position of the bead in the focus.

4:00pm **MB+BI+OF-TuA7 Synthesis and Functionalization of Nanoparticles**, ***A. Ulman***, Polytechnic University **INVITED**

The talk will focus on metal and metal oxide nanoparticles. A one-phase synthesis of thiolate-functionalized metallic nanoparticles will be described, and further chemical reactions, such as surface-initiated polymerization and attachment of DNA bases will be presented. Sonochemical preparation of oxide and mixed oxide nanoparticles will be reported. We have demonstrated, for the first time, that sonication is a very efficient method for coating of γ-Fe_2O_3 and other oxide nanoparticles. The attachment of enzymes to γ-Fe_2O_3 nanoparticles will be described.

Manufacturing Science and Technology
Room: C-109 - Session MS+MM-TuA

Manufacturing Issues in MEMS and Related Microsystems
Moderator: E.G. Seebauer, University of Illinois

2:00pm **MS+MM-TuA1 Silicon Micromachines for Science and Technology**, ***D. Bishop***, Bell Laboratories, Lucent Technologies **INVITED**

The era of silicon micromechanics is upon us. In areas as diverse as telecommunications, automotive, aerospace, chemistry, entertainment and basic science the ability to build microscopic machines from silicon is having a revolutionary impact. In my talk I will discuss what micromachines are, how they are built and show examples of how they will have a revolutionary impact in many areas of science as well as technology.

2:40pm **MS+MM-TuA3 Silicon Nano-biotechnology**, ***G. Timp***, University of Illinois, Urbana **INVITED**

Silicon nanotechnology can now manufacture logic that incorporates more than 43 million Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) into a monolithic integrated circuit (IC). Some of these MOSFETs have a gate or control electrode that is only 130nm long with a gate oxide that insulates the control electrode from the current-carrying channel that is as thin as 1.7nm. Moreover, we have recently shown that further miniaturization is practical. We have produced nanometer-scale MOSFETs or nano-transistors with a gate electrode as shorter than 40nm and a gate oxide thinner 1nm. Inexorably, within the next ten years (according to the ITRS roadmap) the electronics industry is expected to integrate over a billion nanotransistors into a ~3-10cm2 area chip, packing about 5-10 nano-transistors/mm2. Integration on this scale, along with the facility for nanofabrication, will enabled new types of ICs. For example, we will show that it is now possible to fabricate ICs so small that they could inserted inside a living cell. Since the cell is the key to biology, such a chip combined with sensors could provide unprecedented access to it. We will also show how silicon nanofabrication technology can be used to produce sensors out of nanometer-scale pores (~2nm in diameter) in an ultra-thin glass membrane (~2nm thick), which function like ion channels in the membrane of a living cell. Such devices may ultimately be used in proteomics or for rapid sequencing of minute amounts of DNA to discover the genetic origin of a disease.

3:20pm **MS+MM-TuA5 Manufacturing Issues in MEMS and Related Microsystems**, ***B.P. Gogoi***, Motorola **INVITED**

MEMS(MicroElectroMechanical Systems) use IC(Integrated Circuit) manufacturing technology for the fabrication of sensors and actuators that utilize a wide variety of transduction principles to interact with the physical world. The three dimensional aspects of the sensor require some additional process technology that is not available in conventional IC technology. Also, since many of these sensors and actuators require the presence of intentional gaps in which mechanical motion is initiated, MEMS technology also require methods to form these intentional gaps. Using this enabling technology, a number of high volume sensors have been developed for the mainstream market in the automotive, consumer, industrial and medical segments. However, as the trend in IC manufacturing has progressed towards more shallower and planar technology, the trend in MEMS technology has moved towards high aspect ratio structures. The issues related to manufacturing of sensors and actuators using MEMS technology will be discussed. Some of the specific requirements of the process technology to enable well-controlled high volume manufacturing of sensors will be presented. In addition, examples of failure mechanisms that result from the interaction of design and the fabrication process will be discussed. The choices in the integration of these sensors and actuators with the system circuitry will also be presented.

4:00pm **MS+MM-TuA7 MEMS Technology Challenges for Volume Manufacturing**, ***V. Rao***, Intel Corporation **INVITED**

MEMS(Micro Electro Mechanical Systems) is a silicon technology for fabricating miniature mechanical devices made mostly of beams, membranes and channels. These mechanical devices are integrated with electronics to form Microsystems which find use in Communications and computing, Inertial sensing, environmental sensing and Biomedicine. MEMS devices are particularly attractive in the personal communications space because they can provide significant benefits such as energy efficiency and small footprint. However as these are high volume markets the technology must provide the required reliability and cost characteristics for these applications. In RF systems today many passive devices are discrete and off chip. MEMS technology provides a way to integrate the high value passive elements (such as switches, filters and high Q inductors) thereby reducing footprint and enhancing performance. Another example in the communication space is in the use of micromirrors for all optical switching. This is very compelling as light signals can be switched directly in the optical domain by moving mirrors avoiding the expensive Optical to Electrical to Optical conversion as is currently done. This paper will discuss some of the key manufacturing hurdles that must be overcome to realize the reliability and cost benefits that MEMS technology must meet. We will start by discussing key process modules that differentiate MEMS technology from traditional CMOS. We will then describe the stare of the art for these modules today and discuss the technological hurdles that must be addressed for future volume manufacturing.

4:40pm **MS+MM-TuA9 Manufacturing Issues of Automotive Sensors produced at Bosch**, ***M. Offenberg***, Robert Bosch GmbH, Germany **INVITED**

An ever increasing number of electronic systems in vehicles helps to increase the safety and comfort of the driver as well as to increase fuel efficiency and to reduce toxic emissions. Sensors are enabling components for the functionality of these electronic systems. Over the last decade microfabrication technologies have contributed to reduce the cost of these sensors - and thus overall system cost - while at the same time increasing their functionality and reliability. This paper describes selected micro sensors that have been successfully introduced to the market such as pressure sensors, mass flow sensors, acceleration and angular rate sensors. Manufacturing aspects and processes with and without monolithic integration are illustrated for a surface micro-machining process. The embedding of MEMS manufacturing in an existing 6-inch ASIC production environment to achieve an optimized low-cost process is described. Key process steps such as deposition of mechanical-grade thick poly-silicon layers, trench etching, sacrificial oxide etch and hermetic sealing are illustrated. Some of the key processes require dedicated equipment that was developed in collaboration with equipment manufacturer. High rate silicon deep silicon etcher in cluster tools ensure low cost of ownership. Process monitors for mechanical stress and stress gradient will be presented and manufacturing issues such as cross contamination and particle protections are discussed using inertial sensors as an example.

Nanometer Structures
Room: C-207 - Session NS+EL-TuA

Quantum Dots
Moderator: J. Nogami, Michigan State University

2:00pm **NS+EL-TuA1 Peter Mark Memorial Award Address: Mechanisms of Semiconductor Nanostructure Formation**, ***R.S. Goldman****, University of Michigan **INVITED**

Recently, semiconductor nanostructures have shown significant promise for a wide range of electronic, optoelectronic, and magnetic applications. In this

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***** Peter Mark Memorial Award Winner

talk, I will discuss the formation mechanisms of a variety of semiconductor nanostructures, including phase separation-induced alloy nanostructures and strain-induced self-assembled quantum dots. I will show how we have used data from cross-sectional scanning tunneling microscopy, in conjunction with x-ray reciprocal space maps, to develop new models for self-ordering of InAs/GaAs quantum dot superlattices[1] and spontaneous lateral phase separation in InAlAs alloys.[2] I will also describe our recent investigations of the role of elastic anisotropy in semiconductor nanopatterning, towards the formation of three-dimensional quantum dot crystals. These mechanisms are likely to be applicable to a wide range of heteroepitaxial semiconductor nanostructures.

This work was supported in part by the National Science Foundation (CAREER Award and Nanoscale Exploratory Research Program) and the Army Research Office (MURI Program)

[1] B. Lita, R.S. Goldman, et al, Appl. Phys. Lett. 75, 2797 (1999); Surface Review and Letters 7, 539 (2000).

[2] B. Shin, A. Lin, K. Lappo, R.S. Goldman, et al Appl. Phys. Lett . 80, 3292 (2002).

2:40pm **NS+EL-TuA3 Strain Effects and Inter-Dot Coupling in Self-Assembled Quantum Dot Arrays**, ***H.T. Johnson***, *R. Bose*, University of Illinois at Urbana-Champaign, *B.B. Goldberg*, Boston University, *H.D. Robinson*, University of California at Los Angeles **INVITED**

A computational model is used to simulate optical properties of self-assembled InAlAs/AlGaAs quantum dot arrays. Array sections containing up to 30 dots of varying size, shape, and spacing are considered. Comparisons are made to experimental results for arrays characterized using near-field scanning optical microscopy (NSOM). The experimental and computational studies both measure emission/absorption spectra with energy resolution that shows the effects of individual dots in the array. In the computational approach, the optical properties are computed from the spectrum of electron and hole states found for the ensemble. The energies and wave functions in the spectrum are first computed using a strain-modified k-p Hamiltonian approach; the spectrum includes confined electron and hole states associated with individual dots in addition to some delocalized states associated with coupled dots as well as the wetting layer. By modeling the entire ensemble of dots simultaneously, it is possible to consider effects related to long range field interactions between dots, such as linear elastic fields and extended quantum mechanical states. Two key results are of interest. First, it is found that even minor contact between the optical fiber tip and the sample surface leads to indentation strain large enough to substantially shift emission wavelengths of individual dots in the array. Second, extended states in groups of neighboring quantum dots lead to sharp, well-defined resonances in the emission spectra for the arrays. Results of the simulations clearly show these effects that are also observed in the experimental data.

3:20pm **NS+EL-TuA5 Growth of Ge Quantum Dots on Si(100) Without a Wetting Layer [1]**, *K. Yoo*, Oak Ridge National Laboratory, *F. Flack*, University of Wisconsin - Madison, *H.H. Weitering*, Oak Ridge National Laboratory, *M.G. Lagally*, University of Wisconsin - Madison, *Z. Zhang*, ***J.F. Wendelken***, Oak Ridge National Laboratory

When Ge atoms are deposited directly onto a Si(100) substrate, the growth follows the Stranski-Krastanov growth mode in which three-dimensional Ge islands, or quantum dots (QDs), are formed on top of three monolayer thick wetting layers. For many optical and electronic device applications, Ge QDs without the wetting layer may be highly preferred. Using a buffer-layer assisted growth approach,[2] we have achieved the formation of Ge QDs on Si(l00) without a wetting layer. These QDs are shown to possess a narrow size distribution and are also substantially smaller than the QD hut clusters that are formed with the normal SK growth mode. Using the buffer layer approach, Ge QDs have been grown in a single layer and in multiple layers with silicon spacer layers as has been done with multilayers of conventionally grown Ge hut clusters. Due to the fact that growth in the buffer layer approach is well isolated from any stress effects associated with a preceding layer of QDs, it is not expected that the QDs in separate layers will exhibit any layer to layer alignment effects as observed for SK growth. However, the smaller size of the QDs obtained with the buffer layer approach may be expected to exhibit stronger quantum size effects. Initial tests with samples prepared by this approach show a strong photoluminescence signals in the IR that exhibit striking differences from PL results[3] obtained from Ge QDs grown by conventional means with a wetting layer.

[1] Work supported in part by the U. S. DOE at Oak Ridge National Laboratory, managed by UT-Battelle, LLC under Contract DE-AC05-00OR22725, and in part by the NSF at the University of Wisconsin through the MRSEC program.

[2] J. H. Weaver and G.D. Waddill, Science 251, 1444 (1991).

[3] M.W. Dashiell, U. Denker, and O.G. Schmidt, Appl. Phys. Lett. 79, 2262 (2001).

3:40pm **NS+EL-TuA6 Spontaneous Generation of Free-Standing Ge Quantum Dots on Silicon-on-Insulator**, ***E.A. Sutter***, *P.W. Sutter*, *P. Zahl*, Colorado School of Mines

The growth of heteroepitaxial materials on engineered composite substrates such as silicon-on-insulator (SOI) opens a new route for controlling the structural and electronic properties of materials at the nanoscale. Local lattice strain induced by Ge quantum dots grown coherently on SOI - a composite of an ultrathin monocrystalline Si template supported by amorphous SiO_2 on a conventional Si wafer, causes significant local distortion in the Si template and can be used as a tool for nanoscale band structure engineering of the Si substrate. The Ge islands themselves form on SOI initially as huts and then transform into domes, similar to the sequence of epitaxially constrained shapes they assume on bulk Si (100). While the shape sequence of epitaxial Ge islands on bulk Si ends here, we observe further dramatic morphological changes on ultrathin SOI: a spontaneous transformation to free-standing Ge islands accompanied by a breakup of the thin Si slab. We use a combination of atomic force microscopy (AFM) and transmission electron microscopy (TEM) to document the sequence of shape transformations of Ge islands on SOI. We investigate in detail the island shape evolution and redistribution of the substrate material between the islands both before and after the breakup of the ultrathin Si slab of the SOI substrate.

4:00pm **NS+EL-TuA7 Production and Structure of Gas-phase Prepared Germanium Nanocrystals**, ***C. Bostedt***, *T. van Buuren*, *T.M. Willey*, *J. Plitzko*, Lawrence Livermore National Laboratory, *T. Moller*, Hasylab at DESY, Germany, *L.J. Terminello*, Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials, which exhibits promising novel properties. Germanium nanoparticles are particularly interesting, as the cubic as well as the tetragonal crystal phases have been reported for particle sizes below 5 nm, depending on the production method. We have developed a gas-aggregation based production method for germanium nanoclusters, with which nanocrystals in the bulk-like cubic phase from 1 to 10 nm in size can be produced. The clusters are condensed out of supersaturated Germanium-vapor, which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. The particle sizes and phases have been well characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD) and atomic force microscopy (AFM). The crystal phase - production method relationship is discussed. Only little is know about the surface structure of nanocrystals. Information about the surface structure is difficult to obtain. No distinct particle boundaries can be imaged with TEM. Photoemission spectroscopy (PES) has been shown to be a powerful tool to investigate bulk-crystal semiconductor surfaces. PES experiments have been performed on Ge nanocrystal films and a disordered surface shell around a crystalline core is deduced for the nanoparticles. .

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contractW-7405-ENG-48, LLNL.

4:20pm **NS+EL-TuA8 Surface Passivation Effects of Deposited Ge-Nanocrystal Films Probed with Synchrotron Radiation**, *C. Bostedt*, ***T. van Buuren***, *T.M. Willey*, Lawrence Livermore National Laboratory, *T. Moller*, Hasylab at DESY, Germany, *L.J. Terminello*, Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation - often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surfaces can be subsequently passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. X-ray absorption spectroscopy (XAS) and photoemission (PES) were performed on thin films of Germanium (Ge) clusters. Clean Ge nanocrystal films are found to exhibit much stronger quantum confinement effects at the band edges than similar Si particle films. These findings are compared to recent electronic structure calculations. For passivated nanocluster films we find that the passivating agent strongly alters the electronic structure of the clusters. In general the absorption edge shifts to significantly higher energies compared to cluster films without surface passivation. These results will be discussed in terms of a reduction of the cluster-cluster interactions.

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:40pm **NS+EL-TuA9 Growth and Properties of Si Compatible Nanostructures: Si Quantum Dots Grown on CaF_2/Si Films**, ***A. Klust***, *A.A. Bostwick, T. Ohta, Q. Yu, M.A. Olmstead*, University of Washington

Si/CaF_2 is a promising candidate for epitaxial semiconductor/insulator heterostructures for optoelectronic applications because of the low lattice mismatch (0.5%) and large band gap difference (12.4 eV for CaF_2 vs. 1.1 eV for Si). In addition, the strongly dissimilar ionic/covalent bonding character in the system CaF_2/Si allows it to serves as a model system both to study heteroepitaxy of two dissimilar materials and to study the influence of bonding character and electronic structure on scanning probe microscopy. Here, we present an investigation of ultra-thin (1-3 molecular layers) CaF_2 films and Si quantum dots grown on these films using both non-contact atomic force microscopy (ncAFM) and scanning tunneling microscopy (STM). On the one hand, the extremely large band-gap of CaF_2 makes STM measurements difficult; stable imaging is not possible for films thicker than 3-4 molecular layers. On the other hand, STM gives complementary information to that obtained with ncAFM. For instance, scanning tunneling spectroscopy is used to characterize the electronic properties of single Si QD. Furthermore, the contrast during STM imaging of the CaF_2 films depends strongly on the polarity of the bias voltage and the film thickness. Non-contact AFM is used to clarify this behavior to separate electronic and topographic contributions to the STM images. Atomically-resolved ncAFM images of the CaF/Si interface layer will be shown and compared with similar published data obtained from bulk CaF_2(111) crystals.[1] The atomic structure of the CaF/Si interface layer is practically identical to the surface structure of bulk CaF_2(111), while the electronic structure differs. We discuss the influence of the different electronic structure on atomic resolution ncAFM.

[1] A. S. Foster, C. Barth, A. L. Shluger, and M. Reichling, Phys. Rev. Lett. 86 (2001) 2373.

5:00pm **NS+EL-TuA10 Formation of Self-Assembled Copper-Oxide Nano-Dots on SrTiO3(100)**, ***I. Lyubinetsky***, Pacific Northwest National Laboratory

In addition to offering a wide range electrical, optical and magnetic properties, oxide nanostructures can be stable in a range of environments without needing to add protective layers. In this work, we have observed the formation of self-assembled oxidized-copper nanodots on the SrTiO3(100) substrate using oxygen plasma assisted molecular beam epitaxy. The composition and structure were examined by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, x-ray diffraction, and scanning probe microscopy in a wide range of growth parameters (temperature, oxygen pressure, and Cu flux). Under different growth conditions different shapes and/or composition have been found: truncated dots, square pyramids, and multifaceted domes with composition to be Cu2O or containing Cu metal also. Since nanostructure composition changes with temperature, observation made by interrupting growth and cooling may not be adequate. Thus, in addition to scanning probe measurements in ambient conditions, XPS spectra have been acquired at elevated temperatures in step-by-step mode at different stages of nanodots formation. Observed correlations between structural and composition changes will be discussed. Understanding of the evolution of the dot shape, size and composition would allow us to optimize formation conditions to synthesize cooper oxide nanodots with desirable parameters.[1]

[1] This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the Office of Biological and Environmental Research, U. S. Department of Energy.

Nanotubes: Science and Applications Topical Conference Room: C-209 - Session NT-TuA

Nanotubes: Mechanical Properties, NEMS

Moderator: L. Dai, College of Polymer Science and Polymer Engineering

2:00pm **NT-TuA1 Mechanics and Electrostatics of Nanotubes**, ***D.W. Brenner***, *D. Areshkin, J.D. Schall, O.A. Shenderova*, North Carolina State University **INVITED**

This talk will focus on modeling studies that have the aim of optimizing nanotube functionality in a number of applications, including nanocomposites and nanoelectromechanical (NEM) devices. The primary computational tools are a many-body bond-order potential energy function and a self-consistent hybrid density functional/tight binding scheme. The former is used for modeling structural and mechanical properties, including elastic properties of functionalized nanotubes. The latter method, which allows applied fields to be incorporated into a tight-binding Hamiltonian, is used to evaluate nanotube electrostatics and nonequilibrium electron transport. Topics to be discussed include the contribution of electrostatic interactions and nanotube polarizability to mechanical load transfer in nanotube-polymer composites, and alignment, kink formation and non-equilibrium transport in NEM devices.

[1] Funded by the Office of Naval Research and by NASA.

2:40pm **NT-TuA3 Carbon Nanotube/ Polymer Composite: Mechanical and Electrical Properties**, ***H.Z. Geng***, University of North Carolina at Chapel Hill, *B. Zheng*, Duke University, *H. Shimoda*, University of North Carolina at Chapel Hill, *J.L. Liu*, Duke University, *O. Zhou*, University of North Carolina at Chapel Hill

Carbon Nanotubes with elastic modulus ~1Tpa, and fracture strain ~5~10%, is interesting as filler for mechanical enhancement. Due to the poor dispersion and poor interfacial bonding between nanotube and polymer matrix, expected enhancement in mechanical properties by adding nanotube to polymer has by and large not been demonstrated. In this talk we present our results by using fluorinated nanotubes (F-SWNT). Differential scanning calorimetry (DSC) results show that our composite is macroscopically uniform. Tensile stress-strain curve and dynamic mechanical analysis (DMA) results show a significant enhancement of mechanical properties by adding only a few percentage of F-SWNTs. Carbon black particle and carbon fiber filled polymer composites attract a lot of interest due to their Positive Temperature Coefficient (PTC) effect at percolation and therefore their potential application as temperature or current sensors. With large aspect ratio Carbon Nanotubes may offer some advantages over carbon black and carbon fiber, because percolation threshold is believed to be inverse of aspect ratio. In this talk we present our recent results on the dependence of percolation threshold on average length of nanotubes in CNT/polymer composites. Temperature effects on conductivities of composites at their percolations will also be presented.

3:00pm **NT-TuA4 Self-Aligned Mechanical Attachment of Carbon Nanotubes to Surfaces**, ***K. Bylund***, *J.D. Whittaker, D. Kitchen, M. Housley, R.C. Davis*, Brigham Young University

We have investigated self-aligned transition metal silicides and other thin film deposition based processes for the mechanical attachment of carbon nanotubes to silicon surfaces. These processes could aid in the mass production of carbon nanotube based AFM probes and NEMS devices. In each process, thin films are deposited and processed to secure nanotubes to silcon surfaces. An investigation of the efficacy of these processes has motivated fundamental research on the interaction of carbon nanotubes with transition metals and their silicides at varying temperatures. We will present the effects of the metal deposition, silicide formation, and wet chemical etching on the films and the nanotubes as observed by scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS).

3:20pm **NT-TuA5 Self-assembly of Carbon Nanotubes**, ***S.J. Oh***, *H. Shimoda, H.Z. Geng, R.J. Walker, L.E. McNeil, O. Zhou*, University of North Carolina, Chapel Hill

Self-assembly is an efficient process employed by nature to fabricate higher-level architectures of micro- and nano- objects with controlled functionality. Here we report that pre-formed individual CNTs can self assemble into macroscopically ordered films and membranes. Electron microscopy and polarized Raman spectroscopy measurements indicate orientational ordering of the CNTs in these self-assembled structures, which exhibit optical and electrical anisotropy. By controlling the functionality of the substrates, patterned CNT structures were obtained. Self-assembly of the CNTs is explained in terms of heterogeneous nucleation from a locally super-saturated suspension.

3:40pm **NT-TuA6 Fullerene Coalescence as a Junction Engineering for Nanoelectronics**, ***B.I. Yakobson***, Rice University

Relaxation and failure[1] of C or BN[2] nanotubes can be reversed in a well-defined sequence of atomic rearrangements. This process corresponds to cap-to-cap coalescence or welding of two nanotubes. Precise mechanism is revealed by topological analysis[3] and consists exclusively of number of Stone-Wales bond rotations, following the primary jump-to-contact polymerization with covalent bonding. This mechanism explains several "natural" phenomena like diameter doubling of nanotubes, coalescence of C_{60} in peapods, etc. It also generates a series of stable intermediate neck-shaped hetero-junctions with potentially useful electronic properties due to electrostatic dipoles,[4] density of states and conductance all varying along the series of emerging structures.

[1] B. I. Yakobson, Ph. Avouris, Topics Appl. Phys. 80, 287-329 (2001); Ge. G. Samsonidze, Gu. G. Samsonidze, B. I. Yakobson, Phys. Rev. Lett, 88, 065501 (2002).

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[3] Y. Zhao, B. I. Yakobson, R. E. Smalley, Phys. Rev. Lett., 88, 185501 (2002).

[4] T. Dumitrica, C. Landis, B. I. Yakobson, Chem. Phys. Lett. (submitted).

4:00pm **NT-TuA7 Synthesis and Properties of Plasma-polymerized Polypyrrole / Au Nanotube Composite Structures**, ***J. Zhou***, *E.R. Fisher*, Colorado State University

Composite nanostructures have a wide variety of potential applications in microelectronics, chemical sensors, and electrochemical energy production. Here, we report the synthesis of composite plasma-polymerized polypyrrole (PPPy)/Au nanotubes. The characteristics of both the PPPy films and the nanostructured composites have been investigated using FTIR, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and SEM. The gas phase species in the plasma have been investigated with mass spectrometry. The properties of PPPy films mostly depend on the applied plasma parameters, with both ring-opening reactions and the polymerization of pyrrole taking place simultaneously in the plasma. Decreasing the applied plasma power favors the retention of the rings of the pyrrole monomer. Mass spectra suggest that the plasma polymerization of pyrrole takes place on the substrate surface due to the diffusion of radicals produced in the plasma. In addition, thermal treatment after polymerization has been shown to enhance the conductivity of PPPy films. Thermally treated PPPy films can be partially oxidized or reduced electrochemically due to the exchange between cations and anions of PPPy films. From SEM analysis, it is apparent that reconstruction of PPPy films occurs after thermal treatment. However, non-thermally treated PPPy films coated on Au nanotubes demonstrate well-defined redox reversible peaks as results of the increasing of the interface areas between the surface of the PPPy films and electrolyte solution. The implications of these results for potential devices will also be presented.

Organic Films and Devices
Room: C-102 - Session OF+SS+EL+SC-TuA

Organic Molecular Films
Moderator: H. Fairbrother, Johns Hopkins University

2:00pm **OF+SS+EL+SC-TuA1 Reactivity of Polymers Containing Nitrogen and Oxygen Functional Groups with Vapor Phase Metal Atoms**, ***A.J. Wagner***, *G. Wolfe, D.H. Fairbrother*, The Johns Hopkins University

The surface reactions during the initial stages of polymer metallization are crucial in determining bonding and adhesive characteristics with native and plasma treated polymers. In this study, we have compared the reactivity of different nitrogen and oxygen containing functional groups with a variety of vapor phase metal atoms during the initial stages of metallization. The reactivity of different nitrogen containing functional groups during the vapor deposition of Ti, Fe, Ni, Cu and Au on Nylon 6, containing an amide group (-NH-(C=O)-and nitrogen implanted Poly(ethylene) (N-PE) containing a mixture of C-N, C=N and CN groups was studied. In addition, the reactivity of vapor phase metal atoms with specific functional groups was also investigated using a nitrile (CN) terminated self-assembled monolayer (CN-SAM). For each of the metals studied except Au reaction with Nylon 6 and N-PE resulted in the formation of the metal-nitride (MN), although the extent of reaction increased in the order Ti > Fe > Ni ~ Cu, scaling with the M-N bond strength. Experimental evidence, however, indicated that the different nitrogen containing functional groups present in the nitrogen-modified PE were not equally reactive. Ti and Fe also reacted with the C=O functional group in Nylon 6 to form their respective oxides while Cu, Ni and Au were unreactive with the C=O functional group. Metal nitride formation was also observed during evaporation of Ti and Fe on the CN-SAM although Cu and Au were unreactive towards the CN functional group. In contrast, metal carbide production was only evidenced during reactions with Ti. Results from this investigation will be interpreted in terms of the relative bond strengths associated with specific functional groups within the polymer and potential product species (e.g. metal oxide, nitrides).

2:20pm **OF+SS+EL+SC-TuA2 A New Crystalline Form of Pentacene: pi-stacked Thin Films Grown on Au(111)**, ***J. Kang***, *X.-Y. Zhu*, University of Minnesota

The recent demonstration of pentacene and related molecules in high-mobility field effect transistors (FETs), including superconducting FETs, has attracted great interest in this class of organic semiconductors. Carrier mobility is known to depend intimately on crystalline quality. In order to establish a molecular level understanding of structure-property relationship, we have carried out a scanning tunneling microscopy (STM) and spectroscopy (STS) study of the growth of crystalline pentacene thin films on Au (111). The use of high bias voltage (~ 5 V) and low tunneling current (~ 1pA) has enabled us to image, with molecular resolution, the growth of a new crystalline phase of pentacene well beyond the first a few layers. High resolution imaging shows that pentacene molecules form a pi-stacked crystalline phase with their long-axis parallel to the surface. This is attributed to the strong molecule-surface interaction, which seeds the growth of this new crystalline phase.

2:40pm **OF+SS+EL+SC-TuA3 Vapor Deposition and Polymerization of Low-k Polycyanurate Films**, ***J.N. Russell, Jr.***, *V.J. Bellitto, B. Bartlett, MJ Brooks, P.G. Santangelo, A.W. Snow*, Naval Research Laboratory **INVITED**

Future microelectronics will require advanced materials and processes for smaller, faster and more robust devices. Polymers address these needs and range from ultra-low permittivity materials to molecular semiconductors. Developing and understanding solventless deposition processes such as vapor deposition polymerization is important for producing conformal, voidless polymer films. One class of low-k polymers, polycyanurates, shows promise as a vapor depositable material. Yet little is known about the surface chemistry of the cyanate functionality and the conditions required for surface polymerization. Initially the surface chemistry of key functionalities in the monomer and polymer are examined using model compounds such as phenyl cyanate and triazine on Al(111). Aluminum was chosen because it is used for interconnects in microelectronics. Then, the in situ vacuum deposition and polymerization chemistry of NCO-CH2(CF2)6 CH2-OCN (F6Cy) is studied on Al, Cu, and Si surfaces. The vapor deposited F6Cy monomer film undergoes a photo-induced cyclotrimerization process to form cross-linked cyanurate networks with a permittivity of 2.1 at 1 GHz.

3:20pm **OF+SS+EL+SC-TuA5 Formation of Chemically Patterned Surfaces using Gas-Phase Oxalyl Chloride**, ***M.C. Asplund***, *G. Husseini, M.R. Linford, E.T. Sevy*, Brigham Young University

Optical lithography is a common technique for the formation of electronic devices on semiconductor substrates. Here we show an analogous technique that allows the introduction of a reactive functional group (-COCl) onto an alkylated Si substrate, or onto any substrate that contains C-H groups. The importance of the -COCl group stems from its high reactivity with amino and hydroxyl groups. Our new method consists of exposing a C-H containing surface to a gaseous mixture of N2 and oxalyl chloride ($(COCl)_2$) and then illuminating with 355 nm light. The UV photons form free radicals from the oxalyl chloride that then react with the C-H containing surface. We have shown using wetting, XPS, elipsometry and FT-IR spectroscopies that we have been able to form acid chloride functional groups on surfaces. By using simple optical masks we have shown that this functionalization occurs only where the sample is exposed to light. The key step to understanding the reaction mechanism for the surface reaction is understanding the formation and subsequent reaction of the radicals formed from the oxalyl chloride. Previous liquid phase reaction studies of oxalyl chloride with adamantane led to the suggestion that at 266 Cl is the primary radical formed, while at 355 nm the primary radical is the COCl radical. We have looked at the formation of radicals as a function of wavelength to analyze dissociation mechanism, and product energy distributions as well as the effect of pressure on radical formation. The minimum feature size which can be made using this method is given by the diffusion length of the radical. Thus the quenching must be understood and optimized to have controlled patterning of surfaces.

3:40pm **OF+SS+EL+SC-TuA6 Characterization of Ultrathin Organic Films via Near-edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, University of California Davis and Lawrence Livermore National Laboratory, *A.L. Vance, T. van Buuren, C. Bostedt, A.J. Nelson, L.J. Terminello*, Lawrence Livermore National Laboratory, *C.S. Fadley*, University of California Davis and Lawrence Berkeley National Laboratory

Self-assembled monolayers (SAMs) and other thiol compounds adsorbed on Au(111) surfaces have become increasingly important for achieving surface attachment and orientation of complex molecules. Surface-attached molecular species containing catenanes and rotaxanes promise to play a vital role in achieving molecular-scale electronics and other devices.[1] Only through a rigorous understanding of the structure and properties of such molecular monolayer species can a rational synthesis of these hybrid materials be realized. Orientation of chemical bonds and thus the orientation of molecules can be precisely determined with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Here, we present NEXAFS results on the configuration of surface-attached fundamental building-blocks of such systems, including a simple surface-attached rotaxane and its constituents. This rotaxane consists of a crown ether ring, threaded by a molecule bound to the gold at one end and providing an athracene stopper at the other.[2] Investigating films of the stopper molecule only vs. the complete rotaxane we confirm the presence of the crown ether in the complete molecule. We present the orientation of the anthracene stopper and crown ether ring with respect to the surface by deconvoluting their respective features in the NEXAFS.

Acknowledgements: This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; at the ALS under contract number DE-AC03-76SF00098 at LBNL; and at the SSRL under contract number DE-AC03-76SF00515 at SLAC.

[1] Collier et al., Science 289, 1172-5

[2] Kolchinski et al., Chem. Commun., 1998, 1437-8

4:00pm **OF+SS+EL+SC-TuA7 Interfaces with Evaporated Short Chain Polyaniline**, ***B. Xu****, *A.N. Caruso, M. Bai, Y. Ovchenkov, S. Ducharme, B. Doudin, P.A. Dowben*, University of Nebraska-Lincoln

The interface properties of evaporated short chain polyaniline (PANI) were investigated by X-ray photoemission spectroscopy (XPS), inverse photoemission spectroscopy (IPES), as well as angle integrated photoemission spectroscopy (UPS). With sodium doping, the valence bands, conduction bands as well as the characteristic core levels show consistent shifts to the higher binding energy. Sodium, as an electron donor, when added to the polyaniline system, results in increased electron populations in the polyaniline bands --- effectively filling the almost completely filled band. In the case of iodine doping, all the states shifted to lower binding energy. Iodine, as an electron acceptor, effectively depletes the electron population in the occupied bands polyaniline. There is no abrupt interface formed between sodium or iodine and polyaniline, as demonstrated by the angle-resolved XPS. By comparison, the interface between polyaniline and another polymer poly(vinylidene fluoride with trifluoroethylene) copolymer (PVDF-TrFE) is quite abrupt. A P-N diode was made by evaporating PANI (p type) on the top of PVDF-TrFE (n type). The results presented here should apply to the problems associated with improving heterojunction polymer devices.

4:20pm **OF+SS+EL+SC-TuA8 Controlled p-Doping of Organic Molecular Films**, ***W. Gao**, A. Kahn*, Princeton University

We investigate the controlled electrical p-doping of the hole-transport organic molecular material α-NPD with the strong electron acceptor tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) using ultraviolet and inverse photoelectron spectroscopies (UPS/IPES), and in-situ I-V measurements. We previously examined p-doping of ZnPc co-evaporated with F_4-TCNQ,[1] and found an excellent energy match between the ionization energy (IE) of ZnPc (5.28eV) and the electron affinity (EA) of F_4-TCNQ (5.24eV), demonstrating host HOMO-to-guest LUMO charge transfer. The ZnPc thickness dependence of I-V data further demonstrated a 7 orders of magnitude increase in hole current injected from Au due to tunneling through the doping-induced narrow depletion region at the metal/organic interface.[2] In the present study, we show that α-NPD (IE=5.52eV) is also efficiently doped with F_4-TCNQ. The hole injection current increases by almost 5 orders of magnitude when only the first 80Å of α-NPD away from the metal/organic interface is doped, and increases by another factor of 10 when the entire organic film is uniformly doped. However, the doping-induced movement of E_F toward the HOMO appears to be more restricted than in ZnPc. Having excluded extrinsic effects like surface photovoltage, we propose that the substantial (~0.2 eV) ionization-induced relaxation of molecular energy levels moves the "doped" α-NPD HOMO upwards, and thus pins E_F deeper into the gap than for ZnPc, which is a planar molecule with a negligible relaxation energy (< 0.05eV). This interpretation is further confirmed with UPS study of the host material growth on a film of the dopant molecules. We also show that molecular level alignment at organic/organic interfaces is controllable by doping-induced dipole. Work supported by the NSF (DMR-0097133).

[1] W. Gao and A. Kahn, Appl. Phys. Lett., 79, 4040 (2001)

[2] W. Gao and A. Kahn, Organic Electronics (in press).

4:40pm **OF+SS+EL+SC-TuA9 Processable Optically Transparent Thin Films of Conducting Polymers**, ***B.D. Martin**, N. Nikolov, R. Shashidhar*, Naval Research Laboratory

A major problem in the area of electronically conducting polymers is that attempts to enhance their electrical conductivity by adding ionic dopants are always accompanied by a decrease of optical transparency. In this study we show how molecular self-assembly of small carbohydrate molecules can decouple the optical transparency and electrical conductance of conducting polymer films. When a carbohydrate such as glycerol, which is essentially a non-ionic hydrogen bonding dopant, is added to a commercially available conducting polymer suspension (Baytron P), the carbohydrate forms an intercalated, hydrogen bonded sandwich between the ionic pairs of the conducting oligomer unit and its supporting polymer suprastructure. This results in a pronounced increase of the distance between the ion pairs, and hence, to decreased electrostatic interaction. As a consequence there is an enhanced mobility of the ions and hence an increased conductivity without an accompanying increase in optical absorption. This behavior, which is in striking contrast to the normally observed trends in conducting polymers doped with traditional ionic dopants, is very important to the development of plastic liquid crystal displays (LCDs) and organic light emitting diode (OLED) displays.

5:00pm **OF+SS+EL+SC-TuA10 Optical Properties of Ordered Ultrathin Films of PTCDA**, ***R. Nitsche**, H. Proehl, S. Mannsfeld, T. Dienel, T. Fritz*, TU Dresden, Germany

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 is 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, therefore displaying well defined physical properties. In our contribution we will discuss the special optical properties of ultrathin films of an archetypal organic material, namely PTCDA (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride). Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBE with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy) both ex situ and in situ has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which in turn match the results known for long from polycrystalline samples. The results are further compared to thin films grown on mica to discuss the influence of different substrates.

Plasma Science
Room: C-103 - Session PS1-TuA

Microdischarges
Moderator: M.L. Steen, IBM T. J. Watson Research Center

2:00pm **PS1-TuA1 Microhollow Cathode Discharges**[1], ***K.H. Schoenbach**, M. Moselhy, W. Shi, R. Bentley*, Old Dominion University **INVITED**

By reducing the dimensions of hollow cathodes into the hundred micrometer range, stable, direct current, high (atmospheric) pressure glow discharges in rare gases, rare gas-halogen mixtures and in air could be generated. The electron energy distribution in these microdischarges is non-maxwellian, with a pronounced high-energy tail. The high electron energy together with the high gas density, which favors three-body collisions, is the reason for an efficient excimer generation in rare gas and rare gas-halogen microplasmas. Excimer efficiencies of up to 8% have been measured for Ar, Xe, ArF, and XeCl with a radiant excimer emittance on the order of 1 W/cm^2. Pulsing Xe discharges with 20 ns electrical pulses has led to an increase in radiant excimer emittance to 15 W/cm^2, and a simultaneous increase in efficiency to more than 20%. Operating the discharges in an abnormal glow mode has allowed us to generate microdischarge arrays without individual ballast. Stable atmospheric pressure plasmas are not only obtained with microhollow cathodes but also in electrode geometries with planar cathode, and large diameter, ring-shaped anodes, separated by approximately 100 µm. Discharges in such geometries show for pressures on the order of 100 Torr self-organized regular plasma patterns. With increasing pressure the individual plasma structures merge into a homogeneous surface plasma with similar excimer emission characteristics as that obtained with microhollow cathode discharges. Applications of these plasmas are excimer lamps, potentially micro-excimer lasers, and electron emitters.

[1] This work is supported by the NSF under Grant # CTS-0078618 and INT-0001438.

2:40pm **PS1-TuA3 Hollow Cathode Sustained Atmospheric Plasma Microjets**, ***R.M. Sankaran**, K.P. Giapis*, California Institute of Technology

Microhollow cathode discharges (MHCDs) or microdischarges have gained recent attention for their high-pressure operation and intense UV radiation. They are normally formed between two metal foils, a cathode with a pin-hole (diameter~100 µm) and an anode of arbitrary shape. To more easily incorporate these discharges in materials processing, we have recently

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* Morton S. Traum Award Finalist

extended their operation to a tube geometry where gas flow can be directly coupled to the electrodes. Discharges are formed in the tube hole similar to a static case, but the flow carries the plasma outside the tube to form a microjet. In this talk, we will present features of this novel source and discuss possible applications in thin film growth and effluent gas treatment. Plasma microjets are ignited in direct current mode using a stainless steel capillary tube with a 178 µm diameter hole as the cathode and a metal grid or plate as the anode. Optical characterization has confirmed that it is necessary to shrink the hole size to below 200 µm in diameter to operate inert gases at atmospheric pressure in the hollow cathode mode. Argon microjets can be operated in ambient air at 760 Torr with voltages as low as 260 V for cathode-anode gaps of 0.5 mm. Increasing the gap and extending the plasma microjet results in an increase in the plasma voltage. The current-voltage characteristics of the plasma microjet are also influenced by the gas flow rate. For a given interelectrode distance and plasma current, increasing the flow rate reduces the plasma voltage by as much as 200 V. These effects suggest that the diffusion of air into the argon plasma stream is important. Plasma microjets offer a simple tool to perform rapid materials optimization by operating arrays of discharges. As a proof-of-concept, we have demonstrated that CH_4/H_2 plasma microjets can be used to grow diamond with fine control of the film properties by changing the gas composition.

3:00pm **PS1-TuA4 Microhollow Cathode Discharge Microreactor Chemistry**, ***D.D. Hsu***, *D.B. Graves*, University of California, Berkeley

The peak neutral temperature of a microhollow cathode discharge (MHCD) has been found from optical emission spectroscopy to be on the order of 2000 K, although adjacent temperatures rapidly drop off to near room temperature. These thermal properties suggest that MHCDs are suited to promote endothermic chemical reactions. Thin-film resistive heaters often are employed to heat reactants in microreactors. Unlike resistive heaters, the electrical power of the microdischarge heats the gas directly, offering the possibility of higher peak temperatures and greater energy efficiency. Ammonia decomposition is a highly endothermic reaction, and such a reaction could be used as a source of hydrogen for a microfuel cell. Pure ammonia was flowed through a 200 µm diameter microhollow cathode at flowrates up to 64 sccm and pressures up to atmospheric pressure. Ammonia conversion was measured by FTIR, and production of hydrogen and nitrogen was monitored by a mass spectrometer. A discharge at 490 V and 9 mA converted 16 percent of ammonia flowing at a rate of 2.5 sccm at 100 Torr. Conversion was largely dependent on the residence time of the gas in the plasma. Based on published kinetic data, the conversion and residence time data are consistent with thermal decomposition at temperatures near 3000 K. We discuss the behavior of these microplasmas as reactors for ammonia and other chemistries, and we explore methods for increasing reaction conversion.

3:20pm **PS1-TuA5 One-dimensional Simulation of Glow-like Plasma Phenomena in Parallel-plate Microdischarge Geometries**, *X. Yuan*, ***P. Kothnur***, *L. Raja*, University of Texas at Austin

Recently, 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. While some estimates of properties of microdischarge plasmas are available, a detailed understanding of the plasma dynamics and chemistry is completely lacking. This talk presents results from a self-consistent, one-dimensional computational study of the glow-like phenomena in microdischarges. A dc microdischarge in a parallel-plate geometry with gap distances of the order of 10's-100's of microns is modeled. Results for a noble gas (helium) microdischarge indicates the formation of a relatively large cathode sheath that occupies a significant fraction (~ 50 %) of the micron-sized geometry with the remaining region being the bulk plasma. The electron temperatures attain significantly high peak values (~ 50 eV) in the cathode sheath with relatively low (~ 1 eV) temperatures in the bulk plasma. Gas temperatures of ~ 1000 K and electron densities in excess of 1e14 /cm^3 are predicted. The results indicate that microdischarge plasmas are quite unique with properties that are somewhat intermediate between classical glow-discharges and thermal arc discharges.

3:40pm **PS1-TuA6 Characteristics of Miniature Microwave Excited Plasma Discharges**, ***T.A. Grotjohn***, *D. Story, S. Zuo, J.J. Narendra, A. Wijaya, 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 10 mm and for a wide range of discharge aspect ratios. The discharge characteristics investigated included microwave power density, plasma density, electron temperature and gas temperature. The outcome of this investigation to be presented is an understanding and quantification of the microwave power density needed to operate small discharges of specific sizes, shapes, densities and gas compositions. Three microwave plasma sources are used to accomplish this investigation including (1) a highly flexible and adjustable coaxial waveguide source with the plasma generated in an adjustable gap located in the center conductor, (2) a microstrip-line based plasma source with the discharge created in a long quartz tube of 0.3 mm to a few mm in inside diameter, and (3) a microwave powered electrode system where the plasma is formed at the end of the electrode and the plasma is either unbounded or confined in a small spherical, long cylindrical or flat disk shaped chamber. The plasma compositions investigated include argon, nitrogen and hydrogen discharges. The diagnostic measurements are 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^3 and the plasma densities are above 10^{13} cm^{-3}.

4:00pm **PS1-TuA7 Materials with a High Secondary-electron Yield Studied in a Macroscopic Discharge Cell**, ***T.J. Vink***, *R.G.F.A. Verbeek, A.R. Balkenende, H.A.M. van Hal, S.T. de Zwart*, Philips Research, The Netherlands

Reduction of the firing voltage in plasma display panels (PDPs) calls for electrode coatings with a high secondary-electron yield. To this end we have selected a range of materials that have a low electron affinity and thus potentially a high electron emission yield. Among these materials are MgO, used as a default in PDPs, MgF_2, Al_2O_3, CsI, Rb-halogenides etc. The materials, in thin film form, were tested in a so-called macroscopic discharge cell, with dimensions that are 50 times larger than those of a discharge cell in a real PDP. Compared to the real PDP the product of pressure times electrode gap width is kept constant, and the capacitance of the dielectric layer above the electrodes is scaled accordingly. Furthermore, because of its relatively large size the macroscopic discharge cell enabled us to prepare some of the more chemically reactive materials in situ, which is crucial for measuring surface sensitive electron emission properties properly. It is shown that the firing voltages measured in the macroscopic discharge cell compare quantitatively with respect to values obtained from a PDP test panel. A 50% reduction in the firing voltage relative to the best quality MgO can be achieved. The measured firing voltages correlate well with a relatively simple model based on ionization energy of the gas atom, and band gap and electron affinity of the solid. Finally, the occurrence of secondary-electron emission yields above the Auger limit of 0.5 are discussed in terms of ion- and photon-induced processes.

Plasma Science
Room: C-105 - Session PS2-TuA

Plasma Surface Interactions I
Moderator: K.L. Steffens, National Institute of Standards & Technology

2:00pm **PS2-TuA1 Plasma-Wall Interaction Studies during Gate Etch Processes**, ***G. Cunge***, CNRS/LTM, France, *M. Kogelschatz, N. Sadeghi*, CNRS/LSP, France, *L. Vallier, O. Joubert*, CNRS/LTM, France

During a CMOS gate etch process, requirements in terms of Critical Dimension Control are more and more severe and the process reproducibility from wafer to wafer is becoming a serious issue. Process drift are commonly observed in high density plasma sources operating in $HBr/Cl_2/O_2$ and $HBr/Cl_2/O_2/CF_4$, and originate from the deposits of SiOX and SiO-CFX layers on the reactor walls. In the present paper, mass spectrometry and optical emission have been used to investigate the influence of the reactor walls' chemical nature on the recombination rate of halogen atoms, and on the surface loss rate of silicon etch by products. To begin with, the chemical nature of the layers deposited in various chemistry has been characterized by time-resolved actinometry: after a gate etch process, the layer deposited on the reactor walls is sputtered by a pure argon plasma and the emission from etch product and halogen atoms monitored as a function of time. The results gives insight on the chemical nature of the layer as a function of its thickness. Complementary experiment where the layer is sputtered in an $Ar-O_2$ plasma also provides information on the layer deposition mechanism, which proceeds through re-deposition and oxidation of halogenated silicon etch products. As a result, we will show that when a carbon source is provided to the gas phase of an $HBr/Cl_2/O_2$ plasma (either through CF_4 addition, or in the presence of photo-resist) the layer composition change from SiOCl to a mixture of SiOCl-C(F) species. Mass spectrometric measurement demonstrates that the presence of carbon in the layers is accompanied by a drastic increase of the Br and Cl atoms recombination coefficient, whose concentration in the gas phase consequently drops.

2:20pm **PS2-TuA2 Effect of Plasma Chamber Wall Conditions on Atomic Chlorine Concentration and Polysilicon Etch Rate Uniformity**, ***T.W. Kim********, *E.S. Aydil*, University of California, Santa Barbara

The effect of reactor wall conditions on atomic chlorine concentration and polysilicon etch rate uniformity was studied in a high-density inductively coupled plasma reactor. Experimental measurements of etch rate and two dimensional ion flux distributions on the wafer are combined with a simple transport and reaction model for Cl atoms in the plasma to elucidate the effect of reactor wall conditions on the etch rate uniformity. Specifically, we focus on the effects of wafer-to-wafer drifts from the wall conditions and effects of such drifts on the uniformity of etching. The spatially averaged etch rate across the wafer surface increases with time as etch products react with residual oxygen in the chamber and coat the reactor walls with a thin layer of silicon oxychloride film. Etch rate is highest at the center of the wafer when the anodized aluminum reactor walls are maintained in a "clean" state, free of silicon oxychloride deposits. In contrast, the etch rate peaks at the edges of the wafer with a local maximum near the pumping port when the reactor walls are coated with the silicon oxychloride film. The spatially averaged ion flux increases slightly while ion flux uniformity does not change as the reactor walls are covered with the silicon oxychloride film indicating that the drift in etch rate and etch uniformity is primarily due to the drift in atomic chlorine concentration and its spatial distribution. The increase in atomic chlorine concentration is due to its lower recombination probability on the silicon oxychloride film surface as compared to the "clean" anodized aluminum wall. As the reactor walls are coated with the silicon oxychloride film the etch rate distribution changes from a center-fast profile to a edge-fast profile due to a change in the dominant atomic chlorine depletion mechanism from wall recombination to recombination on the wafer surface.

2:40pm **PS2-TuA3 Abrupt Changes with Mixture Composition in the Surface Coverage and Etch Rate During Si Etching by Cl_2-Ar Plasmas**, *N.C.M. Fuller*, ***I.P. Herman***, Columbia University, *V.M. Donnelly*, University of Houston

Laser desorption of the adlayer, with laser-induced fluorescence and plasma-induced emission detection of the desorbed adsorbates, has been used to investigate Si etching in inductively coupled Cl_2-Ar plasmas. These techniques show that the relative coverage of $SiCl_x$ species and etch rate increase and the coverage of Si decreases very abruptly as the chlorine fraction is increased for a 75% Cl_2 plasma with the bias set for 80 eV ions. The Cl_2 fraction required to produce this abrupt change increases with an increase in ion energy. There is no corresponding abrupt change in the Cl, Cl^+, and Ar^+ densities or electron temperature at this mixture condition, as measured by optical emission spectroscopy. The implications of these results and the reaction mechanism will be discussed. This work is supported by NSF Grant No. DMR-98-15846.

3:00pm **PS2-TuA4 Generating High-efficiency Neutral Beams by Using Negative Ions in an Inductively Coupled Plasma Source**, ***S. Samukawa***, *K. Sakamoto*, Tohoku University, Japan, *K. Ichiki*, Ebara Research Co., Ltd., Japan

To minimize radiation damage caused by charge build-up or ultraviolet and x-ray photons during etching, we developed a high-performance neutral-beam etching system. The neutral-beam source consists of an inductively coupled plasma (ICP) source and parallel top and bottom carbon plates. The bottom carbon plate has numerous apertures for extracting neutral beams from the plasma. When a direct current (DC) bias is applied to the top and bottom plates, the generated positive or negative ions are accelerated toward the bottom plate. Most of them are then efficiently converted into neutral atoms, either by neutralization in charge-transfer collisions with gas molecules during ion transport and with the aperture sidewalls in the bottom plate, or by recombination with low-energy electrons near the end of the bottom plate. We found that negative ions are more efficiently converted into neutral atoms than positive ions. The neutralization efficiency of negative ions was almost 100%, and the maximum neutral flux density was equivalent to 4.0 mA/cm^2. A neutral beam can thus be efficiently produced from the ICP source and apertures in our new neutral-beam source.

3:20pm **PS2-TuA5 Direct Detection of Radical and Stable Species Impacting and Desorbing from Surfaces**, ***Y. Kimura***, *J.W. Coburn*, *D. Fraser*, *D.B. Graves*, University of California, Berkeley

We present results from a new vacuum beam apparatus that has been designed to measure directly the radical and stable species fluxes impacting surfaces and the products that form as a result of these interactions under high vacuum conditions. The Radical- and Ion-Surface Interaction Analysis System (RISIAS) is equipped with an external plasma source that creates a beam of radicals, and a threshold ionization quadrupole mass spectrometer (TIQMS) that is aligned with the beam's line of sight. This setup allows us to measure all the radical and stable species in the beam. The TIQMS is vertically translatable to allow a horizontal insertion of a sample surface into the beam path via a load lock. With the sample surface in place, all species desorbing from the surface can also be detected with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and product components. The addition of ion bombardment from a separate ion source on the chamber before or during radical beam exposure allows us to simulate processes with substrates in direct contact with a plasma. We demonstrate operation of RISIAS with O, N, NH, and F radicals impacting a variety of surfaces. In particular, we report the etch product composition for a nanoporous silica film (hydrogen silsesquioxane, or HSQ) etched with fluorine. The products include SiF_4, SiH_4, O_2 and a variety of carbon-containing species, apparently due to carbon contamination in the film.

4:00pm **PS2-TuA7 Film Formation, CF_2 Reactivity and Ion Effects in Fluorocarbon Plasma Systems**, ***I.T. Martin***, *E.R. Fisher*, Colorado State University

Fluorocarbon plasmas are widely used for the deposition of fluoropolymer films possessing a variety of useful properties, such as hydrophobicity, chemical inertness, and low surface energies. Ions play an important role in plasma film deposition, either as precursors to film deposition or as bombarding species that sputter or cross-link the depositing film. In order to better understand the mechanisms of film formation, gas phase and gas-surface interaction studies are combined with the results of the characterization of films deposited from C_3F_8 and C_4F_8 plasmas. Plasma Ion-Mass Spectrometry (PI-MS) is used to identify nascent ions in the plasma systems at different RF powers, which can then be linked to film structures and reactivity measurements. Plasma conditions that minimize the formation of ions lead to the deposition of less cross-linked fluorocarbon films; conditions that enhance fragmentation of the parent gas lead to higher deposition rates within the plasmas. In addition to film characterization, we have used our Laser Induced Fluorescence (LIF) based imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF_2 molecules with Si substrates during plasma processing. CF_2 surface loss coefficients determined for 25-100 W C_3F_8 and C_4F_8 plasmas show relatively high levels of scattering, which indicates that CF_2 molecules are produced at the surface in these systems. Overall, scatter coefficients measured in the C_4F_8 system are higher than those measured in the C_3F_8 system. These data are correlated with the identity of the nascent ions in the plasma systems. Results for ion free conditions are also discussed. Collectively, the data presented provide a fairly comprehensive picture of these fluorocarbon systems, from the gas-phase to the material to the plasma-surface interface.

4:20pm **PS2-TuA8 Surface Reaction Analyses for Si/SiO_2 Selective Etching Processes using Molecular Dynamics Simulations**, ***S. Hamaguchi***, Kyoto University, Japan **INVITED**

Molecular dynamics (MD) simulations are used to study surface reaction dynamics during dry etching processes of Si and SiO2 surfaces. First simulation results of Si and SiO2 etching by Cl and F beams are presented. In these processes Si is selectively etched over SiO2, the mechanism of which can be easily understood from the observation of surface conditions obtained from MD simulations. We also discuss the difference between beam etching and plasma etching (where a large number of low-energy charge-neutral reactive species exist) for these processes. Secondly we present simulation results of SiO2 etching by CxFy. Thirdly enhanced surface diffusion effects by relatively low-energy ion bombardment (the energy of which is below etching threshold) are presented. To perform these MD simulations, we have developed classical interatomic potential functions using potential energy data obtained from ab initio calculations of electronic states for various molecules and radicals. To model Si and SiO2 etching by halogens, we have constructed Stillinger-Weber type potentials for Si-O-Cl and Si-O-F systems. The potential functions for SiO2 and Si etching by CxFy, are of hybrid type of Stillinger-Weber type functions and Abell-Tersoff-Brenner type functions. The details of these potential functions are also discussed in the presentation.

5:00pm **PS2-TuA10 Subsurface Diffusion and Reaction of Fluorine Atoms in Photoresist**, ***F. Greer***, *D. Fraser*, *J.W. Coburn*, *D.B. Graves*, University of California, Berkeley

Radicals created in plasmas are known to play important roles in thin film etching, deposition, cleaning, stripping and surface modification. The present study is aimed at developing a more quantitative model of radical-

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***** PSTD Coburn-Winters Student Award Finalist

surface interactions. Room temperature measurements of F atoms abstracting D atoms from a deuterated photoresist surface to form DF were made in a vacuum beam apparatus, with simultaneous monitoring of film mass change with a quartz crystal microbalance. These measurements were interpreted as abstraction of D by F, followed by F saturation of dangling bonds previously occupied by D. However, the rate of DF formation and mass uptake due to F saturation showed a relatively long-lived tail, inconsistent with surface-only reactions. After the initial stage, subsequent DF formation and mass uptake appeared to be limited by F atom diffusion into the sub-surface since the measured rate of mass change and DF flux from the surface both varied inversely as $t^{1/2}$. The surface abstraction probability of D by F was inferred to be 0.25, and the value of the F atom diffusivity was consistent with values reported for diffusion in polymers. These results will be discussed in terms of studies with other halogen radicals as well as nitrogen radicals. The application of these results to atomistic scale models of plasma etching will also be discussed.

Surface Engineering
Room: C-111 - Session SE+TF-TuA

Systems Design of Functional Coatings
Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE+TF-TuA1 Mechanical Design of Coated Systems Based on Elastic Surface Contacts**, ***T. Chudoba***, Federal Institute of Materials Research and Testing, Germany, *N. Schwarzer, I. Hermann, F. Richter,* TU Chemnitz, Germany **INVITED**

Problems in contact mechanics can be solved very conveniently using analytical solutions, even for layered systems and non-axissymmetric systems involving friction. The calculation time is much lower than for finite element calculations, especially for non-axissymmetric problems, and allows an optimization in a large parameter field, which is difficult to achieve with other methods. In many cases, with a foreknowledge of the type of failure to be avoided, the elastic stress fields computed permit critical values of stress to be avoided by a change in input parameters. One of the key requirements of an analytical solution to a contact problem is the availability of accurate and representative values of material properties. Such properties are not generally available for thin film systems where mechanical properties may not be the same as the bulk properties. The present work shows how elastic modulus and yield stress can be obtained experimentally using nanoindentation techniques for films down to a thickness of some nanometres. Results are given for several film substrate combinations. The parameters can be used for a mechanical modelling to optimize film thickness or to find the required mechanical properties of an intermediate layer to withstand a Hertzian contact at the surface. This is demonstrated by some calculations. In another example ternary (B,C,N) films on Si and fused silica produced by magnetron sputtering with a modulus range of 130 GPa to 300 GPa are used. The mechanical properties so obtained are then used as inputs in an analytical model to determine the optimum thickness and properties of an interlayer for a particular loading configuration, that of contact with a spherical indenter. The work extends the analytical treatment to nearly any cases of indenter shape by showing how the results of individual elastic analytical solutions can be assembled and solved using boundary element methods.

2:40pm **SE+TF-TuA3 A Combinatorial Sputtering Approach to Properties Modification in Polaron Conducting Films**, ***R.R. Owings***, *P.H. Holloway,* University of Florida, *C.F. Windisch, Jr., G.J. Exarhos*, Pacific Northwest National Laboratory

The influence of sputtering parameters and cation composition on measured resistivity and optical transparency of mixed transition metal spinel oxides (AB_2O_4) has been systematically studied. A two-cathode system was used to deposit films having continuously variable compositions onto glass, silicon, and sapphire substrates (25 mm in length) as a function of process gas composition and pressure, target to substrate distance, substrate temperature, sputtering power, and sputtering time. The intent was to correlate transparency and conductivity with composition, phase purity, grain size, film thickness, and cation oxidation state. Both mixed metal oxide and metal alloy targets (nickel, cobalt, rhodium, palladium) were used for sputter deposition with variable gas mixtures of argon and oxygen. Post deposition annealing of sputtered films was found to lower film resistivity but had little effect on optical transparency. Film resistivity returned to its original value upon standing in air for two weeks. However, partial substitution of lithium for cobalt was found to not only improve the conductivity and increase transparency but also to significantly reduce property variations when subjected to post deposition annealing in air. Results suggest that the presence of lithium stabilizes higher oxidation states of the resident transition metal cations leading to lattice compression and diminished oxygen transport.

3:00pm **SE+TF-TuA4 Profile Coatings and Their Applications**, ***C. Liu***, *L. Assoufid, A. Macrander,* Argonne National Laboratory, *G. Ice, J. Tischler,* Oak Ridge National Laboratory, *K. Zhang*, Illinois Institute of Technology

We report a method of profile coating to achieve a certain pre-selected thickness profile of a thin film coating using dc magnetron sputtering. In profile coatings, the substrate is passed over a contoured mask at a constant speed to obtain a desired profile along the direction perpendicular to the substrate-moving direction. The shape of the contour depends on the desired profile and the thickness distribution directly above the gun at the substrate level. Four-inch-diameter Si wafers were coated through a 100 x 152 mm^2 aperture on the top of the shield can. The thickness distribution was then obtained using a spectroscopic ellipsometer with computer-controlled X-Y stages. A model has been developed to fit the measured thickness distribution. The relative thickness weightings are then digitized at every point 1 mm apart for the entire open area of the aperture. When the substrate is moving across the shield can during depositions, the film thickness is directly proportional to the length of the opening on the can along the moving direction. By equating the summation of relative weighting to the required relative thickness at the same position, the length of the opening at that position can be determined. By repeating the same process for the whole length of the required profile, a contour can be obtained for a desired thickness profile. The contoured mask is then placed very close (~1 mm) to the substrate level on the shield can opening. The number of passes and the moving speed of the substrate are determined according to the required thickness and the growth rate calibration. This method of profile coating has been applied to coat laterally graded W/C multilayers for tunable x-ray double-monochromator and x-ray fluorescence detection applications. It has also been applied to coat Au on a cylindrical mirror to obtain an elliptical mirror for x-ray focusing applications. Test results for these applications will be presented.

3:20pm **SE+TF-TuA5 Nano-Structure Substoichiometric Zirconium Nitride Coatings with Unique Metallic Colors and Superior Abrasion and Corrosion Resistance**, ***G. Chen***, Vapor Technologies, Inc., *J.S. Lipe, P.B. Jonte,* Delta Faucet Company, *S. Moysan*, Baldwin Hardware Company

Low temperature arc vapor deposition (LTAVD) is one of the widely applied techniques for industrial production of decorative and functional coatings. Nickel and stainless steel color protective coatings were deposited using substoichiometric nano-crystal size zirconium nitride and oxynitride. Generally the total amount of nitrogen and oxygen is between about 14 to about 50 atomic percent with a nitrogen content of at least about 6 atomic percent. The slightly nitrided or nitrided and oxidized color layer is mainly comprised of nano-phase to amorphous metallic refractory metal with textured metal nitride phase, as determined using x-ray diffraction. For example, zirconium nitride primarily oriented in (111) plane and smaller than 50 nm in grain size, or metallic zirconium primarily oriented in (112) plane and smaller than 80 nm, depending on the proportion of oxygen in total gas flow. Such types of structures are produced at relatively low processing pressures, ranging from 1 to 5 millitorr. These nano-phase coatings have superior abrasion resistance and corrosion resistance over the relative large crystal size coatings have the same atomic percent of nitrogen content.

3:40pm **SE+TF-TuA6 The Adhesion Behavior of Alumina-based Ceramic Nanocoatings and Nanostructures**, *M.V. Kireitseu, I.A. Nemerenco, L.V. Yerakhavets,* ***M. Istomin***, Institute of Machine Reliability, NAS, Belarus

The adhesion behavior of alumina-based ceramic coatings and alumina-based nanostructures involved CrC nanoparticles in contact with themselves, metals and polymer surfaces is strongly dependent upon the chemistry of the ceramic surface and that of the solids with which contact is made. With clean alumina-based ceramic coating surfaces in contact crystallographic orientation influences adhesion as determined by friction force measurements. Friction force measurements are especially effective in gaining quantitative information on interfacial bond strengths. Ceramics, just as has been observed with metals, exhibit the smallest adhesive bond forces and accordingly the lowest friction for the high atomic density low surface energy crystallographic planes. This has been observed with oxide ceramics such as aluminum oxide and nanocomposites based on alumina matrix and chrome carbide nanoparticles. For metals contacting alumina-based ceramic coatings again the chemical activity of the metal is important to adhesive behavior. With noble metals silver and gold interfacial adhesive bonds were sufficiently weak so as not to result in separation of damage to the surfaces of the contacting solids. With other metals that form stable oxides, the interfacial adhesive bonds were sufficiently strong so as to result in fracture of single crystal sapphire when cleavage planes were parallel to the contact interface. Metals undergo shear when the alumina-based ceramic coatings is poly-crystalline aluminum oxide matrix of alpha and gamma phases and attempts are made to, by tangential motion, to fracture the adhered interface. Adsorbates reduce singificantly adhesion and friction forces.

4:00pm **SE+TF-TuA7 Adhesion Fundamentals and Nanomechanics in Alumina-diamonds Nanocomposites**, ***M.V. Kireitseu***, *L.V. Yerakhavets, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

When alumina-based ceramic coatings are brought into contact with a ceramic, a polymer, or a metal, strong bond forces can develop between the materials. The bonding forces will depend upon the state of the surfaces, cleanliness and the fundamental properties of the two solids, both surface and substrate. Adhesion between alumina-based ceramic coatings and another solid are discussed from a theoretical consideration of the nature of the surfaces and experimentally by relating bond forces to the interface resulting from solid state contact. Surface properties of alumina-based ceramic composites correlated with adhesion include orientation, reconstruction, and diffusion as well as the chemistry of the surface specie. Where a ceramic is in contact with a metal their interactive chemistry and bond strength is considered. Substrate properties examined include elastic and plastic behavior in the surficial regions, cohesive binding energies, crystal structures, and crystallographic orientation. Materials examined with respect to interfacial adhesive interactions include alumina composite hardened by chrome carbide nanoparticles and diamonds nanoparticles and aluminum oxide. The surfaces of the contacting solids are studied both in the atomic or molecularly clean state and in the presence of selected surface contaminants.

4:20pm **SE+TF-TuA8 Nanoindentation of Alumina - Chrome Carbide and Alumina - Ultra Dispersed Diamonds nanoComposites**, ***L.V. Yerakhavets***, *M.V. Kireitseu, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

Nanoindentation experiments have been done on alumina-chrome carbide and alumina-ultra dispersed diamonds nanocomposite coating on different substrates like steel, aluminum and corundum. Films with thicknesses between 60 and 300 ?m prepared at various current intensities were indented with spherical indenters with nominal radii of 10, 50, and 150 ?m. The influence of deposition current and drying conditions were investigated using SEM. The suitability of this technique to determine morphology and the use of small spherical-tipped indenters to evaluate the mechanical properties of powder compacts was established. The revealed results may be summarized as follows: (1) The structure, grain size and morphology strongly depend on deposition current although the film density does not. At low current intensity, the grain size is found to be close to the initial particle size, whereas at higher current intensity an apparent coarser grain size occurs that, however, also contains pores and internal voids. (2) it is expected that the higher over potential results in the coarser grain size and formation of pores at higher current intensity that caused the onset of electrolysis of the aqueous medium. The localized electrolysis and oxygen evolution near the anode, resulting in a localized change in pH of the aqueous suspension, produced particle agglomeration as well as bubble formation. (3) Spherical indentation technique is found to be effectively measured contact pressure and effective elastic modulus as a function of penetration depth. The difference in contact pressure and elastic modulus vs. the indenter depth could be adjusted by the modulus vs. the ratio of the contact radius to the film thickness. The errors in the data could be also associated with radial cracks within the contact area. (4) Evidence of residual tensile stresses within the film manifested itself in the form of radial cracks from pores. The thicker films showed a greater influence of the cracks.

none

4:40pm **SE+TF-TuA9 Rheological Behaviour of Alumina-Diamonds-Polymer NanoComposite Structure**, ***I.A. Nemerenco***, *M.V. Kireitseu, L.V. Yerakhavets*, NAMATEX System Division, Institute of Machine Reliability, Russia

To predict strength and deformation of the alumina-diamonds-polymer nanocomposition under Hertzian indentation the rheological model has been developed. The model is based on combined simple rheological elements that in general gives accurate results in comparison with one obtained in Hertzian indentation technique. Based upon the investigations we have suggested the following requirements to be used in rheological model of the nanocomposite structure: 1. Since the composite include hard alumina layer and steel substrate that exhibit plasticity, the irreversible deformations has to be considered as plastic in nature. Deformations develop only after excess of some critical yield strength for the particular layer of the composite. 2. if the deformations are smaller then yield strength, the deformations at constant stress have to grow up step-by-step to final value; 3. Cyclic loading increases summarized plastic deformation of the composite; 4. Curve of deformation vs. time at constant load exhibits a linear dependence in one of plotted region. 5. At unloading the retardation of deformations (elastic return) has to be observed; 6. Stress at constant deformations is relaxed. The selection of model that adequate to the studied composite material is determined by comparison of developed models and experimental results. The composite of hard alumina-diamonds-aluminum can be presented as elastic-tenacious-plastic rheological model of the composite. The mechanical prototype of the model is described in a book. Structural equations of the integral model of the composite looks like (H || N || St-V) - (H-N || H). In general, the kind of the rheological equation depends on a level and form of stress applied on model. The polymer layer can be presented as the rheological model consisting from two elastic elements and one tenacious element. As a prototype of the model, we can consider connection of the Maxwells' model and elastic element. The composite exhibits linear relation of stress curve, whereas unloaded composite shows retardation of deformations (elastic return) shown as downfall segment of the curve. The plotted relations of experimental data and calculated data have revealed very close agreement of developed rheological model and real mechanical behavior of the composite. The above stated conditions are found to be used in investigations of mechanical and rheological properties of the alumina-aluminum-polymer-steel composite systems. The rheological properties and perspectives to be considered in development of such nanocomposite structure have been discussed.

5:00pm **SE+TF-TuA10 Adhesion of Alumina-based Nanocomposites to Polymer Substrate**, ***A.G. Fedaravichus***, *M.V. Kireitseu, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

Adhesion bonding of alumina-based nanostructures to several polyimides has been studied as a function of technological parameters of the layers deposition and polymer surface modification by ion beam and chemical pretreatment. The effects of the alumina-based layer deposition method and parameters have also been examined. The materials of interest include a low thermal expansion polyimide derived from 3,3,4,4-biphenyl tetracarboxylic acid dianhydride-p-phenylene diamine (BPDA-PDA) polyamic acid, and pyromellitic dianhydride-4,4-oxydianiline (PMDA-ODA) polyimide, formed from polyamic acid or polyamide ethyl ester precursors. The alumina/polyimide adhesive strength was determined by the scratch peel test, while the interfacial regions were examined using x-ray photoelectron spectroscopy and ellipsometry. It is found that for PMDA-ODA systems, exposure to low energy Ar + and/or O2+ ions improves adhesion of the alumina-based nanooverlayer, while for BPDA-PDA polyimide, the role of O2+ is more significant. The fracture location is found to lie 20-300 A within the polymer, depending upon the ion beam dose and the specific polyimide employed.

Surface Science
Room: C-108 - Session SS1-TuA

Ultrafast Phenomena & Dynamics at Surfaces
Moderator: B.D. Kay, Pacific Northwest National Laboratory

2:00pm **SS1-TuA1 Electron Dynamics at Surfaces**, ***T. Fauster***, University of Erlangen, Germany **INVITED**

Two-photon photoelectron spectroscopy permits the study of the time evolution of electronic states at surfaces with femtosecond resolution. Image-potential states at metal surfaces provide examples for various fundamental processes in electron dynamics: exponential decay, dephasing, quantum beats and interband scattering. At semiconductor surfaces the relevant time scales can be of the order of picoseconds. For dangling bond states on Si(100) intraband and interband scattering lead to a delayed build-up and slow decay of the electron population.

2:40pm **SS1-TuA3 Observation of Isotope Effect in Femtosecond Laser-Induced Desorption of O_2/Pd(111)**, ***D.P. Quinn***, *T.F. Heinz*, Columbia University

A significantly higher yield for femtosecond laser-induced desorption is observed for $^{16}O_2$ than for $^{18}O_2$ in the saturated co-adsorbed $^{16}O_2$ + $^{18}O_2$/Pd(111) system. Similar isotope effects[1] have been reported for conventional photochemistry and electron-stimulated desorption. Such isotope effects have also been used to examine reaction mechanisms for femtosecond laser-induced surface processes.[2,3] In the present case, investigations of the O_2/Pd(111) system have demonstrated that the desorption process is mediated by the substrate electronic excitations induced by the femtosecond laser pulses. The observation of a significant isotope effect is compatible with such an electronic mechanism, but implies that the adsorbed molecules are out of equilibrium with the electronic degree of freedom of the substrate during the desorption process. We consider this phenomenon in the context of both DIMET[4] and electronic friction models of the adsorbate-substrate coupling.

[1] T.E. Madey et al., J. Chem. Phys. 52, 5215 (1970).

[2] R.J. Finley et al., Chem. Phys. Lett. 274, 499 (1997).

[3] M. Bonn et al., Science 285, 1042 (1999).

[4] J.A. Misewich et al., Phys. Rev. Lett. 68, 3737 (1992).

3:00pm **SS1-TuA4 Time Resolved Femtosecond Laser Desorption from Ionic Crystals**, ***W.P. Hess***, *A.G. Joly, K.M. Beck*, Pacific Northwest National Laboratory, *J.T. Dickinson*, Washington State University

We have used femtosecond laser pulse pairs to measure the positive ion yield, from wide band-gap single crystals, as a function of time-delay between pulses. The two-pulse technique allows direct observation of solid state and surface dynamics on a femtosecond timescale. We find the ion yield, from 265 nm irradiated MgO, KBr, and LiF, depends critically on the time delay between pulses. For example, the Mg+ desorption yield displays three distinct features; a coherence peak, followed by rise, and decay features. In contrast, the yield of K+ and Li+ from KBr and LiF display only the coherence peak and picosecond decay features. The observed thresholds suggest, that although the ion desorption mechanism is dominated by defect photoabsorption, significant electron-hole pair production may contribute to the desorption mechanism following femtosecond excitation. The picosecond lifetimes correspond well with known electron-hole lifetimes in each material. We hypothesize that fs laser desorption may be related to the creation of electron hole pairs. By determining the ultrafast time-dependence we hope to reveal details of the ion desorption mechanism.

3:20pm **SS1-TuA5 On the Detection of Chemically-Induced Hot Electrons in Surface Processes: from X-ray Edges to Schottky Barriers**, ***J.W. Gadzuk***, National Institute of Standards and Technology

The potential involvement of electron-hole pair excitations in atomic/molecular processes such as sticking/adsorption/dissociation at metal surfaces has long been debated, particularly by those previously involved with similar issues in electron spectroscopies of localized core levels in solids. Of special relevance here are the fundamental studies of Müller-Hartmann et al.[1] on the dynamic response of Fermi systems to transient localized perturbations as subsequently applied to problems in non-adiabatic surface dynamics.[2] Recent experiments have detected hot electrons produced when various gases were adsorbed on a thin metal film that formed a Schottky barrier with an n-type Si substrate upon which the film was deposited.[3] Drawing on analogies with electron-hole pair shakeup in spectroscopic processes which lead to the x-ray edge singularity, a theoretical model for the electronically non-adiabatic effects is presented here that accounts for the observed initial hot electron production, roughly 10^{-3}-10^{-2} electrons per incident strongly-interacting adsorbate such as O, H, and NO_2 on Ag. Since the fundamental physical content of the x-ray edge model is the Fermi-level phase shift associated with the localized perturbation and the rate at which it is switched on, straightforward connections with friction-based models[4] are easily established in an intuitively satisfying way.

[1] E. Müller-Hartmann, T. V. Ramakrishnan, and G. Toulouse, Phys.Rev.B 3,1102(1971).

[2] J. W. Gadzuk and H. Metiu, Phys.Rev.B 22,2603(1980); ibid. 24,1866(1981).

[3] B. Gergen, H. Nienhaus, W. H. Weinberg, and E. W. McFarland, Science 294,2521(2001); H. Nienhaus, Surface Sci. Repts. 45,1(2002).

[4] K. Schönhammer and O. Gunnarsson, Phys. Rev.B 27,5113(1983).

3:40pm **SS1-TuA6 Kinetics and Dynamics of CO Oxidation on Oxygen Precovered Gold Nanoclusters Supported on Titania** , ***C.B. Mullins***, *T.S. Kim, J. Stiehl, C.T. Reeves, R.J. Meyer*, University of Texas at Austin **INVITED**

Studies of the kinetics and dynamics of carbon monoxide oxidation have been carried out on a titania single crystal surface with a (110) orientation and decorated with gold nanoclusters. The investigations employed molecular beam surface scattering techniques as well as thermal desorption mass spectrometry and Auger electron spectroscopy. An rf-powered plasma jet source was used to create a beam of atomic oxygen which was used to populate the surface with oxygen adatoms. After the surface was prepared a molecular beam of carbon monoxide was directed at the surface in order to study oxidation of CO as a function of oxygen coverage and surface temperature. There is a maximum in the reactivity as a function of oxygen coverage and surface temperature. Competing processes, such as adsorption and desorption, will be discussed as well as the effect of adsorbed oxygen upon the surface reactivity of the gold nanoclusters.

4:20pm **SS1-TuA8 O_2 and NO Island Formation on Al(111)**, ***J.Z. Sexton***, *A.C. Kummel*, University of California, San Diego

The oxidation of aluminium is a fundamentally important process that is not well understood. Scanning tunneling microscopy was employed to study the mechanisms for the oxidation of Al(111) with thermal O_2 and NO at medium to high oxygen coverage regime (20-50% ML). The STM-UHV studies provided the following observations: 1) Oxygen islands on the Al(111) surface, prepared with thermal oxygen, are elongated and non-compact. 2) Al(111) step edges change shape upon O_2 chemisorption to relieve strain from oxide islands. 3) Islands produced with thermal nitric oxide (NO) produce round, compact islands in contrast to the non-compact, elongated islands formed with thermal oxygen. 4) Above a critical oxygen coverage (30-40% ML), Al-atom protrusions appear within oxygen islands. These protrusions increase with increasing coverage and indicate the onset of the phase transition from isolated chemisorbed oxygen islands to an ionic Al_2 O_3 amorphous layer. 5) Pre-existing oxygen features can locally enhance the sticking coefficient. This local enhancement of oxygen adsorption on the Al(111) surface is likely due to a perturbation in the local electronic structure surrounding an oxygen feature. The enhanced O_2 chemisorption results from lattice strain coupled to a work-function change in the proximity of pre-existing oxygen islands. The lattice strain at high oxygen coverages eventually yields the phase transition to amorphous Al_2 O_3.

5:00pm **SS1-TuA10 Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100)**, ***Z. Dohnálek***, *R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

The adsorption dynamics and desorption kinetics of Ar and CH_4 on MgO(100) are studied using a combination of molecular beam scattering and temperature programmed desorption (TPD). Both Ar and CH_4 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). 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 CH_4, respectively in agreement with previous measurements and theoretical calculations. The total energy scaling observed for the initial trapping of Ar and CH_4 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). Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Surface Science
Room: C-110 - Session SS2-TuA

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

2:00pm **SS2-TuA1 Surface Chemistry of Size-Selected Soot Nano-Aerosol Particles**, ***J.T. Roberts***, *K.K. Higgins, A. Wensmann, M.R. Zachariah*, University of Minnesota

A method has been developed to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. The measurements encompass broad ranges of particle size, phase, and composition. Results will be presented on the growth and oxidation of soot nanoparticles (particle radius between 10 and 40 nm). The particles are investigated for changes in surface area using on-line nanoparticle characterization instrumentation. Experiments emphasize two classes of reactive conditions: high temperature oxidation by O_2 and NO_x, and room temperature addition of hydrocarbons. We believe these to be the first measurements of soot oxidation and condensation kinetics that have been conducted on size-selected particles. The results are important because soot emission from combustion sources is dictated by the competing surfaces processes of growth and oxidation. More generally, the results represent one of the first kinetic and mechanistic studies of gas-phase nanoparticle reactivity.

2:20pm **SS2-TuA2 Uptake and Reaction of Ozone on NaCl and Bromide-doped NaCl**, ***J.N. Newberg***, *J.C. Hemminger*, University of California, Irvine

Sea-salt significantly affects the chemistry and composition of the marine boundary layer. For example, gas-phase bromine compounds resulting from sea-salt aerosol particles and sea ice have been implicated in tropospheric ozone depletion events in the arctic spring time, as well as in the deposition of mercury from the atmosphere in the marine troposphere. While there have been significant advances in our knowledge of gas-phase and bulk aqueous-phase reactions of sea-salt, little is known about the fundamental surface interactions of sea-salt with important gas-phase constituents (e.g., O_3 and OH) at the air-particle interface. This is due in part to the paucity of conventional atmospheric chemistry methods with the ability to monitor surface reactions on a fundamental molecular-level. Using X-ray photoelectron spectroscopy (XPS), we monitored the surface chemistry of solid sea-salt substrates upon exposure to ozone. Past studies under steady-state conditions indicate that O_3 is essentially unreactive towards dry and aqueous NaCl in the dark. Our results show unequivocally that under UHV conditions and continuous exposure to O_3, oxygen uptake occurs on NaCl. For NaCl doped with bromide, an increase in oxygen uptake was observed. Moreover, as the amount of doped bromide increased, the total uptake of oxygen increased. Based on our experimental results and ab initio calculations, it is suggested that the products of the surface reaction of O_3 on dry bromide-doped NaCl yield ClO^- and BrO^-. Neither of these species has been reported in the XPS literature. Exposing the bromide-doped NaCl samples to water vapor leads to the segregation of Br^- to the salt surface. Exposure of this surface enriched Br^- to ozone leads to enhanced uptake of oxygen, likely in the form of BrO^-.

2:40pm **SS2-TuA3 XPS Study on Surface Segregation of Bromide in Bromide-doped NaCl Crystals by Water Vapor Exposure**, ***K. Inazu***, *J.T. Newberg, J.C. Hemminger*, University of California, Irvine

Drastic decrease of trophospheric ozone in the Arctic at polar spring has been observed accompanying an increase of particulate bromide.[1] The chain reactions involving sea salt bromide were proposed to be responsible for the ozone depletion.[2] While current model calculations for the tropospheric ozone depletion have applied the available abundance of bromide for the atmospheric reactions estimated from the bromide concentration in bulk sea water, the availability of bromide in sea salt particles must be reevaluated if the selective surface enrichment of bromide takes place on sea salt particles. In order to verify the feasibility of the surface bromide enrichment in sea salt particles, water-vapor exposure experiments were conducted for bromide-doped NaCl (100) single crystals with different bromide concentration using X-ray photoelectron spectroscopy and scanning electron microscopy. Segregation of bromide to the surface of the NaCl crystals uniformly doped with bromide at Br/Cl ratio below the level in sea water was observed even when the crystals were exposed to water vapor at lower pressure than the deliquescence points of NaCl and NaBr. The initial segregation rate of bromide was dependent on water vapor pressure and steeply increased when the employed water vapor pressure approached the deliquescence point of NaBr. At the initial stage of the segregation, segregated NaBr crystallites were highly dispersed on the crystal with ca. 0.2 µm on a side. As segregation proceeded by further water vapor exposure, the NaBr crystallites fused each other to achieve three-dimensional growth similarly to the case of water-induced reorganization of the ultra thin nitrate film formed by the reaction of NaCl single crystal with nitric acid.[3]

[1] L. A. Barrie et al., Nature, 334, 138(1988).

[2] K. W. Oum et al., Geophys. Res. Lett., 25, 3923-3926(1998).

[3] J. C. Hemminger, Int. Rev. Phys. Chem., 18, 387(1999).

3:00pm **SS2-TuA4 Chemical Reactions Induced by Ionizing and Electron-beam Irradiation in Organohalide/Water (Ice) Films**, ***C.C. Perry***, Johns Hopkins University, *N.S. Faradzhev*, Rutgers, The State University of New Jersey, *A.J. Wagner, C. Vecitis, G. Wolfe, D.H. Fairborther*, Johns Hopkins University, *T.E. Madey*, Rutgers, The State University of New Jersey

We report on the reactions of organohalides (CCl_4, $CHCl_3$, CH_2Cl_2, PhCl, CF_2Cl_2) in water (ice) films (~50 nm) at ~100K under the influence of ionizing and electron beam irradiation using reflection-absorption infrared spectroscopy, X-ray photoelectron spectroscopy and mass spectrometry. The final neutral gas phase products of electron-stimulated degradation of chlorocarbons CCl_4, $CHCl_3$, CH_2Cl_2, and PhCl, were identified as CO_2, CO, and HCl. Product species identified in the film include a thermally stable partially chlorinated (C_xCl_y) overlayer, CO_2, H_3O^+ and Cl^-. Phosgene ($COCl_2$) was also observed except in the case of PhCl. For CCl_4/H_2O mixtures, the product branching distributions are sensitive to the film's initial H_2O/CCl_4 composition. In CCl_4 rich films, the dominant reaction products in the film were C_2Cl_4 and the C_xCl_y overlayer; CO was the dominant gas phase species. In H_2O rich films, CO_2 becomes dominant at the expense of C_2Cl_4 and C_xCl_y species. For films concentrated with CCl_4 chlorine is lost principally into the gas phase while in water rich films chlorine is partitioned principally as HCl, producing H_3O^+ and Cl^-. In contrast, Freon-12 (CF_2Cl_2) / water mixtures subject to e-beam or X-ray irradiation produced carbonyl fluoride (COF_2), a major source of fluorine in the stratosphere. H_3O^+ and CO_2 were also detected as stable reaction products as well as Cl^- and F^-, consistent with a recent study of negative ion yields in ESD from CF_2Cl_2/water films. The decomposition rate of different organohalides in ice film under electron beam irradiation varied dramatically (~100): Freon being much more sensitive to electron exposure than the chlorocarbons.

3:20pm **SS2-TuA5 Heterogeneous Uptake of HNO_3 in the Troposphere: From Sand to Cirrus**, ***M.A. Tolbert***, University of Colorado, Boulder **INVITED**

One longstanding issue in tropospheric chemistry is the observation that the ratio of HNO_3/NO_x often shows atmospheric values two to ten times lower than those modeled. This implies either a missing sink of HNO_3, a missing source of NO_x species, or a missing conversion from HNO_3 to NO_x in the models. There are several dominant particle types in the free troposphere that may provide surfaces for loss of HNO_3. In this paper, we present laboratory studies of HNO_3 uptake on two systems modeling global tropospheric particulate: ice surfaces representative of cirrus clouds and mineral particles representative of atmospheric dust. The results from current laboratory experiments will be discussed and, where possible, comparisons with recent atmospheric data will be presented.

4:00pm **SS2-TuA7 Surface Chemistry of Oxide and Carbonate Particles in the Atmosphere**, ***V.H. Grassian***, *B.J. Krueger, S. Carlos-Cuellar*, University of Iowa

While there is a growing body of evidence which suggests that reactions on mineral aerosol may play an important role in the troposphere, there is very little understanding of what chemistry occurs on the surface of these particles. The focus of this talk is on recent laboratory studies of surface reactions of inorganic and organic acids found in the atmosphere on oxide and carbonate particles. These particles are used as laboratory surrogates for mineral aerosol. Kinetic measurements are made of these potentially important atmospheric reactions so as to quantify the rates of these reactions. Spectroscopic measurements along with atomic force and scanning electron microscopy provide additional information about surface reaction mechanisms. The laboratory data are then used as input into atmospheric chemistry models in order to assess the importance of these surface reactions in the troposphere.

4:20pm **SS2-TuA8 Variable-Temperature Studies of Sulfur Dioxide Reactions with Carbon Clusters**, *W.T. Wallace*, Georgia Institute of Technology, ***A.J. Leavitt***, State University of West Georgia, *M.G. Arredondo*, Georgia Institute of Technology, *D. Doby*, State University of West Georgia, *R.L. Whetten*, Georgia Institute of Technology

The variable-temperature reactions of SO_2 with thermalized carbon cluster anions, C_N^-, are reported. Carbon clusters were produced via laser vaporization of a graphite rod and exposed to a dilute SO_2:He mixture in a pulsed variable-temperature flow tube reactor (FTR). The products of these reactions were detected using time-of-flight mass spectrometry. A series of reactions were monitored at FTR temperatures of 96 °C, 73 °C, 55 °C, 47 °C, 38 °C, and 24 °C. At all temperatures, the products C_NO^- and $C_NO_2^-$ were detected corresponding to the depletion of the parent C_N^- concentration in the mass balance for selected values of N = 8 to 40. At each increasing temperature, the reaction was driven closer to completion when compared to $C_N^-:SO_2$ reactivity at room temperature. These studies probe the reactive nature of atmospheric soot with SO_x that are linked to respiratory problems.

4:40pm **SS2-TuA9 Heterogeneous Reactivity of Ozone on Mineral Oxides**, ***A.E. Michel***, *C.R. Usher, V.H. Grassian*, University of Iowa

Mineral aerosols, or wind-blown soil particles, are emitted into the atmosphere where they can provide numerous sites for the heterogeneous reaction, physisorption and chemisorption of tropospheric gases. Understanding the role of mineral aerosol in the troposphere is important for its potential impact on chemical processes in the atmosphere. Laboratory measurements of the various processes are desired for the development of accurate atmospheric computer models. The uptake of ozone on various mineral oxide particles was observed using a Knudsen cell apparatus equipped with a quadrupole mass spectrometer. Mineral oxide samples included both commercially available powders (α-Al_2O_3, α-Fe_2O_3 and SiO_2)

and authentic dusts (Saharan sand and China loess). Initial reactive uptake coefficients, γ_{BET}, were measured for the various particles and ranged from 10^{-5} to 10^{-4}. In this investigation, it was observed that both the mineral oxide powders and authentic dusts exhibited catalytic behavior towards the destruction of ozone. Additionally, variations in the reactivity of the authentic dusts were observed as a function of sample treatment.

5:00pm **SS2-TuA10 Alkali Halide Nanocrystal Growth and Etching Studied by AFM and Modeled MD Simulation**, ***S. Garcia-Manyes***, *A. Verdaguer*, University of Barcelona, Spain, *P. Gorostiza*, University of California at Berkeley, *F. Sanz*, University of Barcelona, Spain

Adsorption of water on alkali halides single crystals plays a key role in many fields ranging from interstellar dust grains, biochemistry, industrial applications and environmental processes, such as nucleation of clouds or sea salt spray. To understand the atomistic details of the wetting and dissolution processes that take place in, we combined Atomic Force Microscopy and Molecular Dynamics to study the adsorption of water vapor on a stepped (100)-oriented crystals surface prepared by cleavage. The AFMicroscope, placed in a humidity-controlled chamber is used to induce local step nanostructures forming hillocks. A few seconds of contact between the cantilever tip and the crystal surface are enough to create a hillock of a few monatomic steps due to the water neck formed on account of capillary forces. The shape and distribution of the monatomic steps in the formed hillock follows the minimization of the interface free energy established between the aqueous ionic solution and the air phase in order to reduce surface tension. After hillock creation the AFM tip is retracted and the hillock starts to dissolve and ions migrates until the hillock disappears. Terraces in the hillock disappear one by one, from the upper one to the lowest in order to minimize again the free energy of the whole system. We have studied creation and free evolution of hillocks for alkali halides single crystals by AFM under chosen humidity conditions. Imaging during experiments is performed in tapping mode so as to reduce the surface perturbation. We performed molecular dynamics simulations of the interface between the single crystal and water using a hillock-like surface model and results are compared with experimental data in order to understand the dynamics of the system. Ionic migration, steps mobility and dissolution directly calculated by the simulations have been used to modeling the hillock evolution according to experimental data.

Surface Science
Room: C-112 - Session SS3-TuA

Metal/Oxide Surfaces
Moderator: C.A. Ventrice, Jr., University of New Orleans

2:00pm **SS3-TuA1 High Quality Nanoscale Interfaces between Metals and Metal/Oxides: Co on Fully Hydroxylated Sapphire**, *S.A. Chambers*, *T. Droubay*, Pacific Northwest National Laboratory, ***D.R. Jennison***, *T.R. Mattsson*, Sandia National Laboratories

We present experimental and theoretical results that show Co metal deposited on fully hydroxylated alpha-Al2O3(0001) at room temperature produces a chemical reaction that leads to laminar growth of the metal film. A fraction of the initial metal dose is oxidized, and a concomitant amount of hydroxyl is reduced, resulting in hydrogen being released. The resulting Co cations are within the top layer of the oxide. These bind ionically to the substrate, but are also bound to neighboring metal atoms. Stronger interfacial binding results and near layer-by-layer metal growth is achieved, with good metal morphology just beyond the third layer. We propose direct hot reactions are responsible and many other metals and oxides should display this phenomenon. All work was supported by the US Dept. of Energy.

2:20pm **SS3-TuA2 The Interaction and Reactivity of Hydrocarbons on Hydroxylated g-Al_2O_3/NiAl(100)**, ***K.A. Layman***, *J.C. Hemminger*, University of California, Irvine

γ-Al_2O_3 is an important industrial catalyst and catalyst support. The surface OH groups on bulk γ-Al_2O_3 influence the Brönsted acidity and metal dispersion on these catalysts. However, the detailed understanding of Al_2O_3 surfaces has been limited because of the complexity of the surface hydroxyl groups. We are able to grow highly-ordered and well-defined thin films of hydroxylated γ-Al_2O_3 which model bulk γ-Al_2O_3 by exposing the NiAl(100) substrate to 100 L H_2O at 1000 K. Unlike bulk γ-Al_2O_3, these films exhibit a single OH stretch at 3711 cm^{-1} (FWHM approximately 100 cm^{-1}). This frequency is indicative of non-interacting OH groups bonded to 2 or 3 Al atoms. We have used HREELS to study the interaction and reactivity of hydrocarbons, such as acetonitrile, pyrazine, 2,6-dimethylpyridine, and ammonia, on our thin films of hydroxylated γ-Al_2O_3 following adsorption at 140 K. These molecules interact with surface OH groups, forming acid-base complexes. Complex formation causes the OH bond strength to decrease and the OH stretch to shift to lower frequency. We have observed that the magnitude of the OH shift depends on both the basicity and adsorption orientation of these hydrocarbons. Correlation of the OH frequency shift with the gas basicity of the adsorbate allows us to assign a pK_a to the surface OH groups. The hydrocarbons can also interact with the surface Al^{3+} cations. In the case of ammonia, this interaction leads to disruption of an N-H bond and the formation of surface NH_2 and OH species.

2:40pm **SS3-TuA3 Calculations of the Free Energy and Structure of Alpha-Alumina (0001)**, ***M. Finnis***, *A. Marmier*, Queens University, UK **INVITED**

We report a study of the excess free energy of this surface using two different shell models (S1 and S2) and an ab initio (AI) model in which the total energy was obtained from self-consistent pseudopotential calculations using the local density approximation. We apply the quasi-harmonic approximation to estimate the phonon contribution to the free energy. The surface energies with S1 and S2 bracket the AI result. They also show that only two k-points are needed to sample the phonons in the Brillouin zone with good accuracy. A six layer slab is thick enough for obtaining all contributions to the surface free energy, which converges faster with slab thickness than the mean square amplitudes of atomic vibration, and in fact the latter diverges for a finite slab. Anharmonicity is insufficient to account for the discrepancy beween calculated and experimental surface relaxations. A stoichiometric Al-terminated surface is predicted to be stable over all but very low (close to decomposition of the oxide) and very high (> 1 atmosphere) oxygen partial pressures, in agreement with experiment.

3:20pm **SS3-TuA5 Effect of Annealing on the Crystallization of Ultrathin Al_2O_3 Film on NiAl(110)**, ***T.T. Lay***, *M. Yoshitake*, National Institute for Materials Science, Japan

Al_2O_3 is a wide band gap insulator and it is reported that clear band gap exits in 0.5nm-thick well-ordered Al_2O_3 grown on NiAl(110).[1] It has high potential of application in metal-insulator-metal(M-I-M) electron emitter which needs wide gap insulator. Oxygen dose rate, oxidation temperature and annealing are important parameters for well-ordered film. In our previous work, good crystalinity of Al_2O_3 layer was obtained by optimizing the dose rate and oxidation temperature.[2,3] In the present work, change in crystalinity and surface composition due to annealing time is analyzed. NiAl(110) single crystal was put inside the UHV system and 1200L oxygen was introduced under pressure 5 x 10^{-7} torr at 670K. After oxidation the specimen was annealed at 1070K. The oxide layer was amorphous before annealing and crystalline Al_2O_3 appeared after annealing. Crystal structure and surface composition were measured by LEED and XPS every hour during annealing. Intensity ratio of Al_2O_3 and NiAl spots was measured from LEED patterns. The intensity ratio is directly related to crystalinity and it increases linearly with annealing time. After 6 hours annealing, the ratio became saturated and there was less change by further annealing. The surface composition of O, Al and Ni changed only at the early stage of annealing and were almost constant one hour later. It is likely that the amount of oxygen contributed to well-ordered crystalline oxide is almost decided at oxidation. Annealing at 1070K for certain period of time is important for epitaxial growth of well-ordered oxide layer.

[1] R.M. Jaeger, H.Kuhlenbech, H.J.Freund, M.Wuttig, W. Hoffmann, R. Franchy and H. Ibach, Surf. Sci., 259,235(1991),

[2] M. Yoshitake, B. Mebarki and Thi Thi Lay, Surf.Sci. Lett., in press.,

[3] Thi Thi Lay, M. Yoshitake and B. Mebarki, J.Vac. Sci. Technol., submitted.

3:40pm **SS3-TuA6 Ab-Initio Calculations of Pristine and Doped ZrO_2 Tilt Grain Boundaries**, *Z. Mao*, Northwestern University, *E.C. Dickey*, The Pennsylvania State University, ***S.B. Sinnott***, University of Florida

The structure of the cubic-ZrO_2 symmetrical tilt sigma 5 (310)/[001] grain boundary is examined using density functional theory within the local density and pseudopotential approximations. Several pristine stoichiometric grain boundary structures are investigated and compared to Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy results. The lowest-energy grain boundary structure is found to agree well with the experimental data. When Y^{3+} is substituted for Zr^{4+} at various sites in the lowest-energy grain boundary structure, the calculations indicate that Y^{3+} segregation to the grain boundary is energetically preferred to bulk doping, in agreement with experimental results.

4:00pm **SS3-TuA7 Role of the Stress in the Epitaxy of Silver on the Basal Planes of Zinc Oxide**, ***J. Jupille***, Groupe de Physique des Solides, France, *S. Djanarthany*, Laboratoire des Geosciences, France, *D. Abriou*, Laboratoire CNRS/Saint-Gobain, France, *N. Jedrecy*, Laboratoire Mineralogie-Cristallographie, France, *R. Lazzari*, *G. Renaud*, CEA-Grenoble, France

In general late transition metals and noble metals poorly wet oxide surface oxides. However, rather high values of the critical coverage (onset of the formation of the second atomic layer [Campbell, Surf. Sci. Rep. (1997)]) have been observed for platinum, copper and silver. The present paper reports on two different $(0001)_{ZnO}//(111)_{Ag}$ epitaxies for silver on the oxygen- and zinc-rich basal planes of zinc oxide. The $[20\text{-}20]_{ZnO}//[220]_{Ag}$ orientation relation (OR I), corresponding to a misfit of + 2.75 %, is obtained on surfaces which are only prepared by annealing under oxygen. The $[11\text{-}20]_{ZnO}//[220]_{Ag}$ orientation relation (OR II, rotated by 30° with respect to OR I) is observed after an ion bombardment of the surfaces. It corresponds to a misfit of 11 %. The two epitaxies show both a perfect reproducibility and a good thermal stability. Low energy electron diffraction, transmission electron microscopy and X-ray diffraction (XRD) measurements demonstrate that (i) the ion bombardment strongly increases the size of the surface domains (narrowing of diffraction spots and rods) and that (ii) OR II, which corresponds to within 0.11 % to a 9Ag/8ZnO lattice coincidence, does not show any stress even at the onset of the film growth. It is concluded that the OR II is favoured by large ZnO domains while the OR I, which shows a better fit on short range, appears on surfaces of poor crystalline quality.

4:20pm **SS3-TuA8 Vanadium Oxide Nanostructures on Rh(111): Novel Oxide Phases at the Interface**[1], *J. Schoiswohl, S. Surnev, S. Eck, M.G. Ramsey*, ***F.P. Netzer***, Karl-Franzens University Graz, Austria

Ultrathin layers of materials develop novel physical and chemical properties due to confinement and interfacial proximity effects, which are not shared by their respective bulk phases. Here we report a study of thin vanadium oxide layers on Rh(111) surfaces using STM, STS, LEED, and XPS with synchrotron radiation. We have fabricated vanadium oxide nanostructures on Rh(111) by reactive evaporation of vanadium metal in an oxygen atmosphere onto the heated substrate surface and have characterised the atomic structures of the V-oxide with STM (STS) and LEED; the oxidation state of the oxide layers have been followed by XPS. We find a complex phase diagram of oxide structures as a function of oxide coverage and temperature, and observe a range of well-ordered two-dimensional oxide phases with novel structural properties. At submonolayer coverages higher oxidation states ($\geq 4^+$) prevail [$(\sqrt{7}\text{x}\sqrt{7})$ and/or $(\sqrt{13}\text{x}\sqrt{13})$ structures], whereas the oxidation state converges to 3^+ and a bulk-type V_2O_3 phase forms for thicker layers (> 2-3 ML). The monolayer phase is distinguished by a Moiré-type STM structure, resulting from the lattice mismatch between the ordered oxide overlayer and the substrate. Reduced oxide phases are obtained after vacuum annealing treatments, displaying a fascinating structural complexity, with e.g. (5x5), $(5\text{x}3\sqrt{3})$, (9x9) and other structures.

[1] Supported by the Austrian Science Foundation.

4:40pm **SS3-TuA9 Room Temperature Growth and Thermal Sintering of Ag and Pd on Flat Ultra-thin SiO_2 and MoO_2 Films**, ***A.K. Santra***, *B.K. Min, D.W. Goodman*, Texas A&M University

The initial growth morphology of Ag and Pd particles has been investigated on epitaxial ultra-thin MoO2(100) and SiO2 films using STM. The room temperature growth of Ag and Pd particles is invariant with respect to the thickness of the SiO2 film, however, with increasing surface temperature the Pd particles undergo a 3DÃ¨ 2D transition on a 0.5nm thick SiO2 film and increase in particle size on films with a thickness >0.8nm. In contrast, Ag particles on a MoO2(100) substrate show striking differences with respect to the particle size distribution as a function of the oxide film thickness at room temperature. These results indicate that the initial growth and thermal sintering of metal particles depend critically on the strength of the metal-support interaction. The preparation procedure for these flat ultra-thin films on Mo(112) will be discussed relative to the LEED and highly resolved STM data. Furthermore, STS data indicate that a minimum thickness (3 - 4 Si-atomic equivalent layers) is necessary to obtain a bulk-like band-gap for SiO2 ultra-thin films, in excellent agreement with results recently reported by Muller and co-workers [Nature 399 (1999) 758] for Si/SiO2/Si gate-oxide samples.

5:00pm **SS3-TuA10 Structure and Properties of SnOx Wetting Layers and Crystallites on Pt(111)**, ***J. Kim***, University of Southern California, *M. Batzill*, Tulane University, *D. Beck*, University of California-Los Angeles, *B.E. Koel*, University of Southern California

Tin-oxide films were grown on Pt(111) substrates by oxidation of Sn/Pt surface alloys using NO_2 exposures or by deposition of Sn in an NO_2 ambient gas. Based on the wide variety of structures of tin-oxide films that we have reported previously [Phys. Rev. B 64, 245402/1 (2001)], we now report detailed characterization of the vibrational and electronic properties of each structure using XPS, UPS, ELS, and HREELS. XPS confirmed the existence of three Sn states that have been labeled previously as metallic, "quasimetallic", and oxidic Sn. We conclude that the "quasimetallic" state results from oxidized Sn that is still alloyed within the Pt surface layer. UPS identified a SnO_2 stoichiometry for multilayer tin-oxide films. HREELS was used to identify characteristic vibrational modes for the different monolayer films. SnO_2 crystallites, although only a few monolayers high and tens of nanometers in width, remarkably exhibit bulk-like vibrational and electronic properties.

Thin Films
Room: C-101 - Session TF-TuA

Atomic Layer Deposition - Oxides
Moderator: S.M. George, University of Colorado at Boulder

2:00pm **TF-TuA1 Growth Kinetics and Scaling of High-K Materials Deposited by Atomic Layer Deposition**, ***R.J. Carter***, IMEC, Belgium **INVITED**

The aggressive scaling of MOS devices is quickly reaching the fundamental limits of SiO_2 as the gate insulator. The replacement of SiO_2 with a high dielectric constant (high-k) material allows for an increase in the physical thickness of the gate insulator, while maintaining a low equivalent oxide thickness (EOT) and low direct tunneling current. The high-k material of choice will likely be a deposited film, which makes the replacement of SiO_2, a thermally grown layer, even more challenging. Atomic layer deposition (ALD) is a well-controlled surface saturating process using gas-solid interactions to deposit thin films. The technique results in covalent bonding between the gaseous precursors and the surface bonding sites. ALD provides highly uniform layers and the possibility to deposit mixed oxides. We have observed that the starting surface is extremely important to deposit high quality films with ALD. The surface termination of the substrate affects the growth kinetics of high-k materials in terms of a growth inhibition time. Longer inhibition times have shown detrimental effects when depositing ultra-thin high-k layers, e.g. films are not fully closed. Our results show that the ideal starting surface for ALD is an OH-terminated silicon surface, which is readily achieved with a chemical oxide. In terms of scaling, the benefit of using a high-k material is compromised if a lower dielectric constant insulator is also present in the gate stack. In order to scale to EOT's below 1 nm with a chemical oxide present, the thickness of the high-k material must be significantly reduced. As a result the tunneling current through the gate stack will increase. By optimizing the surface preparation, we have achieved sub-1 nm EOT's while maintaining leakage currents below 1 A/cm2 at -1 volt. Poly-Si integration with high-k materials remains a challenge. The flexibility of ALD to deposit mixed oxides provides options to fabricate scalable Poly-Si/high-k gate stacks.

2:40pm **TF-TuA3 Effect of Growth Temperature on the Properties of ALD Grown ZrO_2 Films**, ***G. Scarel***, *E.K. Evangelou, S. Ferrari, S. Spiga, C. Wiemer, M. Fanciulli*, Laboratorio MDM-INFM, Italy

Zirconium dioxide films, 15 nm thick, are grown by atomic layer deposition (ALD) using zirconium tetrachloride and water as precursors. A relatively high dielectric constant (22), wide band gap and conduction band offset (5.8 eV and 1.4 eV respectively) indicate zirconium dioxide as one of the most promising candidates to substitute silicon dioxide as gate dielectric in complementary metal-oxide-semiconductor devices. However, crystallization occurring both during deposition and after annealing treatment affects charge mobility and induces flat band voltage shifts. Chlorine ions might contribute to the same effects and also to an increase of leakage current related to the introduction of extra levels in the band gap. These ions are produced during the stage of the ALD cycle in which the ZrCl4 precursor reacts with the growing surface. To address the structural and morphological properties and their effects on the electrical ones, ZrO2 films are grown at different substrate temperatures: 150 C, 200 C, 250 C, 300 C and 350 C. Relevant modifications of film structure with changing the substrate temperature during growth are expected because the density of the reactive sites (mainly Si+1 - (OH)-1 bonds) decreases with increasing temperature (Y.B. Kim et al., Electrochem. and Solid State Lett. vol. 3 (2000) p. 346). Preliminary results suggest, for example, that the amorphous component of the films increases with higher density of Si+1 - (OH)-1 bonds in the starting growth surface obtained at lower substrate temperatures. The size and consequences of these modifications are investigated in this work using x-ray diffraction and reflectivity, far infrared transmission spectroscopy and atomic force microscopy. Time of flight - secondary ion mass spectrometry is used to study chlorine and oxygen diffusion and to what extent the behavior of these two species is related. Electrical properties are determined from C-V and J-V characteristics.

3:00pm **TF-TuA4 ZrO_2 Thin Film Growth by CVD from Tetrakis-diethylamino-zirconium for High-k Gate Dielectrics**, ***I. Nishinaka***, *T. Kawamoto*, *Y. Shimogaki*, University of Tokyo, Japan

In order to improve the performance of ULSI, the scale of MOS (Metal-Oxide-Semiconductor) transistor tends to be reduced. Gate dielectric scaling will require new insulating materials with high dielectric constants to provide increased capacitance without increasing the gate leakage current by direct tunneling. ZrO_2 films were investigated as high-k gate insulators for possible gate dielectric applications. We employed tubular CVD reactor system to investigate the kinetics of ZrO_2-CVD from tetrakis-diethylamio-zirconium (TDEAZ) as zirconium source. The growth rate profile in the tubular reactor strogly indicated that TDEAZ directly deposited on the surface and the decomposition of TDEAZ by gas phase reaction did not occur. The step coverage was constant independent of the substrate position, and the sticking probability at 340°C estimated from the step coverage profile by Monte Carlo simulations was 0.004. The as deposited film structure was amorphous at 300-340°C. As the films were subjected to the rapid thermal oxidation, the film structure changed amorphous into monoclinic and then into amorphous again by increasing the annealing temperature. This structural change resulted from the decrease of the residual nitrogen and carbon, and the increase of the silicon that diffused from the substrate into the ZrO_2 films. After annealing at 1000°C, Si concentration in the film was about 40%, and Zr was 10%. The initial growth process of CVD by TDEAZ was investigated by changing the deoposition time, and surface coverages of Zr and Si were examined using XPS. The time dependencies of XPS signal intensities of these elements revealed that the ZrO_2 film growth from TDEAZ is not island-like growth, but is layer-by-layer growth. This initial growth behavior may be applicable to ALD (Atomic Layer Deposition).

3:20pm **TF-TuA5 Atomic Layer Deposition of Zirconium Silicate Films Using Zirconium Tetrachloride and Tetra-n-butyl Orthosilicate**, ***S.W. Rhee***, *W.K. Kim*, *S.W. Kang*, Pohang University of Science and Technology, Republic of Korea, *N.I. Lee*, *J.H. Lee*, *H.K. Kang*, Samsung Electronics Co., Ltd., Republic of Korea

Atomic layer chemical vapor deposition (ALCVD) of zirconium silicate films with a precursor combination of $ZrCl_4$ and TBOS (tetra-n-butyl orthosilicate) was studied for high dielectric gate insulators. Deposition conditions, such as deposition temperature and pulse time for purging and precursor injection, on the deposition rate per cycle and composition of the film were studied. At 400°C, the growth rate was saturated to 1.35 Å/cycle above 500 sccm of the argon purge flow rate. The growth rate, composition ratio ((Zr/Zr+Si)), and impurity contents (carbon and chlorine) were saturated with the increase of the injection time of $ZrCl_4$ and TBOS and decreased with the increase of the deposition temperature from 300 to 500°C. The growth rate, composition ratio, carbon and chlorine contents of the Zr silicate thin film deposited at 500°C were 1.05 Å/cycle, 0.26, 3.3 at.%, and 1.5 at.%, respectively. It seemed that by using only zirconium chloride and silicon alkoxide sources, impurity content of carbon and chlorine could not be lowered below 1%. Also it was found that the incorporation rate of metal from halide source was lower than alkoxide source. The electrical properties were characterized by C-V and I-V measurements. Interface was also observed with high resolution transmission electron microscopy (HRTEM).

3:40pm **TF-TuA6 Characteristics of ZrO_2 and HfO_2 Gate Oxides Deposited by Atomic Layer Deposition (ALD) Using Metal Organic Precursors with Various Reactant Gas Sources**, ***J. Han***, *J. Koo*, *S. Choi*, *Y. Kim*, *H. Jeon*, Hanyang University, Korea

High dielectric constant materials have recently gained considerable attention as a possible alternative to SiO_2 gate dielectric. The main advantage of high dielectric constant materials is increasing the physical thickness to reduce the tunneling leakage current and thus improve the reliability while scaling the capacitance equivalent oxide thickness below the direct tunneling limit of SiO_2. Among the high-k materials, ZrO_2 and HfO_2 are considered as a potential alternative to SiO_2 gate dielectric below 2nm scale due to the relatively high dielectric constant, large band gap, and compatibility with the manufacturing of integrated circuits. For these reasons, we investigated the physical, chemical and electrical characteristics of ZrO_2 and HfO_2 gate dielectrics deposited by the atomic layer deposition (ALD) method. ZrO_2 and HfO_2 films were deposited using $Zr(Net_2)_4$ and $Hf(Net_2)_4$ as the Zr and Hf-precursors with various reactant gas sources such as the oxygen gas, oxygen plasma and water vapor. ZrO_2 and HfO_2 films after deposition were rapid thermal annealed at 800°C for 10 seconds in N_2 ambient and post-metallization annealing (PMA) was performed in an H_2+N_2 atmosphere at 450°C for 30minutes. The microstructure and interface morphology of ZrO_2 and HfO_2 films were investigated using cross-sectional transmission electron microscopy (XTEM), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) were utilized to analyze the chemical composition variations, impurity contents, chemical bonding characteristics, and surface morphologies. The electrical properties and reliability characteristics including equivalent oxide thickness, hysteresis, leakage current and capacitance were analyzed by current-voltage (J-V) and capacitance-voltage (C-V) measurements.

4:00pm **TF-TuA7 Trimethylaluminum-initiated ALD Growth of Al_2O_3 on Si: An In-situ Infrared Study**, ***M. Frank***, Agere Systems and Rutgers University, *Y.J. Chabal*, *G.D. Wilk*, Agere Systems

The initial phase of alternative gate dielectric growth on Si by atomic layer deposition (ALD) is critical for the final Si-dielectric interface properties. The ubiquitous and deleterious presence of an interfacial SiO_2 layer has motivated deposition on H-terminated Si surfaces. However, even for these surfaces a thin SiO_2 layer is formed during growth. It is believed to arise from the initial reaction of water (forming OH and Si-O-Si), and to be necessary for subsequent metal precursor reaction. We have designed a model reactor to perform an in-situ infrared absorption study of Al_2O_3 growth on both HF-etched and oxidized Si from trimethylaluminum (TMA, $Al(CH_3)_3$) and water at 300°C. We have thus observed all relevant species (CH_3, OH, Si-H, oxides) present at the surface up to 16 ALD cycles. We find that H-terminated Si(100) surfaces are neither oxidized nor hydroxylated by water, in contrast to what is expected (yet, D_2O experiments show H-D isotopic exchange and similar O_2 exposures lead to oxidation of the H-terminated surface). Instead, TMA exposure leads to the formation of both Al-CH_3 and Si-CH_3 groups, with varying kinetics. Transfer of CH_3 to Si predominantly occurs at Si step sites, and is absent on atomically smooth H/Si(111)-(1x1). Once Al is deposited, three reactions take place upon water exposure, each with different kinetics: replacement of Al-bonded CH_3 by OH; transfer of CH_3 from Al to Si; and the catalytic oxidation of Si. In contrast, Si-CH_3 remains unaffected by water, and may therefore be responsible for C contamination at the Si/oxide interface. During subsequent TMA-water cycles, more interfacial SiO_2 is formed, while Al_2O_3 growth proceeds according to the well-known self-terminated mechanism on all Si substrates. This leads to the formation of Al_2O_3 films equivalent to what is grown in commercial ALD reactors.

4:20pm **TF-TuA8 Atomic Layer Deposition of Aluminum Oxide Using Dimethylaluminum Isopropoxide and Water**, *K-S. An*, *S.S. Lee*, *W.T. Cho*, Korea Research Institute of Chemical Technology, South Korea, *J.M. Kim*, Korea Institute of Machinery & Materials, South Korea, *K. Sung*, ***Y. Kim***, Korea Research Institute of Chemical Technology, South Korea

Dimethylaluminum isopropoxide (DMAI), $(CH_3)_2AlOCH(CH_3)_2$, a precursor originally developed for the metal organic chemical vapor deposition of alumina, was adopted as a new precursor for growing aluminum oxide thin films on HF-treated Si and chemically-induced SiO_2/Si substrates by atomic layer deposition (ALD). This precursor is stable for a prolonged period of storage time under inert atmosphere (such as in nitrogen or argon) and does not react vigorously in air, and therefore is easy to handle and safe, without causing hazards. The self-limiting ALD process by alternate surface reactions of DMAI and H_2O was confirmed from thickness measurements of the aluminum oxide thin films as a function of DMAI pulse time and also as a function of the DMAI-H_2O cycle. The growth rates on HF-treated Si and chemically-induced SiO_2/Si were saturated to about 1.04 Å/cycle at the substrate temperature range of ~120-150 °C. Dependence of growth rate on H_2O pulse time as well as substrate temperature was also monitored. The grown Al_2O_3 thin films were characterized for surface roughness, stoichiometry, and electrical properties by atomic force microscopy, Rutherford backscattering spectroscopy, and I-V measurements, respectively. X-ray photoelectron spectroscopy was also employed to investigate the oxidation states of the interfaces between the HF-treated Si substrates and the aluminum oxide films. In conclusion, our preliminary results verify the validity of dimethylaluminum isopropoxide as a new ALD source for aluminum oxide.

4:40pm **TF-TuA9 Atomic Layer Deposition of HfO_2 / Al_2O_3 Laminate Structure for Gate Dielectric Applications**, ***J. Koo***, *J. Han*, *S. Choi*, *Y. Kim*, *H. Jeon*, Hanyang University, Korea

Hafnium oxide (HfO_2) and aluminum oxide (Al_2O_3) have been widely investigated as an alternative gate oxide in sub-100nm metal-oxide-semiconductor technology due to its large band gap, good thermal stability, and relatively higher dielectric constant compared to SiO_2[1]. For these reasons, we investigated the characteristics of HfO_2 / Al_2O_3 laminate structure as well as its physical, chemical and electrical properties for gate dielectric applications. HfO_2 / Al_2O_3 films were deposited on p-type Si (100) substrate by atomic layer deposition (ALD) method. All samples after deposition were rapid thermal annealed at 800°C for 10 seconds in nitrogen ambient. And the platinum (Pt) layer with the thickness of about 1000 Å was deposited by e-beam evaporator and patterned to form the gate electrodes. Forming gas anneal was performed in an H_2+N_2 atmosphere at 450°C for 30 minutes. The electrical properties including equivalent oxide thickness, hysteresis, leakage current and dielectric constant were calculated and analyzed by using capacitance-voltage (C-V) and current density-voltage (J-V) measurements. For the evaluation of the physical and chemical characteristics of HfO_2 / Al_2O_3 films were analyzed by cross-sectional transmission electron microscope (XTEM), atomic force microscope (AFM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). This paper will discuss the systematic analysis of HfO_2 / Al_2O_3 laminate films deposited by ALD for gate dielectric applications.

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5:00pm **TF-TuA10 Room Temperature NH_3-Catalyzed SiO_2 Atomic Layer Deposition Using Sequential Exposures of TEOS and H_2O**, ***J.D. Ferguson***, *S.M. George*, University of Colorado

The atomic layer deposition of SiO_2 has employed $SiCl_4$ and H_2O and required high temperatures and long exposure times. Amine catalysts have been shown to reduce the exposure lengths, lower the growth temperature to 300 K and increase the SiO_2 growth rate. However, the reaction product, HCl, readily reacts with the amine catalysts to form a salt. The salt formation problem can be avoided using organometallic silicon precursors. NH_3-catalyzed SiO_2 ALD was accomplished using tetraethoxysilane (TEOS) based upon the following AB reaction sequence: A) $SiOH^* + Si(OCH_2CH_3)_4$ --> $SiOSi(OCH_2CH_3)_3^* + CH_3CH_2OH$ B) $Si(OCH_2CH_3)^* + H_2O$ --> $SiOH^* + CH_3CH_2OH$ SiO_2 films were grown on high surface area ZrO_2 and $BaTiO_3$ particles using alternating exposures of TEOS and H_2O at 300 K with NH_3 as the catalyst. The sequential surface chemistry was monitored in a vacuum chamber using in situ transmission FTIR spectroscopy. The particles initially contained OH* surface species that were converted to $Si(OCH_2CH_3)_x^*$ species by the first TEOS/NH_3 exposure. The subsequent H_2O/NH_3 exposure converted the $Si(OCH_2CH_3)^*$ species to SiOH* species. Alternating TEOS/NH_3 and H_2O/NH_3 exposures yielded $Si(OCH_2CH_3)_x^*$ and SiOH* species, respectively, that sequentially deposit silicon and oxygen with atomic layer control. The repetition of the TEOS and H_2O exposures in an ABAB... reaction sequence led to the appearance of bulk SiO_2 vibrational modes that increased with the number of AB reaction cycles. After SiO_2 deposition, the ZrO_2 and $BaTiO_3$ particles were examined using transmission electron microscopy (TEM). The TEM images revealed extremely uniform and conformal SiO_2 films on both types of particles and growth rates of ~0.7 Å per AB cycle.

Vacuum Technology
Room: C-104 - Session VT-TuA

Vacuum System Architecture and Specialized Analytical Techniques
Moderator: J.L. Provo, Sandia National Laboratories

2:00pm **VT-TuA1 Present Status of the KEKB Vacuum System**, *K. Kanazawa, S. Kato,* ***Y. Suetsugu***, *H. Hisamatsu, M. Shimamoto, M. Shirai*, High Energy Accelerator Research Organization (KEK), Japan

The KEK B-Factory (KEKB) is an electron-positron collider with an asymmetric energies consisting of two rings, that is, the High Energy Ring (HER) for 8.0 GeV electrons and the Low Energy Ring (LER) for 3.5 GeV positrons. The design beam currents are 1.1 A and 2.6 A with 5120 bunches for HER and LER, respectively. Each ring has a circumference of 3016 m and most of beam chambers are made of oxygen free copper for its ability to withstand the intense heat load and to shield effectively the radiation from high beam currents. The pumping scheme is a combination of Non-Evaporable Getter (NEG) pumps and sputter ion pumps. The commissioning of KEKB started in December 1998. At the end of March 2002, the achieved stored currents were about 0. 93 A and 1.44 A for HER and LER, respectively, with 1200 bunches. The KEKB is now able to serve the world-record luminosity of 7.2 nb^{-1} s^{-1} for the BELLE detector. The vacuum system has been operating satisfactorily. The average pressure of about $1x10^{-7}$ Pa is achieved now for both rings during the operation. The coefficient of the photon stimulated gas desorption (PSD) decreased steadily to almost $1x10^{-6}$ molecules $photon^{-1}$ at the integrated linear photon flux of about $3x10^{25}$ photons m^{-1}. Most of vacuum components, such as Helicoflex sealing (Le Carbone Co. Ltd.) and the vacuum bellows with RF-shield structure, have been working well. The severest trouble had been the beam-induced troubles of the movable masks, but the newly developed masks were installed and are now in use without serious problem. One of the latest issues is the excess heating of bellows, chambers or pumps coming from the electromagnetic filed excited by the intense bunched beam. A non-linear dependence of pressure on beam current has been observed in LER. That seems to deeply relate to the electron multipactoring, which causes the electron cloud instability. Here we will summarize the experiences and the present status of KEKB vacuum system, and touch briefly the future plan.

2:20pm **VT-TuA2 Development of Sputtering System for Large-Area Deposition of $CuIn_{1-x}Ga_xSe_{1-y}S_y$ Thin-Film Solar Cells**, ***N.G. Dhere***, *A.H. Jahagirdar, A.A. Kadam, V.S. Gade, H.P. Patil*, University of Central Florida

Manufacturing cost of $CuIn_{1-x}Ga_xSe_{1-y}S_y$ (CIGS) thin-film modules is expected to become cheaper than that of crystalline silicon modules within 5 years. At present, commissioning and reaching full production of thin film modules is delayed because of the non-availability of turnkey manufacturing plants. Few university laboratories are conducting research on design and construction of PV plants. CIGS thin-film solar cells are being prepared routinely at FSEC on glass and metallic foil substrates for terrestrial and space applications. Earlier the size was limited to 3x3 cm^2. This paper presents results of development efforts in design and construction of large-area sputtering system for large-area (15x15 cm^2) CIGS thin-film solar cells. The system has the potential of serving as a nucleus of a pilot plant for fabrication of CIGS minimodules. It could be used for simulating full-scale production set-up. Stepper-motor controlled, linear substrate movement and uniform argon distribution set-ups were designed and built. RF tuning network was modified for optimum impedance matching. Initial problems of bowing of the backing diaphragm, possible formation of air pockets, restriction of effective water flow and consequent heating of the target material were resolved by increasing the thickness of the backing plate and redesigning the structural members. Thickness distribution was optimized by modifying the magnetic field distribution in the middle 15-cm portion of the 10x30 cm^2 magnetron sputtering sources by selectively removing nickel-coated soft-iron pieces at the rear. The present optimum configuration has resulted in thickness variation of ±3% over 11.5x10 cm^2 for Mo, CuGa, In, ZnO, and ZnO:Al layers. Magnetic field is being boosted at extremities to avoid precipitous ~15% drop beyond 11.5 cm and to achieve thickness uniformity of better than ±2% over 12.7x12.7 cm^2 and ±3% over 15.3x15.3 cm^2 areas.

2:40pm **VT-TuA3 Ultra-sensitive Detection of Helium Release from Metal Tritides**, ***J. Poths***, *T.J. Venhaus, EJ. Steinkruger*, Los Alamos National Laboratory **INVITED**

Static noble gas mass spectrometry has been in use for ultra-sensitive analysis of samples in the geological community for almost 5 decades. We have been using a magnetic sector instrument created by Al Nier at the University of Minnesota in both geological and nuclear research. In static mode of operation, the sample is equilibrated into the volume of the instrument with no pumping, rather than flowing through the source and into a pump as in a standard dynamic mass spectrometry. Thus, static operation provides a factor of 10,000 increase in sensitivity. We have recently applied this technique to analyzing the release of helium-3 from erbium ditritide films. The increased sensitivity has allowed us to compare helium release on timescales ranging from 5 minutes to 100 days. We confirm that helium release is highest at the beginning of an erbium ditritide film's lifetime, then decreases after a few months to a steady rate. Interestingly, during this period of steady-state release, the helium release rate seems to be independent of the buildup of helium-3 levels in the film. This observation suggests that at the moment of tritium decay a helium-3 atom is either immediately released or is trapped and no longer accessible for release. At steady-state, the ratio of helium released to helium decayed during storage is about 0.008.

3:20pm **VT-TuA5 Quantification of Mass Spectra in Experiments with Deuterium**, ***B. Zajec***, *V. Nemanic, M. Zumer*, Institute of Surface Engineering and Optoelectronics, Slovenia

For monitoring the interaction of gaseous hydrogen with surfaces or bulk materials, deuterium is frequently applied as a tracer gas for the quadrupole mass spectrometer (QMS) analysis. In fast and steady processes, the major peak at mass number 4 is frequently a good indicator of deuterium involved reactions while peaks at mass numbers 2 and 3 may be neglected. In slow and transient processes, the weak peaks at mass numbers 2, 3 and 4 must be considered for a quantitative analysis. Tracing reactions where deuterium molecules dissociate is troublesome since the mass number 2 overlaps with the hydrogen background. The problem to eliminate the QMS artefacts is usually solved by calibration of the instrument with a suitable low deuterium flux, but any further resolution of the background hydrogen originated from the chamber surfaces is very inaccurate. We present the results of a calibration procedure of two QMS mounted on a well outgassed UHV system, realised in a specific way. Each of the QMS was pumped in line but could be also separated from the system by a valve. A constant deuterium or hydrogen inflow was set from 10^{-8} mbar l s^{-1} to 10^{-6} mbar l s^{-1} by observing the pressure rise in the chamber by means of a calibrated capacitance manometer. The calibration of both QMS was taken in the dynamic mode for both gases. Further on, the spectra of deuterium accumulated in the UHV system for a defined period of time were compared to the calibration spectra. From the difference, we could resolve the extent of mass numbers 2 and 3 produced in the QMS from the contribution of the deuterium participated in surface reactions at the chamber wall. It was thus shown that after admittance of pure deuterium into the UHV chamber at 10^{4} mbar, its exchange with the adsorbed hydrogen led in some hours to a noticeable changed proportion of mass numbers 2, 3 and 4. This could not be predicted from the low background outgassing rate.

3:40pm **VT-TuA6 Mass Spectrometric Determination of Hydrogen and Hydrogen Isotopes from Thin Films**, ***J.F. Browning***, Sandia National Laboratories

The absolute measurement of hydrogen and hydrogen isotope concentrations in materials is of interest to many areas of both applied and fundamental research. In this work we describe a technique for the high accuracy determination of hydrogen concentration in thin films. The technique involves the thermal desorption of hydrogen from the film at a temperature of 900°C. Application of the ideal gas law to such experiments is questionable at best due to the extreme temperature range existing between the thermal desorption system and the mass spectrometer inlet system. To overcome issues associated with such extremes in temperature we use a response function technique to quantitate the total molar quantity of gas evolved from the film followed by high resolution mass spectrometric determination of the constituent components. Molar concentrations in the range 10^{-8} to 10^{-5} are routinely determined to an overall uncertainty of ±1%.

4:00pm **VT-TuA7 Quantification of Gas Load from Ultra-small GDP Capsules**, ***S.D. Balsley***, Sandia National Laboratories

A-priori knowledge of the gas composition of 10^{-8} liter capsules manufactured by General Atomics Corporation (GA) and used in inertial confinement fusion (ICF) experiments at Sandia National Laboratories' Z-pinch facility is important to experimentalists and modelers. These Z-pinch driven capsules are larger than any ever fielded by any other ICF program, and as such are part of an ongoing research program at GA and Sandia. Total pressure determinations via burst tests, although useful, lack information regarding the composition of gas mixtures. Here we present a novel technique for quantitatively determining partial pressures of gas loaded capsules whereby a low-background vacuum fixture for capsule bursting is coupled with a Finnigan-MAT 271 mass spectrometer. Typically, capsules consist of a 50µm thick polymer coated with a 3µm polyvinyl alcohol layer. Capsules are diffusion filled with a deuterium-argon mixture that is pre-defined by model calculations. Nominal fill pressures for deuterium-argon capsules are 17atm and 0.075atm, respectively. Other gas fills are also used, including deuterated methane (CD_4) mixed with minor quantities of argon or tetramethylsilane. Initial test results from several argon filled capsules agree well with stated fill pressures. Subsequent analysis of sister capsules similar to those imploded at Z-pinch in 2002 show good correlation between stated fill quantities and expected deuterium loss due to diffusion. It is envisioned that application of this technique will be important for gas fill validation of target capsules to be used in the National Ignition Facility, scheduled to begin testing in 2003-2004.

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.

4:20pm **VT-TuA8 How to Have Clean Surfaces in an Unclean World**, ***R. Robinson***, *D.D. Allred*, *A. Guillermo*, *R. Sandberg*, *A Jackson*, Brigham Young University, *M.K. Newey*, University of Maryland

Clean surfaces that are exposed to the atmosphere rapidly become dirty. Even though a surface may be carefully prepared and well characterized in its preparation or deposition environment, there is no guarantee that it will remain unchanged minutes after it is exposed to the air. We will report our measurements on the amount of contamination a sample acquires from various activities including handling with various kinds of gloves, sitting face up or down in the lab for several hours, storage in wafer carriers etc. We will also discuss the use of several cleaning techniques: UV light+ozone, plasma ashing, and polymer (Opticlean) for removing dust and/or the contamination layers in preparing materials for EUV/VUV (8-110 eV) and/or AFM measurements. Experience from silicon-based microelectronics is instructive but not definitive here. Answers depend in part on the identity of the surface. XPS shows the presence of carbon and oxygen in most contamination layers. Spectroscopic ellipsometry's advantages include: it can be used in air, measurements are rapid and it is sensitive to the relative thickness of layers even in the sub nm range. Measurement is the first step to understanding which can lead to control. We are making materials for VUV and EUV (8-100 eV) optical applications where the presence of a few nanometers of carbon and/or oxygen containing materials can have a remarkable effect on the performance of the surface. A companion group is doing AFM. Here the presence of organic contamination can clog the tip. We will report our answers to questions such as: How fast does a surface acquire its accidental carbon-containing overcoat? What can be done to block or ameliorate deterioration? Can the sample be handled, cut and stored for several hours before the next measurements? How can a sample be restored or recleaned without losing its essential characteristics? When does storage introduce its own problems?

Applied Surface Science
Room: Exhibit Hall B2 - Session AS-TuP

Topics in Applied Surface Science

AS-TuP1 Observation of Preferably Electrical Activation of Boron Implanted at Low Energy by Scanning Capacitance Microscopy, ***M.-N. Chang***, National Nano Device Laboratories, Taiwan R.O.C., *D.-H. Deng*, National Tsing Hua University, Taiwan R.O.C., *C.-Y. Chen*, National Nano Device Laboratories, Taiwan R.O.C., *J.-H. Liang*, National Tsing Hua University, Taiwan R.O.C., *F.M. Pan*, National Nano Device Laboratories, Taiwan R.O.C.

Ultrashallow doping is one of the technical trends on ultra large-scale integrated circuit. Low energy ion implantation combined with rapid thermal annealing (RTA) is necessary to obtain required ultrashallow doping profiles. It is well known that scanning capacitance microscopy (SCM) is a promising technique providing two-dimensional (2D) doping profiles. In this work, we have provided a new method employing plane view SCM images to investigate the lateral carrier distribution in ultrashallow p^+ junctions formed by BF_2^+ implantation at low energies. RTA processes were performed at 550, 850 and 1050 °C for different anneal times from 5 to 120 seconds in N_2 ambient. The width and pitch of the designed grating pattern are 0.8 and 2 μm, respectively. The SCM image clearly shows the existence of a transition region at each pattern edge of which the width reveals the carrier concentration gradient of the lateral p-n junction. For the same anneal time, the sample annealed at 850 °C exhibits a wider transition region than the one at 1050 °C, indicating that more electrically active boron atoms can be obtained at higher anneal temperatures. The SCM signal intensity, i.e., dC/dV, is a function of the free carrier concentration of the implanted region. Comparing the dC/dV profiles across the implantation pattern for the samples treated under different RTA conditions, one can find that less implanted boron atoms at the pattern edge are electrically activated than at the center region. According to this study, the edge effect will significantly affect the lateral carrier concentration distribution upon RTA processes when the pattern size decreases.

AS-TuP2 Development of a Large Area XPS Imaging Instrument, *T. Tazawa, M. Kato, M. Kudo,* ***Y. Iijima***, *K. Tsutsumi*, JEOL Ltd., Japan

Recently, the photoelectron image measurement by XPS has become a very general surface analysis method. However, the measurement over the whole sample surface is very difficult because the measurable image region by the micro analysis in XPS is small. We developed an XPS instrument which is able to measure the region covering from 30x30μm^2 to 50x18mm^2. The photoelectron image measuring method is the stage scanning method. The minimum image resolution of this instrument is 30μmm or less. For this instrument, a newly designed magnetic lens was developed to achieve a better performance than the static lens system. This magnetic lens to measure a micro area is placed under the sample stage. In addition, the X and Y axes of sample stage can be operated by an accuracy of 1μm. The maximum operation ranges of the X and Y axes are 0-50mm and 0-18mm, and they are controlled by a PC system. We obtained photoelectron images of a polymer surface and a hard disk surface with this XPS instrument, polymer surface and hard disk surface. The results show that the large area XPS imaging analysis is very effective in the measurement of element distribution and chemical states of the sample surface by surface analysis. So we can say this instrument as "Chemical state image XPS". Moreover, the total reflection XPS (TRXPS) measurement function was added to this XPS instrument. TRXPS is a new surface analysis method, has sensitivity several times higher than XPS in surface analysis of the semiconductor such as Si wafers.

AS-TuP3 Compensating for the Ubiquitous Hydrocarbon Overlayer to Enable Quantification of the Elemental Composition from XPS; the Air-formed Film at the Aluminium Surface, *M.R. Alexander, G.E. Thompson,* ***X. Zhou***, UMIST, UK, *G. Beamson*, Daresbury Laboratories, UK

Air-formed and anodic films at the surface of aluminium are of considerable technological importance. The chemistry of the surface is relevant to the performance of coated and bonded aluminium; XPS is a powerful tool in characterising this surface.[1] Unfortunately, when an overlayer of hydrocarbon contamination is present on the air-formed oxide film, quantification of the elemental composition using XPS requires a correction to account for the greater attenuation of lower KE photoelectrons. Different methods have been developed to correct for this effect that do not require etching or angle resolved measurements. These include the Ebel model and modifications of this approach,[2] the Evans approach[3] and the Vereecke and Rouxhet method.[4] Application of these methods is compared for a range of overlayer thickness using a plasma polymerised hexane coating (ppHex) as a model for hydrocarbon contamination. The thickness was measured using in situ quartz crystal microbalance, XPS signal attenuation and TEM. A stable and reproducible hydrothermally-formed pseudoboehmite (AlOOH) sample is used with hydrocarbon contamination as low as [C]=1 at%.[5] Application to relevant systems is considered.

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AS-TuP4 Multivariate ToF-SIMS Image Analysis of Patterned Protein Surfaces, ***B. Wickes***, *D.G. Castner*, University of Washington

Novel biomaterial surfaces are being developed to specifically interact with their biological environments. These surfaces are patterned with multiple species of biomolecules to generate regions of differing bioactivity. The chemical structure of these surfaces must be characterized at high spatial resolution. Static Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) imaging offers a modality for simultaneously visualizing the spatial distribution of multiple surface species. Because ToF-SIMS images yield a full mass spectrum at each pixel, it is possible to use characteristic mass fragments to identify and differentiate regions of different chemistry with a spatial resolution of approximately one micron. However, these datasets can be challenging to analyze because of their large size, complex chemistries and low ion counts per pixel. The combination of spectral data denoising and multivariate image analysis provides a convenient method to process ToF-SIMS images. Wavelet filtering followed by Principal Components Analysis (PCA) was applied to ToF-SIMS images. For example, the raw image data from a patterned poly(ethylene oxide) (PEO)-protein surface showed contrast in over 50 peaks; the resulting PCA model compressed the contrast from the raw data into two variables describing the variation between the protein- and PEO-regions, and the background and a defect region, respectively. Applying PCA to filtered image matrices removes user bias in peak selection and allows use of the full mass spectrum at each pixel. It highlights the peaks important in the chemical image and yields a new set of variables identifying the chemistries responsible for the image contrast.

AS-TuP5 Thermally Isolated Support Membrane for Low-noise Si JFET Amplifiers, ***Y. Bae***, *J. Podosek, M. Yun, J. Bock, K. Sukhatme, E. Jones*, Jet Propulsion Laboratory

A thermally isolated JFET module was fabricated at JPL to work with a high-sensitivity Bolometer that operates at a low temperature, ~300mK. The JFET module provides 24 differential pairs of JFETs, which need be warmed to 130K to provide optimal noise performance, 7nV/rtHz. Each channel has 2 feedback resistors and source, drain, gate, etc. electrical leads. However, power from the JFET electronics is dissipated on the 10K helium vapor-cooled stage of the Herschel cryostat, and the dissipation needs to be minimized to not affect the hold time and temperature of the liquid-helium. Although the JFETs are capable of satisfying the noise and power requirements, the design of the thermal isolation stage dominates the thermal dissipation requirement and presents a significant design challenge. We have devised a novel suspended nitride membrane to provide thermal isolation while satisfying the vibration and thermal cycle environment of a cryogenic space borne instrument. The JFET module needs to meet Bolometer's setup requirements: 1) a voltage noise performance less than 7nV/rtHz/JFET and 2) heat dissipation less than 3.5mW/module. Siliconix U401 JFET differential amplifiers must be heated to 130K to meet the 7nV/rtHz noise requirement. The silicon nitride membrane acts as a 2-D heat flow, so minimizing its thermal conductance is best achieved by reducing the membrane thickness or perforating the membrane. We present tests of the thermal conductance of several membrane architectures, and have carried out through testing of a complete 1.8micron silicon nitride assembly populated with JFET dies. The complete JFET module was characterized in functions of the power and voltage noise. The module passed shock environment test, 15g 400 - 2500Hz sine sweep, and passed thermal cycling to 77K, however it exceeded the heat dissipation requirement. Our test data on thinner membranes indicates we can meet the dissipation requirement with a 1.0micron membrane.

AS-TuP6 Non-destructive Depth Profiling Analysis of Surface Oxidation of b-FeSi$_2$ Thin Film on Si (100) by SR-XPS, ***T. Saito***, *H. Yamamoto, K. Yamaguchi,* Japan Atomic Energy Research Institute, *M. Haraguchi,* Ibaraki University, Japan, *T. Nakanoya,* Japan Atomic Energy Research Institute, *M. Imamura, N. Matsubayashi, T. Tanaka, H. Shimada,* National Institute of Advanced Industrial Science and Technology, Japan, *K. Hojou*, Japan Atomic Energy Research Institute

The formation process of iron silicid (β-FeSi$_2$) films on Si single crystal surfaces has been extensively studied because of their excellent characters as semiconductors. It is well known that stable β-FeSi$_2$ films are not oxidized even under ambient atmospheres. However, the oxidation behaviors of the topmost surface layer of β-FeSi$_2$ are not well understood. In the present study, we investigated the surface oxidation of β-FeSi$_2$ thin films formed on a Si (100) surface by means of synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) to obtain the information on the surface chemical state and the depth distribution of chemical components. The β-FeSi$_2$ films (10 - 100 nm) were formed by ion beam sputter deposition method (IBSD) or solid phase epitaxy method (SPE) at a substrate temperature of 973 K. After formation of β-FeSi$_2$ phases, the samples were exposed to oxygen or air at room temperature. SR-XPS depth-profiling analyses revealed formation of β-FeSi$_2$ islands on the substrates. The comparison of experimental results with simulation results using inelastic mean free paths (IMFP) of photo-electrons in Si and Fe revealed that about 50 - 70 % of the substrates surface were covered by β-FeSi$_2$ phases. In addition, the topmost surface of β-FeSi$_2$ and exposed Si substrates are almost completely covered by uniform thin SiO$_2$ layers. The thicknesses of the oxide layers were estimated at about 1.0 nm. These results indicated that thin surface SiO$_2$ layers behaved as a protective layer for further oxidation of β-FeSi$_2$ surfaces.

AS-TuP7 Surface Characterisation of Fluorinated Polyether Ionomers from Aqueous Dispersions, ***R. Canteri***, *G. Speranza, M. Anderle,* ITC-irst Centre for Scientific and Technological Research, Italy, *S. Turri, S. Radice,* Ausimont Spa Research & Development Centre, Italy

The introduction of perfluoropolyether (PFPE) bifunctional macromers, in polyurethane coatings[1,2] has lead to a substantial improvement of the durability characteristics and surface properties of the material, while maintaining the advantage of an easy application technology in a variety of environmental conditions and temperatures.[3] In this work we present a surface characterisation by TOF-SIMS and XPS of a new series of polymer thin films containing PFPE macromers, applied in form of PolyUrethane Aqueous Dispersions (PUAD). In fact, environmental issues are forcing the development of waterborne polymer systems (dispersions or emulsions) in order to reduce the problems of solvent emissions in the atmosphere. The PUAD systems presented in this work can be defined as polyurethane ionomers, since self-dispersion in water is achieved by using co-monomers containing a NR$_3$ or a -COOH group, which can be salified with acids or bases. It is known that many of the performances of the coating, like low surface energy (water and oil repellence), lubrication and low friction etc, are related to the capability of fluorinated structures to stay close to the polymer-air interface. The analysis of the outermost layer of the dried waterborne coatings by TOF-SIMS is compared with analyses by XPS obtained at two different angles (90° and 15° take off angle) for sampling different thickness. These results are finally compared with those obtained on the solventborne crosslinked coatings[4] containing similar PFPE macromers.

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AS-TuP8 A New Transparent Conducting Oxide: Indium Molybdenum Oxide (In_2O_3 : Mo), ***Y. Yoshida***, Colorado School of Mines, *T.J. Coutts, T.A. Gessert,* National Renewable Energy Laboratory

We report our preliminary work on a new transparent conducting oxide, indium molybdenum oxide (IMO, 4% Mo), prepared by radio frequency magnetron sputtering (RF sputtering). Other works have recently reported that thermal reactive evaporated thin films of IMO showed an exceptionally high mobilities of 80 - 130 cm^2 V^{-1} s^{-1}.[1] To study further the functionality of molybdenum in IMO, and to test if the large-area deposition capability afforded by RF sputtering can produce high mobility, we produced In_2O_3 (IO) and IMO films in an argon and oxygen atmosphere at a substrate temperature of 350°C. Electrical properties were studied as a function of the ratio of oxygen to argon (O_2/Ar) from 0 to 1. We found that the best film properties resulted when a small O_2/Ar ratio was used (≤ 0.3). IMO films grown at 0.005 O_2/Ar achieved a mobility of 37.5 cm^2 V^{-1} s^{-1}, a carrier concentration of 1.16 x 10^{20} cm^{-3}, a resistivity of 5 x 10^{-3} Ω-cm, and ~70% transmission in a visible range (400nm - 900nm). IO film quality was optimized at ~0.025 O_2/Ar, resulting in a mobility in the range of 20 - 30 cm^2 V^{-1} s^{-1}, carrier concentration of 2.03 x 10^{18} cm^{-3}, and resistivity of 9.98 x 10^{-2} Ω-cm. IMO films showed much better electrical properties than the undoped IO films grown under the same range of conditions. X-ray photoelectron spectroscopy (XPS) confirmed the presence of molybdenum 6+ in the films. X-ray diffraction (XRD) analysis confirmed phase purity in the films and possible texture changes due to variations of the amount of oxygen in the system.

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AS-TuP9 SIMS Analysis of Copolymers: A Test for Statistical Ordering, *A.G. Shard,* University of Sheffield, UK, ***S. Clarke***, *M.C. Davies*, University of Nottingham, UK

Statistical copolymers of lactic and glycolic acids (PLGA) have been investigated by SIMS. The composition of the copolymer can be determined through analysis of the intensities of secondary ions which contain several monomer units, as described previously for non-statistical copolymers.[1] We describe here a method for determining whether the SIMS data are consistent with the copolymer being statistical. This method is applicable to any copolymer, the only requirement being the detection of secondary ions containing two or more monomer units. This information is used to determine the relative ion yields of selected secondary ions in the SIMS spectra of PLGA and the invariance of ion yields across a large composition range is shown, validating our previous work.

[1] Shard AG, Davies MC, Li X, Volland C, Kissel T, Macromolecules 30, 3051, 1997.

AS-TuP10 Impurity Dopant Profile Measurement and its Quantitative Analysis using Nano Capacitance-Voltage (NCV) Method, ***E.-S. Kang***, *H.-J. Hwang,* Chung-Ang University, Korea, *G.-Y. Lee*, Samchok National University, Korea

It is well known that commercial scanning capacitance microscope (SCM) systems are not easy to obtain the local dC/dV curves over the dopant range of 1020 - 1018cm-3 because of smaller depleted volume charges generated under the surface by SCM tip size. This problem will prevent us from acquiring quantitative carrier depth information correctly. To do this, it needs the developing of robust capacitance sensor and the more powerful SCM modeling. For the more accurate inverted dopant profile in higher dopant area, therefore, we have added some factors such as SCM tip/sample interaction and fully calculated volume charges into previous modeling parameters. In addition, we have developed a new capacitance sensor operating about 1.7GHz frequency bandwidth. The capacitance sensor used in commercial SCM has been using the amplitude modulation method. However, we have taken the frequency modulation technique for increasing the accuracy in higher dopant area. This new capacitance sensor consists of a voltage-controlled oscillator with controlled voltage, a microstrip resonator, and a RF mixer IC and PLL (Phased-Lock Loop) for detecting the capacitance variations. We have called this system Nano Capacitance-Voltage (NCV). This technique will bring a greater enhancement for the current SCM sensitivity and performance.

AS-TuP11 A Quantitative Comparison between Rutherford Backscattering and Time-of-Flight Medium Energy Backscattering, *B.R. Rogers,* ***R.D. Geil***, *Z. Song, D.W. Crunkelton, R.A. Weller, V. Pawar,* Vanderbilt University

Both conventional Rutherford backscattering (RBS) and time-of-flight medium energy backscattering (ToF-MEBS) have been used to determine the thickness and stoichiometry of thin dielectric films (Al_2O_3) deposited on silicon, and a comparison is made between the two ion beam techniques. The characterization of these films is important in optimizing the deposition process and ultimately the film properties. The conventional RBS and ToF-MEBS systems are capable of 1.8 MeV and 270 keV He$^+$ beams, respectively. ToF-MEBS is a lower energy derivative of conventional RBS that offers improved depth resolution and sensitivity at the expense of total analyzable depth and ease of use.[1] Channeling was performed with both systems to suppress the substrate signal and enhance the signal from the thin dielectric film. Grazing angle analysis was performed with the RBS system to increase particle path length in the sample, thereby improving depth resolution. It was found that for films less than about 200 Å RBS had little sensitivity to the thin Al_2O_3 films while ToF-MEBS detected Al and O in films that were tens of angstroms in thickness.

[1] Weller, Robert A. Introduction to Medium-Energy Ion Beam Analysis. Methods in Materials Research (2000) 12b.1.

AS-TuP12 SIMS Depth Profiling of Multilayer Structures, ***A. Godines***, *Yu. Kudriavtsev, A. Villegas, R. Asomoza*, CINVESTAV-IPN, Mexico

In this work we performed a comparative study of the depth resolution function for metal and semiconductor multi-layers in depends on primary ion kind, primary ion energy and angle of incidence. Influence of oxygen flooding on the depth resolution was analyzed as well. Subject of our study was different test semiconductor multi-layers grown by MBE: AlAs/GaAs, AlGaAs/GaAs, GaAsN/GaAs, InGaAs/GaAs, AlGaN/AlN, as well as metal multi-layers (neutron super-mirrors): Co/Ti and Si/Fe. The number of layers has varied from 20 to 200; the thickness of an individual layer has varied from 1 monolayer to about 20nm. Sputtering was performed by cesium and oxygen positive ions. SIMS depth resolution depends on many different factors and effects such as surface roughness and surface roughness caused by ion bombardment, ion mixing effect, radiation enhanced diffusion and so on. In our work the ion mixing was found as the main effect affecting the depth resolution of semiconductor multi-layers. Parameter, which characterizes it, was found being proportional to the root square of the primary ion energy, normalized on the cosine of the angle of incidence, for both metal and semiconductor multi-layers. We did not find any mass dependence of the depth resolution that is in a contrast with the ballistic mixing model. Oxygen ion bombardment leaded to a dramatic reduce of the depth resolution in the case of metal multi-layers, because of a strong surface roughness formation. Moreover, a strong matrix effect was found at the interfaces of metal layers, which was more pronounced in the case of cesium ion bombardment. In order to reduce the matrix effect, we applied the oxygen flooding. This technique: Cs+ ion bombardment with CsM+ (where M is the analyzed element) secondary ions monitoring and with simultaneous oxygen flooding was found as the best method for metal multi-layer depth profiling.

AS-TuP13 Sample Topography Developed by Sputtering in Cameca Instruments: an AFM and SEM Study, ***E. Iacob***, *M. Bersani, A. Lui, L. Vanzetti, D. Giubertoni, M. Barozzi, M. Anderle*, ITC-irst, Italy

Secondary ion mass spectrometry (SIMS) is based on ion sputtering. Removing atoms layer by layer we can get a satisfactory depth distribution analysis. To obtain a suitable depth resolution for semiconductors applications low impact energy and glancing angles are mandatory. However high dose ion bombardments results in a change of surface topography causing problems in quantitative analysis and depth resolution deterioration. The morphological artefacts on the crater surface, depend on various SIMS sputtering parameters and samples conditions. The induced morphology by ion sputtering require detailed characterization. In this work we analysed, by using of Atomic Force (AFM) and Scanning Electron (SEM) Microscopies, the morphological effects induced by ion bombardment on various samples: monocristalline Si <100>, polycrystalline Si and amorphous silicon oxide. Topographic irregularities, induced by SIMS analysis are studied showing the dependence on sputtering condition. We used different instruments (Cameca Sc-Ultra and Cameca 4f) comparing the effect of analytical conditions as impact angle, incidental ion species, ion dose and impact energy. The goal is to determine best parameters to minimize roughness and surface irregularities considering or not the employment of the sample stage rotation.

AS-TuP14 Comparison of Experimental Protocol for Low Energy Sputter Yield Measurements of Advanced Materials as a Function of Sputtering Angle, ***V.S. Smentkowski***, General Electric - Global Research Center, *S. Hu*, Lockheed Martin

We will report two different experimental protocol that can be used to measure the sputter yield of advanced materials as a function of sputtering angle. One protocol uses standard surface analytical instrumentation while the second protocol utilizes a home built system containing a broad-beam (Kaufman) ion source. Low energy (350 eV and below) Xe was used for all measurements. When the samples were sputtered at normal incidence, the data generated using the two protocol agreed, however as the sputtering angle increased a divergence was noted in the data sets. It will be demonstrated that the divergence correlates with a change in the surface topography, which biases the data generated using one of the protocol. As part of this study, we measured the sputtering yield of silicone dioxide thin films obtained from different vendors and noted that the yield varied. Possible explanations for this effect will be reported. We believe that effects such as these are partially responsible for the lack of agreement in other sputter yield measurements reported in the literature.

AS-TuP15 Mathematical Topographical Correction of XPS Images using Multivariate Statistical Methods, ***K. Artyushkova***, *S. Pylypenko, J.E. Fulghum*, Kent State University

For rough heterogeneous samples, the contrast observed in XPS images may result from both changes in elemental or chemical composition and sample topography. Background subtraction is frequently utilized to minimize topographic effects so that images represent concentration variations in the sample. For this purpose, background images are recorded at slightly lower and/or higher binding energies than the main peak for all species of interest. Background-corrected images result from subtracting a background energy map from one acquired at the peak energy. This procedure may significantly increase the data acquisition time. Multivariate statistical methods can assist in resolving topographical and chemical information from images. Principal Component Analysis (PCA) is one method for identification of the highest correlation/variation between the images. Topography which is common to all of the images will be resolved in the 1st most significant component. The score of this component contains spatial information about the topography of the surface, while the loading is a quantitative representation of the topography contribution to each elemental/chemical image. Reconstructing the data using the score and loading for the 1st component will provide mathematical background images. These images, which contain the topographical information for all elemental/chemical images, can be used to correct the images for topography in the same way the experimental background images are used, thereby reducing the time required for data acquisition. The mathematical background correction scheme is developed and validated by comparing results to the experimental background correction for three samples with differing degrees of topography. The first example is a very rough, fossilized sample, the second is a patterned sample with roughness on the order of the XPS sampling depth and the third is a flat polymer blend sample. This work has been partially supported by NSF CHE-0113724.

AS-TuP16 High Spatial Resolution XPS Analysis of Si Samples Prepared using the FIB Lift-out Technique, ***J. Fenton***, *A. Ferryman, J.E. Fulghum*, Kent State University, *L.A. Giannuzzi*, University of Central Florida, *F.A. Stevie*, North Carolina State University

The goal of this project is to assess Ga+ contamination on Si in order to elucidate artifacts due to focused ion beam (FIB) milling. The FIB instrument has witnessed an increase in use from machining and processing to specimen preparation. However, the surface chemistry alterations, gallium implantation damage region, and residual effects of FIB sample preparation are not well understood. It is imperative that we understand the chemical and morphological alterations that this instrument may cause to its target, if correct interpretations regarding structure/property relationships of materials are to be made. FIB is currently most often used to prepare samples for microscopic techniques such as TEM, which have a higher spatial resolution than most surface analysis methods. Improvements in imaging and small area analyses have made X-ray photoelectron spectroscopy (XPS) an increasingly useful characterization technique for such samples, however. Utilizing spectra-from-images capabilities enables the acquisition of spectra from areas of ~ 1 micron in diameter, allowing for surface chemical characterization of FIB lift-out samples. This poster will discuss the use of XPS imaging and small area spectroscopy to characterize surface oxidation and Ga contamination in Si (100) prepared by the FIB lift-out method.

AS-TuP17 Elucidation of Three-Dimensional Structure in Polymer Blends using Correlated Confocal Microscopy and XPS Imaging, ***L.A. Broadwater***, *K. Artyushkova, I. Smalyukh, O. Lavrentovich, J.E. Fulghum*, Kent State University

The complexity of heterogeneous polymeric materials makes it difficult to distinguish between alternative morphologies using a single analytical technique. Knowledge of both polymer surface chemistry and component distribution with depth can be important. In this study, blends of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) have been investigated using confocal microscopy and imaging XPS. Confocal microscopy provides the distribution of phase separated areas as a function of depth (on a scale of microns), while XPS provides the surface distribution of phase separated regions. Conclusions based upon these comparisons will be compared to previous work from our group using imaging FTIR. This has been partially supported by NSF ALCOM and NSF CHE-0113724.

AS-TuP18 Correlative XPS and AFM: Chemical Phase Identification in Polymers, ***J. Farrar***, *K. Artyushkova, J.E. Fulghum*, Kent State University

AFM can be utilized to provide both topographical and phase contrast information from polymeric materials. AFM phase contrast images potentially contain chemical information, although image interpretation can be challenging. XPS images contain chemical phase information, but at a significantly different spatial resolution. In this study we evaluate methods for the correlation of images with varying spatial resolutions, focusing on XPS and AFM. Processing for image correlation includes resizing, image alignment and resolution matching. Following imaging processing, classification methods are used to correlate components present in XPS and AFM images. Data from a variety of polymer samples will be used to demonstrate that classification of XPS and AFM images can be used to identify chemical phases in AFM images. This work has been partially supported by NSF ALCOM (DMR89-20147) and NSF CHE-0113724.

AS-TuP19 Surface Studies of Corrosion of Stainless Steel by Lead-Bismuth Eutectic, ***A.L. Johnson***, *D. Koury, B. Hosterman, D. Parsons,* University of Nevada, Las Vegas, *D. Perry,* Lawrence Berkeley National Laboratory, *J. Farley*, University of Nevada, Las Vegas

The corrosion of stainless steel by lead-bismuth eutectic (LBE) has been studied using various types of surface analysis, including Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectrometry (XPS). The goal is to understand the chemical reaction products and chemical reactions involves in the corrosion. The atomic composition of steel samples has been examined as a function of position. Sputter depth profiling has been employed to study the atomic composition as a function of depth. High resolution XPS studies reveal the oxidation state of the various elements. We have examined both unexposed steel samples and steel samples that have been exposed to LBE for various lengths of time for different temperatures. Crucial differences between the unexposed and exposed samples are demonstrated in the data. For example, nickel is present at the surface of the unexposed samples, but absent from the exposed samples. The latest experimental results will be presented and mechanistic implications discussed. This work was supported by the U. S. Department of Energy under the AAA UPP Program (UNLV) and Contract Number DE-AC03-76SF00098 (LBNL).

AS-TuP20 Initial Tests of a Draft Protocol for Wide Scan XPS Measurements, ***M.H. Engelhard***, *D.R. Baer,* Pacific Northwest National Laboratory

In May 2002 an international workshop on developing an expert XPS system was held in St. Malo, France. One output of that workshop, developed by a task group lead by Prof. James Castle, was a draft protocol for collecting a maximum amount of information from wide scan data. Although similar to approaches already used in some laboratories, the protocol is significantly different than the default wide scan spectra for most instruments and suggests that a significant amount of information can be routinely extracted from wide scan data that is generally ignored or missed. Although parts of the draft protocol (step size, scan width and preliminary charge correction) are common practice for use of our Quantum 2000, other parts (energy resolution, analysis for layered structure) are different than our usual practice. This paper reports our preliminary experience in a manual application of the initial version of this draft protocol to "routine" samples in our laboratory.

This work was conducted in the Environmental Molecular Sciences Laboratory, a U. S. Department of Energy User Facility run by Battelle Memorial Institute.

AS-TuP21 Surface Characterization of Nanoparticles for Cast Dispersion Strengthened Metal Matrix Nanocomposites, ***A.L. Linsebigler***, *V.S. Smentkowski, T. Angeliu,* General Electric Global Research Center

Oxide dispersion strengthened (ODS) metal matrix composites possess very stable nano-particles that provide strength at elevated temperatures, but have found limited commercial application due to complex processing and cost constraints. Solidification processing has been pursued as one of the most cost effective and versatile methods to produce metal matrix composites. However, composites produced by casting have significant challenges in wetting the surface of an oxide particle by molten metal. Particle wetting can be influenced by physisorbed and chemisorbed surface species and oxide stoichiometry. Surface characterization studies have been conducted on as-received and heat-treated alumina nanoparticles by SEM, AES, TOF-SIMS, and TPD methods. The roles of adsorbed species and surface functionalization on the wetting and dispersion of these nanoparticles in metal alloy matrices will be discussed.

AS-TuP22 Basic Characterization of Arcing in Sputtering Targets, ***F.G. Tomasel***, *D. Carter, H. Walde, J.J. Gonzalez, G.A. Roche,* Advanced Energy, Inc.

Arcing in sputtering deposition is a very well known phenomenon that affects quality of thin films. Different strategies have been devised to reduce arcing during the deposition process. However, it is felt that there is still a need for a further description of the basics of arc formation. This article intends to contribute in this subject by presenting a detailed description of the formation and evolution of arcs. The study combines the spatial and time resolved results of ultra high-speed, single frame photographs with an electrical characterization of the current and voltage waveforms for arcs occurring on different sputtering targets. Elaborating on these data, we will present a possible explanation for the results observed.

AS-TuP23 Characterization of Plasma Source Ion Implanted Stainless Steel for High Voltage Applications, ***N.D. Theodore***, College of William and Mary, *C. Hernandez,* Jefferson Lab, *D.M. Manos,* College of William and Mary, *H.F. Dylla,* Jefferson Lab, *R. Moore,* University at Albany Institute for Materials, *T. Siggins*, Jefferson Lab

Properly modifying the surface of stainless steel to increase efficiency or output power is useful in high voltage electrical pieces seen especially in particle accelerators for research and medicine, high-power radar, DC electron guns, and high power microwave tube and waveguide systems. In this study, highly polished stainless steel test pieces were processed in our integrated PSII/PVD system, which is capable of implanting ions while simultaneously depositing high purity SiO_2. Previous studies have shown that the suppression of field emission is enhanced in harder, smoother surfaces, and that nitrogen-implanted stainless steel increases surface hardness. Our recent work has shown that the suppression of field emission increases by an order of magnitude in surface-processed samples.[1] This study compares the surface character of unprocessed stainless steel with nitrogen-implanted stainless steel and nitrogen-implanted, SiO_2-deposited stainless steel using electric field microscopy, atomic force microscopy, micro-hardness testing, and Auger electron spectroscopy. The relative effectiveness of various surface-processing methods in reducing field emission will also be discussed. This work supported by the US Dept. of Energy and the Office of Naval Research.

[1] C. K. Sinclair, et al. "Dramatic Reduction of DC Field Emission From Large Area Electrodes By Plasma Source Ion Implantation." Proceedings of the 2001 Particle Accelerator Conference.

AS-TuP24 Nano-scale Mapping of Surface-photo-voltage by Scanning Tunneling Microscope : Ag/Si(001), ***O. Takeuchi***, *S. Yoshida, H. Shigekawa*, University of Tsukuba, CREST, Japan

It has been a subject of great interest to investigate the nanoscale spatial distribution of surface photo voltage (SPV) on semiconductor surfaces. In general, SPV measurement studies the change in band bending at semiconductor interfaces as a function of the external illumination, which offers information about local band diagram including band gap structure and mid-gap confined states as well as local density, diffusion length and lifetime of carriers. Thus, measurement of SPV with high spatial resolution opens a way for precise control of defect and dopant density in a specific nanostructure and investigation of its characteristics. In this study, we have mapped the nano-variation of SPV for partially covered Ag/Si(001) system with conventional scanning tunneling microscope (STM) from OMICRON, in UHV at 300 K and 80 K. To measure SPV, current-voltage curve (IV curve) measurement was performed while 2 mW HeCd laser beam was focused onto tunneling gap with mechanical chopping at 20 Hz. The spot diameter was about 0.1 mm. Since, the obtained IV curve gives the IV curves on dark and illuminated conditions simultaneously, SPV can be retrieved as lateral displacement of the two IV curves as a function of bias voltage. Spatial mapping was realized by performing the SPV measurement in grid points during conventional STM topograph imaging. Clear dependence of SPV on the distance from the two-dimensional Ag islands as well as linear dependence of SPV on bias voltage with static tunnel gap distance was observed.

Biomaterials
Room: Exhibit Hall B2 - Session BI-TuP

Biointerfaces and Surfaces I

BI-TuP1 Computer Simulation of Water Near Structureless Model Surfaces and Self-assembled Monolayers: Interfacial Behavior and Hydration Forces, ***T. Hayashi***, *A.J. Pertsin, M. Grunze*, Heidelberg Universität, Germany

The hydration forces between both structureless and structured surfaces are calculated using the grand canonical Monte Carlo technique. Primary attention is given to large surface-to-surface separations (40 Å and more), where the oscillations of the hydration force have practically decayed. For simulations of structureless surfaces, both orientation independent and strongly directional potentials are employed. Our results show that water confined between hydrophobic surfaces experiences a capillary evaporation at surface-to-surface separations less than about 58 Å. At larger separations, hydrophobic attraction due to a density depression in the confined region is observed. In cases of hydrophilic surfaces, the sign and magnitude of hydration force are found to be strongly dependent on the presence of orientation dependent terms in the water-surface potential. Simulations of structured surfaces were performed with methoxy tri(ethylene glycol) terminated alkane thiol self-assembled monolayers (SAMs) on the Au(111) and Ag(111) substrates. Although both of the SAMs show a typical hydrophobic behavior similar to that observed with structureless hydrophobic surfaces, there are substantial differences in their interaction with water. The simulation results are discussed in the context of the experimentally observed protein adsorption properties and surface force behavior between the SAMs.

BI-TuP2 Permittivity Responsive Interface for Biosensor in Tissue Engineering, ***P.O. Bagnaninchi***, *M. Tabrizian*, Mc Gill University, Canada

We have designed micro-porous host medium which fit with requirements for permittivity changing interface. The main application is the assessment of the growth of cells in micro-porous matrix for tissue engineering. These biointerfaces will be used with evanescent wave transducer or Inter Digital Capacitance since they are based on the change of permittivity in a surrounding medium. The complex biological medium is heterogeneous and our approach to describe the macroscopic dielectric behaviour of this mixture in terms of the bulk properties of the constituents is based on and derived from the effective medium theory; which is valid as long as the wavelength of electromagnetic wave is larger than the size of heterogeneities. Our method allow us to design permittivity responsive matrix and to improve the sensitivity of the biosensor in order to assess in a non-destructive way the growth of cells in micro-porous matrix. In this study the biointerface is characterized by complex permittivity measurement over a wide frequency range with the aid of a dielectric probe and network analyser.

BI-TuP5 Interaction of Poly(L-Lysine)-g-poly(ethylene glycol) with Negatively Charged Supported Phospholipid Bilayers, ***F. Rossetti***, Swiss Federal Institute of Technology, *I. Reviakine*, University of Houston, *G. Csucs, S.M. De Paul, J. Vörös, N.D. Spencer, M. Textor*, Swiss Federal Institute of Technology

The goal of the study presented in this poster is to develop a general, one-step method for modifying the surfaces of different types of vesicles. The proposed idea is to coat negatively charged phospholipid or polymeric vesicles with functionalised Poly(L-Lysine)-g-poly(ethylene glycol) (PLL-g-PEG), a polyelectrolyte with a positively charged backbone and protein-resistant ("stealth"[1]) side chains. Negatively charged supported phospholipid bilayers (SPBs) were used to investigate the adsorption behaviour of PLL-g-PEG as a function of charge density. The main investigation methods used were the Quartz Crystal Microbalance (QCM-D, including measurement of dissipation) and fluorescence microscopy. The SPB system used consisted of mixtures of a zwitterionic phospholipid (dioleyl phosphatidyl choline - DOPC) and a negatively charged phospholipid (dioleyl phophatildyl serine - DOPS) in a range from 0 (neutral SPB, used as a control) to 18 mol-%. Effects of the buffer composition on the adsorption process (with particular attention to the ionic strength) and the presence or absence of Ca^{2+} ions, which were found to be crucial for the formation of an SPB from DOPC:DOPS vesicles, were also considered.

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[1] Woodle, M.C., Lasic D.D., Biochim. Biophis. Acta, 1992, 1113, 171-199.

BI-TuP6 Derivatization and Surface Characterization of poly(2-hydroxyethyl methacrylate) for Oriented Protein Immobilization, ***J.L. Schwartz***, *S.M. Martin, D.G. Castner, C.M. Giachelli, B.D. Ratner*, University of Washington

When biomaterials are placed in the body they are immediately covered with a random layer of mixed proteins. This may trigger the foreign body reaction leading to collagenous tissue encapsulating the biomaterial. To circumvent this, many schemes have been developed to pre-immobilize a protein or peptide onto the surface intended to subdue the inflammatory response. The goal of this study is to immobilize osteopontin (OPN) in a single orientation such that the active site is presented to the surface for optimal cellular interaction. Proteins can be immobilized via a primary amine from a lysine unit, but due to the number and distribution of lysine in OPN there is no control over the final orientation. A different approach is to immobilize OPN engineered with a polyhistidine tail, which can interact with the coordination sites of a divalent metal ion. The recombinant six-histidine (His-tag) sequence does not hinder protein activity and can be placed at a characteristic site on the protein of interest. The divalent metal ion, Ni^{2+}, binds tightly to nitrilotriacetic acid (NTA), a metal chelating agent covalently attached to poly(2-hydroxyethyl methacrylate) (pHEMA) via a N,N-carbonyldiimidazole (CDI) intermediate reaction step. The choice of pHEMA as the immobilizing substrate was due to the abundance of hydroxyl groups on the surface as well as low non-specific protein adsorption. These surfaces were characterized by XPS and ToF-SIMS before and after chemical derivatization as well as after each reaction step. Derivatization with fluorine containing molecules was used to probe hydroxyl, carboxyl, and imidazole carbamate availability with XPS. The amount of protein immobilized to pHEMA was quantified by ^{125}I radiolabeled OPN and the protein was tested for retained biological activity.

BI-TuP9 Polysaccharide Adsorption on Hydrophobic and Hydrophilic Surfaces, ***K.T. Queeney***, *C. Royce*, Smith College

The interaction of extracellular polysaccharides with solid substrates plays an important role in the adhesion of bacterial cells to a variety of natural and synthetic surfaces. We have used a combination of surface infrared spectroscopy and atomic force microscopy to investigate the fundamental chemical interactions that govern the adsorption behavior of such polysaccharides. The adsorption of xanthan gum, a model polysaccharide, is studied on silicon and silica surfaces that have been modified to present a range of both surface wettability and chemical functionality. Adsorption is monitored both in- and ex-situ, using a custom-designed cell for infrared spectroscopy at silicon/aqueous interfaces. Simultaneous studies of the adsorption characteristics of the constituent monosaccharides of xanthan provide a way to assess the importance of effects such as polymer conformation and polymer-polymer interactions in the adsorption process. For instance, while monosaccharides exhibit similar adsorption characteristics on hydrophilic, silanol-terminated silica and hydrophobic, hydrogen-terminated silicon, xanthan exhibits a marked preference for the hydrophobic surface. The importance of adsorbate-adsorbate interactions in the adsorption of both poly- and monosaccharides is explored through analysis of spectral evolution from mono- to multilayer regimes.

BI-TuP10 Plasma Treatment of Plastics to Reduce Water Adhesion and Bio-fouling, ***M.J. Neumann***, *P.J.A. Fackler, D.N. Ruzic*, University of Illinois at Urbana

Polymers have become a part of our everyday lives for use in a wide range of applications. This is due to polymers exhibiting high strength with little weight, wide range of flexibility, ease of formability, and economics of production. However, processes designed to achieve the desired surface properties of a polymer can comprimise 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. By modifying the surface of a polymeric material so as to impede water adhesion, the ability of bacterial and cell growth and hence, infection, can be minimized on those surfaces that are incorporated into biological systems. Surface modification was accomplished via plasma processing in a commerical size plasma etching device which achieves plasma densities and and electron temperatures up to 10^{11} cm^{-3} and 4 eV. The desired degree of change is controlled by macroscopic external controls, rather than invasive internal modifications. This process lends itself well for use in exisiting plasma processing systems. Water contact measurements have been taken before and after treatment of HDPE that show a change from a pretreatment of 85° to post treatment of near 0° and 0° angles, which corresponds to a dramatic change in surface energy of the polymer. Video of the surface interaction with water shows drops rolling off the material. Applications of the process includ intubation tubes, blood vials, shunts, splints, and many other biomedical devices.

BI-TuP11 Comparison of Polystyrene and Teflon-AF as Model Surfaces for Hydrophobic Adsorption and Biocompatibilization, ***L. Feller***, *N. Tirelli, S.M. De Paul, J.P. Bearinger, A. Napoli, J.A. Hubbell, M. Textor*, Swiss Federal Institute of Technology

The motivation of this investigation is to produce materials for applications in biosensors and biomedical materials via surface modification based on hydrophobic interactions. For this purpose we have used the physical adsorption of amphiphilic poly(propylene sulfide)-block-poly(ethylene glycol) (PPS-PEG), from a polar solvent (methanol, water). Upon deposition on a hydrophobic surface, these polymers display the biocompatible, protein-repellent PEG as the top layer and are believed to maintain this architecture when placed in either water-based model electrolytes or a physiological environment. We have chosen to apply this method of surface modification to two hydrophobic materials, poly(styrene) and Teflon-AF. These materials have already been used in biomedical applications but which require a surface biocompatibilization to reduce unfavorable foreign-body reactions. Both polymers can be produced in form of thin films (20-50 nm thickness) via spin-coating. We studied the properties of thin films of these two hydrophobic surfaces and their behavior in subsequent PPS-PEG adsorption studies. The thickness and uniformity of spin-coated surfaces are sensitive to rotation speed and concentration. For optical waveguide lightmode spectroscopy (OWLS) investigations it is necessary to have an optically transparent homogenous thin layer of ideally 12 nm thickness. We produced a series of both poly(styrene) and Teflon-AF layers of various thicknesses and characterized their homogeneity and thickness using an Atomic Force Microscope (AFM). Layer stability was characterized by dynamic contact angle measurements. The adsorption of PPS-PEG block copolymers through hydrophobic interactions was subsequently studied by OWLS. PPS-PEG demonstrated good adsorption on both surfaces, showing complete and stable coverage under physiological conditions. Preliminary experiments have also shown that the deposited layers strongly decrease the protein adsorption on such substrates.

BI-TuP12 In-situ Single-Molecular Detection of Antibody-Antigen Binding by Tapping-Mode Atomic Force Microscopy, ***L. Li***, *S. Chen, S. Jiang*, University of Washington

Ever since its invention atomic force microscopy (AFM) has been widely used in biotechnology and biomedical research, including imaging, force mapping and sensor application. In this work, we have performed studies on AFM-based single-molecule detection. Target molecules are detected by directly comparing two tapping-mode AFM topographical images at the same location before and after exposing an immobilized antibody to a solution containing its antigen, or vise visa. Two pairs of antigen/antibody systems were investigated: chorionic gonadotropin (hCG) and monoclonal antibody (MAb) to hCG, goat anti-hCG and MAb to goat immunoglobulin (IgG). Antibody molecules are chemically immobilized on uniform mixed self-assembled monolayers (SAMs) terminated with COOH and OH, which allow the detection of the individual antigens, antibodies, and antigen/antibody complexes. The advantages of the in-situ detection at the same location include the detection of antigen/antibody binding at single-molecule resolution and the distinction of non-specific interactions from specific ones. This AFM-based immunoassay is more sensitive and reliable.

BI-TuP13 Transformation of a Single Peptide Molecule Measured with Atomic Force Microscopy, ***M. Kageshima***, *S. Takeda*, National Institute of Advanced Industrial Science and Technology, Japan, *A. Ptak*, Poznan University of Technology, *C. Nakamura, S.P. Jarvis, H. Tokumoto, J. Miyake*, National Institute of Advanced Industrial Science and Technology, Japan

Transformation of protein molecule is a fundamental process in various function of the molecule. Such a transformation is considered to accompany substantial rearrangement of intramolecular hydrogen bonds. In a peptide molecule in an α-helix form, breaking of hydrogen bonds takes place as it is unfolded by a tensile force along its helical axis and results in variation in the longitudinal stiffness of the molecule. Therefore, in order to understand the unfolding process in a single-molecule scale, measurement of the variation in stiffness and the energy dissipated during refolding process is indispensable. In the present study this measurement was implemented by AFM with magnetic modulation technique. An end of a single $C_3(AEAAKA)_6C$ peptide molecule was picked up with the AFM probe and was stretched. The AFM cantilever was modulated with an AC magnetic force with a frequency of 500 Hz via a magnetic particle on its backside. The amplitude and phase shift in the AC component of the cantilever deflection were measured simultaneously with the DC force. The dissipation during one cycle of oscillation and the variation in the stiffness of the molecule was calculated from the measured amplitude and phase. The contribution by the liquid in the measured dissipation was calculated from the amplitude signal and was subtracted. From the dissipation change during the unfolding process, the dissociation energy per one hydrogen bond was determined. Thus, it is shown that both the conservative and the dissipating processes taking place in a single molecule during its transformation can be measured with this technique.

BI-TuP14 Selective Photocatalysis by Means of Molecular Recognition, ***Y. Paz***, Technion- Israel Inst. of Technology, Israel

Titanium dioxide is known to be a non-selective photocatalyst for the treatment of polluted air and water. An approach for obtaining selectivity, thus facilitating its use for the mineralization of hazardous, non-biodegradable contaminants is presented hereby. This approach is based on the construction of molecular recognition sites (MRS) anchored on inert domains in the vicinity of photoactive sites. These MRS are designed to physisorb target molecules and to "shuttle" them to the photocatalytic sites. Care is taken to prevent the photocatalytic degradation of the MRS, since (as we have found before) the photoinduced oxidizing species are, in principle, able to attack molecules anchored in the vicinity of titanium dioxide domains. Here we present several examples of selective photocatalysis by means of molecular recognition, based on the trapping of target molecules on thiolated cyclodextrins sites, followed by surface diffusion and photodegradation of the contaminants. The prospects and limitations of this approach will be discussed.

BI-TuP15 Reflex Arc on a Chip - Directed Neuron Growth, ***M. Poeta***, *G. Jacob, M. Das, P. Molnar, J. Hickman*, Clemson University

The reflex arc is one of the simplest controls systems in the body. Yet it rivals the most complex man-made systems in complexity. The reflex arc is a controls loop consisting of a muscle fiber innervated by a motoneuron. A dorsal root ganglion (DRG) innervates both cells, completing the loop and providing feedback. Our group will look at building this system on a Micro Electrical Mechanical System (MEMS) chip. Currently, we are investigating the directed growth of motoneurons on substrates. We have created patterns of Self Assembled Monolayers (SAMs) on glass cover slips. The patterns have two geometric variables: somal (cell body) adhesion site diameter and axon (signal sending process) track width. The patterns are made of diethylenetriamine (DETA), a SAM cytophilic to motoneurons. The cover slips were then backfilled with tridecafluoro-1,1,2,2-tetrahydrooctal-1-trichlorosilane (13F), a SAM cytophobic to motoneuron growth. Photolithographic techniques are used to create the patterns. We are determining the geometric parameters (somal adhesion site diameter, axon track width) that are most conducive to motoneuron growth. We also will present electrophysiological characteristics of the motoneurons and relate changes in electrical activity to parameters in the neuron local environment.

BI-TuP17 Explorations of the Influence of Electrostatic Interactions on Surface-Peptide Binding by Matrix-Assisted Laser Desorption / Ionization Mass Spectrometry, *G.R. Kinsel*, ***J. Zhang***, *R.B. Timmons, M. Li*, University of Texas at Arlington

Protein-surface interactions play an important role in a variety of fields. The mechanism of these interactions remains unclear, however, due to the extraordinary complexity of the protein-surface interface and the wide range of chemical and morphological properties that may be present. The use of well characterized surfaces and peptides with well-defined properties can alleviate some of these problems and allow the systematic study of the influence of various surface or protein properties on the protein-surface binding interactions. In the present studies surfaces having well characterized chemical and morphological properties have been created by plasma polymerization of allyl amine or vinyl acetic acid leading to surfaces with high contents of amine or carboxylic acid functional groups respectively. Bradykinin, angiotensin I, and buccalin are three small peptides with similar molecular weights but various primary sequences leading to systematic changes in the peptide pI from 12.0 to 6.9 to 3.8 respectively. It is shown that these peptides have increasing binding affinity for plasma polymerized vinyl acetic acid modified PET surfaces, but decreasing binding affinity for plasma polymerized allyl amine modified PET surfaces. These trends may be attributed to electrostatic interactions between the peptides and the chemical groups on the plasma modified surfaces. This interpretation of the observed effects can be further explored by altering the pH of the solution in which the binding interactions take place. For example, it is found that as the acidity of the solution is increased binding of the acidic peptide to the basic surface is reduced, consistent with the peptide being neutralized in low pH solutions. Additional studies that explore the effect of solution pH on peptide surface binding interactions have been performed and are interpreted in terms of the changing electrostatic properties of the peptide and surface.

BI-TuP18 Realisation of Biosensor Interfaces by Surface Reactions on Silanised Tantalum Pentoxide, ***W. Laureyn***, *R. De Palma, F. Frederix, K. Bonroy, J.-M. Friedt, K.-H. Choi, A. Campitelli*, IMEC, Belgium, *G. Maes*, KULeuven, Belgium

Affinity biosensors allow the detection of affinity based interactions between bio-molecules, e.g. in antibody-antigen recognition. The presence of antigens in an analyte can be verified by their binding to complementary antibodies, immobilised onto a biosensor surface. Tantalum pentoxide (Ta_2O_5) is regarded as a promising material for the realisation of affinity biosensors, especially for impedimetric biosensing, because of its high dielectric constant and chemical stability. To date, the main method for the immobilisation of proteins to oxide surfaces has involved reactions with short-chain trialkoxysilanes, leading to heterogeneous and less effective biosensor interfaces. Alkyltrichlorosilanes, on the contrary, generate well-structured Self-Assembled Monolayers (SAMs), when produced under the proper conditions. Unfortunately, most polar functional groups ideal for protein immobilisation (COOH and NH_2) have to be generated from non-polar precursor alkyltrichlorosilanes, after SAM-formation of the latter. In this contribution, several approaches for the introduction of polar functional groups on Ta_2O_5 , silanised with alkyltrichlorosilanes, will be presented. A novel surface reaction for the introduction of COOH and NH_2 groups on SAMs of bromoalkyltrichlorosilane is evaluated and compared to the oxidation of allylalkyltrichlorosilane and the reduction of cyanoalkyltrichlorosilane respectively. The proposed surface reaction consists in a nucleophilic substitution of the bromine termination with functional thiol compounds. The silanisation of Ta_2O_5 and the subsequent surface reactions are characterised by means of contact angle measurements, XPS, infrared spectroscopy and cyclic voltammetry. Finally, the immobilisation of IgG, on the generated functional Ta_2O_5 surfaces, and the subsequent binding of anti-IgG are monitored by means of Quartz Crystal Microbalance and Atomic Force Micrososcopy.

Electrochemistry and Fluid-Solid Interfaces
Room: Exhibit Hall B2 - Session EC-TuP

Poster Session

EC-TuP1 A Potentiodynamic Study of the Influence of Chloride and Chromate on Passive Films on Copper, ***M.A. Hossain***, *M.Y.A. Mollah,* Lamar University*, D.E. Mencer,* Wilkes University*, R. Schennach,* Technical University of Graz, Austria*, H. McWhinney,* Prairie View A&M University*, D.L. Cocke*, Lamar University

Copper is being increasingly studied today because of its use for electronic interconnects, its resistance to corrosion and its structural and alloying properties even though it undergoes pitting corrosion in the presence of aggressive ions including chloride and bromide. In a research program to delineate the physical and chemical processes that control metal and alloy oxidation, we have found it necessary to explore in detail the oxidation of copper. Although the electrochemical oxidation of copper has been much studied, there is a need to examine the nature of the oxidation product films developed in the process in light of recent discoveries of the importance of the intermediate oxide, Cu_3O_2. In this study, the electrochemical oxidation of copper is examined in neutral solution by cyclic voltammetry and linear sweep voltammetry. The influences of chloride and chromate ions have been investigated. Chloride has been found to strongly influence the passive film and to produce additional chemical species in the product films. Chromate influences the electrochemical properties of the passive films by increasing resistance to corrosion and increasing resistance to electrochemical reduction during linear sweep voltammetry. The structural and chemical influences have been examined by SEM and XPS. The chemical and structural changes in the product films will be discussed in terms of the increasing body of information being determined on the nature of oxidation produced films on copper by thermal, electrochemical and plasma means.

EC-TuP2 Electrochemical Characterization and Preparation of Nanoporous Model Catalysts Produced from the Alloy $Cu_{77}Zn_{12}Mn_7Ni_4$, ***M. Kesmez***, *M.A. Hossain,* Lamar University*, D.E. Mencer,* Wilkes University*, H. McWhinney,* Prairie View A&M University*, D.L. Cocke,* Lamar University

In a research program to explore the preparation of model catalysts by the electrochemical oxidation of alloys, we have examined the oxidation of the $Cu_{77}Zn_{12}Mn_7Ni_4$ alloy to produce a nanoporous copper manganese oxide catalyst with supported nickel. This has been accomplished by the selective dezincification of the alloy under oxidative potential control. The electrochemical properties of the alloy have been examined by cyclic voltammetry and linear sweep voltammetry to establish the mechanisms of corrosion and the characteristics of the oxidized films. The electrochemical characteristics needed for catalyst design will be delineated. The structural and chemical properties of the product films have been examined by SEM and XPS before and after thermal treatments to produce the active catalysts. The electrochemical preparation of the model hopcalite catalyst will be discussed in terms of the previous preparation of the catalyst by thermal and plasma chemical means. The potential of electrochemically controlled dezincification of this type alloy will be discussed for the production of new nanoporous model catalysts.

EC-TuP3 The Electrode Processes of Iron at Potentials Beyond the Stability Limits of Water, ***S.R. Pathak***, Lamar University*, J.R. Parga,* Instituto Technologico de Saltillo, Mexico*, D.E. Mencer,* Wilkes University*, G. Irwin, D.L. Cocke*, Lamar University

The increasing use of iron electrodes in electrochemical processes that operate beyond the stability limit of water has created a critical need for the delineation of the irreversible interfacial processes affecting perfomance. These include the production of a range of aqueous iron species, a number of oxyhydroxides and several oxides that are released to the aqueous phase or remain attached to the electrode surfaces. We have examined the performance of iron electrodes in a five electrode arrangement with three bipolar and two monopolar electrode systems. The electrochemical reactor has been examined by the Cell Design 2000 software by LCHEM® to produce potential distribution and current distributions. The local electrodics are compared to the model calculations. The electrode surfaces residues have been examined by linearsweep voltammetry. The solids have been characterized by SEM, XRD, FTIR and Mossbauer Spectroscopy. The iron oxide and oxyhydroxide phases produced display strong dependence on pH. The results will be discussed in the context of the prevalent chemical and physical mechanisms and the influence on the performance of systems such a electrocoagulation, electrodecantation and electroflotation will be delineated.

EC-TuP4 Microstructure in Selective Electrodeposition of Copper on Indium-Tin-Oxide Film, ***S. Asakura***, *M. Hirota, A. Fuwa*, Waseda University, Japan

This paper describes the use of electrodeposition process to fabricate copper micropatterns on indium tin oxide (ITO) surface using patterned self-assembled monolayers (SAMs) as templates. Thin film ITO has good conductivity and excellent transparency in the visible region, but very few attempts have been made on fabrication of SAMs and electrodeposition of copper on ITO substrates. Micropatterned copper, which has been widely used because of its high electrical conductivity and low cost, is a key requirement since copper provides us with the electronic circuit wires which send signals to the functional molecules on them, electrochromic materials like a part of display, and biosensor. In our study, the organosilane SAMs have been prepared from octadecyltrimethoxysilane (ODS) by chemical vapour deposition (CVD) and irradiated through a TEM grid as a photomask by vacuum ultraviolet (VUV, 172 nm) light for removal of selected SAMs region and creation of electrode region for copper deposition. Lateral force microscopy (LFM) has been used to evaluate the friction differences between photoirradiated and unirradiated areas. SAMs and ITO regions have been also characterized by cyclic voltammetry (CV), from which we could decide selectively electrodeposition condition. It has been found possible to have micropatterned copper utilizing SAMs blocking effect in preventing electron transfer from species in solution through electrodeposition.

EC-TuP5 Characteristics of the Polymer formed on via Sidewall during RIE Process and its Removal, ***J. Song***, *J. Kim,* Samsung Electronics Co., Ltd., Korea*, H. Seo, Y. Kim, H. Jeon*, Hanyang University, Korea

Via contact holes, act as electrical connection between the upper and lower metal layers through inter-metal dielectric, are generally patterned by photo lithography and reactive ion etching (RIE) processes, and the patterned photoresist after the formation of via holes is conventionally removed by the combination of remote plasma ashing and wet organic stripping. It is very critical to remove completely polymer formed on via sidewall and bottom during RIE process to have reliable metal filling and good contact resistance. Via holes were formed by using RIE process with CHF_3/CF_4 gas under the same processing conditions for the state-of-the art DRAM process. The surface morphology of polymer before and after cleaning process was observed by using in-line scanning electron microscopy (SEM), vertical SEM and transmission electron microscopy (TEM). The chemical compositions and structures of polymer were analyzed by using energy dispersive spectroscopy (EDS) and Auger electron spectroscopy (AES). TEM and EDS study revealed that the side wall polymer were grown from the cap TiN layer on Al and showed the truncated cone shape with the thickness in the range of 200~400Å. This indicates that via polymer layer becomes a very critical issue when the etch stop layer is TiN. Bottom polymer layer showed double layer structure with two distinct chemical compositions. The lower layer with the thickness of about 50Å showed a similar chemical characteristic to the side wall polymer while the upper polymer layer with the thickness of about 200Å showed no fluorine content. In this study, we will investigate the removal characteristics of polymer during RIE process at various ashing and stripping conditions. Preliminary results indicated that the low temperature remote oxygen plasma ashing and hydroxylammoniumsulfate based wet stripping were very effective to remove polymer formed on the side and bottom of via holes during RIE process.

Magnetic Interfaces and Nanostructures
Room: Exhibit Hall B2 - Session MI-TuP

Aspects of Magnetism

MI-TuP1 Enhanced Magnetoresistance in Ferromagnetic Vertical Single Electron Transistor, ***S. Haraichi***, *T. Wada*, National Institute of Advanced Industrial Science and Technology, Japan

Recently, such novel phenomena as enhancement of magnetoresistance and magneto-Coulomb oscillation have been found in ferromagnetic single electron transistors (SET). However, because the areas of the ferromagnetic-insulator- ferromagnetic (FIF) tunnel junctions were as large as 0.02 ???, extremely low temperature as 20 mK was required to obtain Coulomb blockade and spin-dependent tunneling transport simultaneously. In order to elucidate the mechanism of those phenomena at relatively high temperatures and to realize such novel devices as spin-memories and spin-transistors, FIF tunnel junctions with 10 nm sizes are necessary. We have developed Si based inorganic electron beam resist process suitable for integration by which 10 nm resolution can be achieved. Using this process, nanometer-scale vertical FIF tunnel junctions are fabricated with high reliability. In this paper, we will report a fabrication process for ultra-small ferromagnetic vertical SET by modifying the above inorganic resist process, and the electrical characteristics especially spin-dependent tunneling transport of fabricated devices. The enhanced magnetoresistance changes over several times in the Coulomb blockade (CB) region in magnetic fields of around 100 mT at 14 K, while that changes only several % in the outside of the CB region. This strong enhancement is explained by the higher-order tunneling process.

MI-TuP2 Iron-silicide Phases Formed in Fe/Si Multilayered Films, ***J.S. Park***, Hanyang University, Korea, *Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine, *J. Dubowik,* Institute of Molecular Physics, Korea, *J.Y. Rhee*, Hoseo University, Korea, *Y.P. Lee*, Hanyang University, Korea

Fe/Si multilayers films (MLF) can have the interfacial layers of various iron silicides and were recently discovered to have an antiferromagnetic (AF) coupling in the as-deposited state. An ion-beam mixing (IBM) allows us to overcome either thermodynamic or kinetic barriers by employing the energetic particles, to surpass the limit of solid solubility and to achieve the compositional and structural metastability. Fe/Si MLF with various sublayer thicknesses were made by RF sputtering onto glass substrates and an IBM was also performed. The structural properties before and after the IBM turned out to be very different. A study of the optical and magneto-optical (MO) properties of the as-deposited MLF reveal that neither $FeSi_2$ nor ε-FeSi could be considered as the spacer layer providing the strong AF coupling, but that a B2-phase nonmagnetic metallic FeSi compound is spontaneously formed between Fe sublayers during deposition. The IBM of the Fe/Si MLF has been performed at room temperature (RT) by using Ar^+ ions with an energy of 80 keV, a dose of $1x10^{16}$ ions/cm^2 and a flux of $1.5x10^{-6}$ A/cm^2. The magnetic properties were measured at RT by vibrating-sample magnetometry and ferromagnetic-resonance spectroscopy. The ion-beam treatment has led to noticeable changes in the structural and physical properties of Fe/Si MLF : the formation of a new phase, which is characterized by a crystalline silicide structure, a low coercivity and a Curie temperature of about 550 K. The obtained results can be explained if a metastable $FeSi_2$ silicide with a B2-type structure is supposed.

MI-TuP3 Dynamic and Static Measurements on Epitaxial Fe/Si/Fe, ***B.K. Kuanr***, University of Colorado at Colorado Springs, *M. Buchmeier,* Forschungszentrum Juelich GmbH, Germany, *Z. Celinski, R.E. Camley*, University of Colorado at Colorado Springs

Strong antiferromagnetic interlayer exchange coupling across an insulating spacer is in increasing demand for high-density magnetic recording. For example such structures can be used as artificial antiferromagnets in spin valves. We report here the interlayer exchange coupling of epitaxial Fe(10 nm)/Si(t)/Fe(8 nm) trilayers as a function of Si thickness studied by Ferromagnetic Resonance (FMR), Brillouin Light Scattering (BLS) and Magneto Optic Kerr Effect (MOKE) measurement techniques. A very strong antiferromagnetic (AFM) interlayer exchange coupling (>6 mJ/cm^2) was observed at a spacer Si thickness of 0.7 nm. The bilinear J_1 and biquadratic J_2 coupling constants are determined from (i) the fitting of the angular variation of the resonance field (H_{res}) from FMR (ii) the field variation of the frequencies for the Damon-Eshbach (DE) surface modes (both optic and acoustic with non-zero k) and (iii) the fitting of longitudinal MOKE hysteresis loops. We obtain a higher H_{res} along the easy-axis than along the hard-axis and the magnetizations of the two Fe films are canted. The eight-fold like symmetry of H_{res} as a function of the angle observed at room temperature, is due to the competition between the four-fold anisotropy and AFM interfacial coupling energy. This behavior vanishes at 24 K due to a strong increase of AFM coupling in comparison to four-fold anisotropy. From the fitting of temperature variation of H_{res} curves, we obtain the temperature variation of the bilinear and biquadratic exchange coupling constants. This strong coupling can be related to the highly resistive Si spacer between epitaxial Fe layers.

MI-TuP4 Investigations on the Peculiar Magneto-optical and Magnetic Properties of Au-Fe Alloy Films and Au/Fe Multilayered Films, ***K.W. Kim***, Sunmoon University, Korea, *R. Gontarz,* Institute of Molecular Physics, Poland, *Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine, *Y.P. Lee*, Hanyang University, Korea

In this study, the peculiar magneto-optical (MO) and magnetic properties of Fe-Au alloy films and Au/Fe multilayered films (MLF) were investigated. (3.0 nm Fe / $t_{Au})_{20}$ MLF (where / t_{Au}= 1.0, 2.0, 2.5 and 3.0 nm) were prepared by rf-sputtering onto glass substrates with a Au buffer layer of 20 nm in thickness. We also prepared Au, Fe and $Au_{1-x}Fe_x$ (0 < x < 1) films of about 100 - 150 nm in thickness by face-to-face sputtering onto a glass substrate at room temperature (RT). The structures of Au/Fe MLF and Au-Fe alloy films were analyzed by using the low- and high-angle x-ray diffraction (XRD). The MO equatorial Kerr effect and optical properties of the samples were measured at RT in a spectral range of 248 - 1130 nm (5.0 - 1.1 eV) and 235 - 2500 nm (5.3 - 0.5 eV), respectively. To understand the magnetic properties of $Au_{1-x}Fe_x$ alloy films more quantitatively, the magnetic circular dichroism (MCD) measurement was performed at 2B1 beamline of Pohang Light Source (Pohang, Korea). It was elucidated that alloy-like regions are spontaneously formed near the interfaces between Au and Fe sublayers during the Au/Fe MLF fabrication. The MCD results reveal that the orbital magnetic moment of the constituent Fe atoms in the bcc Fe-Au alloy film is about twice larger than that of pure Fe, which implies a hybridization between Fe and Au atoms. It is thought that the prominent feature observed in the UV range of the MO response of Au/Fe MLF results not from the quantum confinement, but probably from an enhanced magnetic moment of Fe (and/or an induced magnetic moment of Au).

MI-TuP5 Magnetoresistance and Magnetic Behavior of Manganite-based Multilayers, ***M. Sirena***, *M. Granada, L.B. Steren, N. Haberkorn, J. Guimpel*, C.N.E.A., Argentina

We have studied the physical and structural properties of multilayers based on manganite compounds. Different ferromagnetic (FM) spacers, insulator (B1) and metallic (B2), have been used in order to compare the magnetoresistance (MR) effects and interlayer coupling of both kind of systems. Multilayers based on high polarized manganites are specially interesting for developing magnetic devices with high tunneling MR, spin filters, etc. A/B1 and A/B2 multilayers (A: $La_{0.55}Sr_{0.45}MnO_3$, B1: $La_{0.9}Sr_{0.1}MnO_3$ and B2: $La_{0.67}Ca_{0.33}MnO_3$) have been grown by DC sputtering on MgO and $SrTiO_3$ substrates. X-ray diffraction patterns have been fitted to obtain information about the interface and roughness interdiffusion. The results show that the samples grow strongly textured in the c-direction, perpendicular to the sample surface, with a multilayered structure. The similar structure and lattice parameters of the samples make these films specially attractive to build multilayers with interfaces of good quality. We have studied the dependence of the transport and magnetic properties of these systems with the interlayer and top-layer thickness. Both A/B1(B2)/A trilayers present properties similar to those observed for the $La_{0.55}Sr_{0.45}MnO_3$ film. Magnetization vs. field measurements performed in both systems, show a single FM loop indicating that the A layers are always ferromagnetically coupled. The FM nature of the interlayer in the A/B1/A case is probably the origin of the FM coupling. In the A/B2/A trilayers, on the other hand, the FM coupling above its Curie temperature could be mediated by short-range ordered zones in the LaCaMnO interlayer. No extrinsic MR, associated with the multilayered structure was observed in the whole temperature range, probably due to the presence of FM coupling between the metallic layers, as suggested by magnetization measurements.

MI-TuP6 Current Induced Magnetoresistance in Co/Cu/Cu Multilayers, ***J.-D. Suh***, Electronics and Telecommunications Research Institute, Rep. of Korea

We have investigated the magnetic properties fabricated by e-beam lithography from a Co/Cu/Co multilayer. Current induced magnetoresistance properties for current flowing perpendicularly through the layers with a high current density of 10^8A/cm^2 are systematically studied as a function of device size, magnetic layer thickness and temperature. A current induced magnetic switching is observed in multilayer structures with diameters as small as 100 nm. The results are explained by spin transfer model. In this study, we shall discuss the relation between nanostructured geometry of magnetic Co/Cu/Co multilayer and current induced magnetic switching in detail.

MI-TuP7 Patterned Nanostructures of Permalloy on Al_2O_3 Barrier Grown by an Electrodeposition, ***S. Kenane***, *L. Piraux,* Université Catholique de Louvain, Belgium, *J. Carrey, K. Bouzehouane, J.-M. George*, CNRS/THALES, France

Abstract Dots of Ni80Fe20 were grown by electrodeposition on the top of a thin alumina barrier at preferential nucleation centers. The particle sites were induced by indentation with a conducting tip atomic force microscopy (AFM) on the alumina barrier (figure 1). Figure 1 shows regular spheres of Ni80Fe20 which all have practically the same size. The size of the dots (sphere) can be controlled by varying the time deposition. The behavior of the current has been confronted to a theoretical nucleation-growth model. Using a conducting atomic force microscope, we characterize the resistance of the defects on which the dots nucleate. Preliminary electrical transport measurements were performed on the permalloy dots.

MI-TuP8 Magnetism of Ultrathin Co Films on Flat and Vicinal (001) Surfaces, *S. Pütter, N. Mikuszeit, J. Hoyer,* ***H.P. Oepen***, University of Hamburg, Germany

The magnetic properties of ultrathin Co films on Cu(1 1 13) and Pt(001) have been investigated by means of the magneto-optic Kerr effect (MOKE).

Due to the symmetry breaking of the vicinal Cu(1 1 13) a uniaxial magnetic behavior is found. Magnetic anisotropies of first and second order are derived from the hard axis hysteresis curves revealing a field-driven spin-reorientation transition. The thickness dependence of the magnetic anisotropies is explained in the framework of strain relieve. The Kerr ellipticities perpendicular and parallel to the step edges are different. The difference is due to a canting of magnetization that causes a superposition of longitudinal and polar Kerr effect. Utilizing a recently proposed procedure[1] to deconvolute the mixed Kerr signals the canting angle is determined and found to be thickness dependent. By means of MOKE the quasi static magnetic susceptibility is measured during Co growth on Pt(001). The parallel susceptibility was obtained for in-plane orientation of magnetization. Around one monolayer a susceptibility peak indicates the onset of ferromagnetism in the pseudomorphic Co layer. For higher thicknesses the fcc Co film exhibits a fourfold symmetry with <110> as easy axes.

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MI-TuP9 Spin Polarized Vacuum Tunneling in Field Emission from Co-Coated W(111) Tips, ***K.L. Man***, *R. Bryl*, Hong Kong University of Science and Technology, *R. Zdyb,* Arizona State University, *T.C. Leung,* National Chung Cheng University, China, *C.T. Chan,* Hong Kong University of Science and Technology, *E. Bauer,* Arizona State University, *M.S. Altman*, Hong Kong University of Science and Technology

Ultrathin Co films are grown on the W(111) surface as the basis for spin polarized vacuum tunneling in field emission and scanning tunneling microscopy. The growth morphology, structure and magnetism are studied with conventional and spin polarized low energy electron microscopy (LEEM/SPLEEM) and diffraction (LEED) and first principles total energy calculations. Quasi-layer-by-layer growth of thick pseudomorphic Co films is observed at 380K, while Stranski-Krastanov growth and transformation to a (6x6) closed-packed structure are observed at higher temperatures. Pseudomorphic Co/W(111) is ferromagnetically ordered at 380K when film thickness exceeds 7.6 ML. Although only in-plane magnetization is found, a strong influence of substrate atomic steps is seen in the magnetization easy axis and magnetic domain structure. Spin polarization in vacuum tunneling is assessed by a Mott electron spin polarimeter coupled to a field emission microscope. High spin polarization (typically 20%, maximum 50%) in field emission from Co-coated W(111) tips and polarization manipulation achieved by pulsed magnetic field encourage further development.

MI-TuP10 Transition Metal Ion-implanted GaN and Its Magnetic and Structural Properties[*], *J.S. Lee, Z.G. Khim,* ***Y.D. Park***, Seoul National University, Korea, *S.N.G. Chu,* Agere Systems, *G.T. Thaler, M.E. Overberg, C.R. Abernathy, S.J. Pearton*, University of Florida

We report on the magnetic and structural properties of Co, Cr, and V ion-implanted epitaxial GaN films on sapphire substrates. Dilute magnetic semiconductors (DMS) with ferromagnetic ordering near or above room temperatures have been reported in Mn doped GaN[1] and Co doped TiO2,[2] subsequent to predictions from a near-field model for GaN doped with a relatively high concentration of Mn.[3] Theoretical treatment of ferromagnetic ordering in DMS systems have progressed to include low carrier density regimes[4] and incorporation of other magnetic impurities.[5] We have found from SQUID magnetization measurements that (Ga,Co)N and (Ga,Cr)N show ferromagnetic ordering below ~ 78 K and ~ 51 K respectively, while (Ga,V)N shows paramagnetic behavior. Structurally from TEM and Selective Area Diffraction Pattern (SADP) data, we have observed that the ion-implantation and subsequent annealing process leaves the expected residual damage in the form of dislocation loops, but no detectable second phases, which corresponds well with the observed modest coercive fields (~100 Oe for (Ga,Co)N) of the samples. By sharp contrast, the presence of ferromagnetic metallic clusters at dimensions below our detection limits would have expected coercivities in the range of thousands of Oersteds.

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MI-TuP11 The Effect of the Ferromagnet/Antiferromagnet Interface on Magnetic Properties of Fe/KCoF$_3$ System, *L.M. Malkinski, T. O'Keevan, R.E. Camley,* ***Z. Celinski,*** University of Colorado at Colorado Springs, *D. Skrzypek*, University of Silesia, Poland

The Molecular Beam Epitaxy (MBE) system was used to grow Fe/KCoF$_3$ bilayers, a ferromagnet-antiferromagnet system. Depending on deposition conditions the fluoride can be grown on the single crystal Fe layer in either single crystal or polycrystalline forms. Structural properties of our samples were carefully studied using X-rays, Reflection High Energy Electron Diffraction (RHEED) and tunneling electron microscopy. The structure of the fluoride determines the ferromagnet/antiferromagnet interface and significantly modifies magnetic properties, which were measured using Ferromagnetic Resonance (FMR) and SQUID magnetometry. We observed changes in the exchange bias which correspond to different structural states of the antiferromagnet. This could result in different spin compensations at the Fe/KCoF$_3$ interface in single crystal and polycrystalline samples. The interface also had a dramatic effect on the four-fold magnetocrystalline anisotropy of Fe. For the samples with polycrystalline KCoF$_3$, the anisotropy thickness dependence for the single crystal Fe film, with thickness d ranging from 0.9 to 3 nm, showed a deviation from the usual 1/d dependence. The temperature dependence of the four-fold anisotropy of the samples with single crystal fluoride was typical of single crystal Fe films. However, the films with polycrystalline fluoride exhibited a distinctly different temperature behavior. The anisotropy for these samples increases significantly with decreasing temperature. The enhancement of the anisotropy was most pronounced for the samples with the thinnest Fe film changing by a factor of 3 from room temperature to low temperature. This effect is probably due to a specific morphology of the interface between the ferro- and antiferromagnet. In addition, a large rotational magnetic anisotropy, associated with the interaction between Fe and KCoF$_3$, was evaluated from the temperature dependence of the FMR fields.

Nanometer Structures
Room: Exhibit Hall B2 - Session NS-TuP

Nanometer Structures A

NS-TuP1 Calibration Methods for Displacement and Cantilever Stiffness in AFM, *G.A. Matei, E.J. Thoreson,* ***N.A. Burnham***, Worcester Polytechnic Institute, *X. Chen,* University of Nottingham, *C.H. Hodges*, University of Leeds

The laser beam in our AFM was placed half on and half off a cantilever that was hanging freely above a reflective surface. The resulting two beams interfered and the interference could be detected at the photodiode, yielding a simple and accurate means of calibrating the scanner displacement. This approach will be extended to the calibration of the amplitude of oscillating cantilevers. Also, we compared the experimentally determined values of stiffness for ten cantilever probes using four different methods[1]. For rectangular silicon cantilever beams of well-defined geometry, the approaches all yield values within seventeen percent of the manufacturer's nominal stiffness. One of the methods is new, based on the acquisition and analysis of thermal distribution functions of the oscillator's amplitude fluctuations. We evaluate this method in comparison to the three others and recommend it for its ease of use and broad applicability.

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NS-TuP2 Atomic Force Microscope Assisted Oxidation of Zirconium Surfaces, ***N. Farkas***, *G. Zhang, S.F. Lyuksyutov, E.A. Evans, R.D. Ramsier,* The University of Akron, *J.A. Dagata*, National Institute of Standards and Technology

We present results from scanning probe oxidation of zirconium (Zr) surfaces using atomic force microscope tips in air. For both single-crystal and sputter deposited thin-films of zirconium, rapid oxide growth kinetics are replaced by much slower processes as a function of oxidation time (0 - 300 s). We track these kinetics vs. Zr film thickness (10 - 50 nm), relative humidity (25 - 60 %), and applied voltage (0 - 20 V). In addition, we are able to modify the nanolithographic process by incorporating nitrogen into the top 10 nm of the sputtered films. Our results contribute to a more comprehensive description of the nanolithographic process and complement efforts to model and control the oxidation of Zr surfaces.

NS-TuP3 Molecular Dynamics Simulations of Nanofluidics, ***K. Lee***, *S.B. Sinnott*, University of Florida

The design of ultrafiltration membranes using carbon nanotubes to allow gases to selectively pass through the membrane depends on the understanding of the diffusion and adsorption of the gases within the carbon nanotubes. The nanofluidics of hydrocarbons, oxygen, and carbon dioxide has been studied with molecular dynamics simulations in our research. These macroscopic behaviors can be simulated with multiple integrations of the interactions among the atoms in a system. The interatomic forces in the simulations are calculated using a classical reactive empirical bond-order hydrocarbon potential coupled to Lennard-Jones and Coulombic potentials. For a shorter time period, the location, the trace, and the orientation of the gas molecules in the nanotubes are affected by the diameters of the nanotubes, and the structures of the carbon nanotubes. The transport of gas molecules for a longer time period is described by nonequilibrium followed by equilibrium states. Until reaching the equilibrium state, the gas density in a carbon nanotubes increases on and levels off. During the nonequilibrium state, the gas molecules move back and forth through the nanotube. This behavior and the time for the level-off are affected by the concentration of gas molecules both in and outside of the carbon nanotube. It is found that the molecular volumes of the gas molecules and the composition of the gas mixtures also have an important effect on the separation behavior.

NS-TuP4 STM and STS Characterization of Silicon Phthalocyanines for the Molecular Quantum Dot Cellular Automata Implementationn, ***M. Manimaran**, G.L. Snider, V. Sarveswaran, M. Lieberman*, University of Notre Dame

The surface characterization of organic molecules adsorbed on solid surfaces has been investigated intensively in recent years. In particular, the adsorption of long-chain substituted hydrocarbons (CH3(CH2)2X, X= CH3, OH, SH,S,SS, NH2, Cl, Br, I, etc on highly oriented pyrolytic graphite (HOPG) and Au surfaces was well studied because of their importance in wide range of applications in biology and molecular devices such as Quantum-dot cellular automata (QCA). QCA is a computation paradigm based on the Coulomb interactions between the neighboring cells. The prime idea is to represent binary information, not by the state of a current switch, but rather by the configuration of charge in a bistable cell. In its molecular realization the QCA cell can be a single molecule. Si-phthalocyanine (SiPc) is one of the promising candidates for the QCA. In this study, SiPc molecules, which are double-dot-like entities, are deposited on Au and Si(111) substrates initially. These molecules are then observed under UHV-STM to determine if the molecules would self assemble, and also to determine their electronic properties via voltage vs. current (I/V) measurements. In addition to the STM and STS studies, XPS, PL and ellipsometric results will be presented in this paper.

NS-TuP5 Substrate Temperature Dependence of Electrical Conduction in Nanocrystalline CdTe:TiO_2 Sputtered Films, ***S.N. Sharma***, National Physical Laboratory, India, *S. Kohli,* Colorado State University, *S.M Shivaprasad,* National Physical Laboratory, India, *A.C. Rastogi*, University of Massachusetts

TiO_2 thin films with high volume fraction (~ 50-60 %) of CdTe nanoparticles were prepared by rf magnetron sputtering from a composite TiO_2:CdTe target. Variations in the substrate temperature, T_S (room temperature-RT and 373 K), produces two distinct structural regimes with different electrical properties in thermally treated TiO_2 thin films: (i) a metallic regime for low T_S films where the CdTe/Cd grains touch each other and form a metallic continuum. Here, homogeneous, ordered and electrically-continuous structure was obtained. Here, due to the presence of large-scale coalescent islands of CdTe/Cd, three-dimensional network of crystallites could be realized. Such films exhibited positive temperature coefficient of resistance. For metallic regime films, electrical conduction is essentially due to electrical percolation through CdTe/Cd crystallites embedded in an amorphous TiO_2 matrix. XPS studies indicated the segregation of metallic Cd upon thermal treatment which were responsible for metallic-type of conduction exhibited by these films. (ii) a non-metallic regime for high Ts films in which small isolated particles of CdTe/Cd are dispersed in an amorphous matrix. Here, highly disordered and electrically-discontinuous structure was obtained and thus formation of CdTe network could not be realized. The formation of oxides on the surface of the CdTe/Cd crystallites acts as an electrical insulation and thus, the conduction is thermally activated. The electrical conduction in high T_S films is essentially by hopping mechanism thus indicating transfer of charge carriers via thermally activated tunneling. Such films exhibited negative temperature coefficient of resistance.

NS-TuP6 Nanolithography and Biofunctionalisation for Cell Adhesion Studies, *A. Szucs,* ***M. Arnold****, Ch. Geierhaas, J.P. Spatz*, University of Heidelberg, Germany

Periodic and artificial lateral nanostructures with micrometer or nanometer spacings have been prepared through the combination of a top-down approach (electron beam lithography) with a bottom-up approach (formation and compartmental localization of metallic and semiconductor nanodots within block copolymer micelles). E-beam lithography was used to construct patterned templates with characteristic spacings greater than 200 nm of coarse prestructures. Within these structures, Au nanoparticles and/or quantum dots (Q-dots) (CdS, CdSe and CdTe) in the size range of 2-8 nm could be positioned with a precision of approx. 10 nm by means of a self-assembling polymer micelle. The particle size was controlled by the length of the reverse micellar core constructing polymer and the salt loading inside the core. Specifically, it was obtained by casting a solution of HAuCl4 and/or Cd salt loaded block copolymer micelles onto the prestructured resist film. Due to capillary effects and steric hindering, the particles are centered within the prepatterned holes and at the edges of prestructured lines. Subsequent lift-off of the resist allows the removal of all micelles with the exception of those that are in direct contact to the underlying substrate. The block copolymer is then removed by plasma etching, which strips the polymer micelle and reduces the gold salt to gold thereby leaving behind nanoscopic dots or lines of gold in a defined array. These nanostructured interfaces are used as platform for biofunctionalisation of solid interfaces. The surfaces are used as a tool to investigate cluster formation of focal adhesion associated proteins of fibroblasts.

NS-TuP7 In situ STM Study on Electrochemical Formation and Desorption of Self-assembled Monolayer in Ethanol Solution Containing KOH and Alkylthiol, ***K. Uosaki****, H. Wano*, Hokkaido University, Japan

Oxidative formation and reductive desorption of self-assembled monolayer (SAM) of alkylthiol in ethanol solution containing KOH and various concentration of alkylthiol was investigated by in situ STM. Cyclic voltammograms show the formation process is slower than the desorption process. When the concentration of the thiol was very low (~ micro M), no vacancy island (VI) was observed even in positive potential region where SAM formation is expected. As more thiol was added at the positive potential region, the growth of VIs, i.e., SAM, was observed. The VIs disappeared and herringbone structure appeared on the surface as potential became more negative than the certain value, showing the restoration of the reconstructed, i.e., clean, surface. The herringbone structure became clearer with time. When the potential was scanned positively, disappearance of the herringbone structure and the growth of the VIs were observed. Drastic change of step lines reflecting the higher mobility of gold atoms was also observed during the formation and desorption of the SAM.

Nanotubes: Science and Applications Topical Conference Room: Exhibit Hall B2 - Session NT-TuP

Poster Session

NT-TuP1 Vertically Aligned Carbon Nanotubulated Fibers Grown by Microwave Plasma-Enhanced Chemical Vapor Deposition, *M. Hiramatsu,* ***K. Ito****, K. Kato,* Meijo University, Japan, *C.H. Lau, J.S. Foord*, University of Oxford, UK

Carbon nanotubes have attracted attention for several applications because of their unique properties such as high field electron emission capability and capacity for the storage of large amount of hydrogen. Carbon nanotubes with different structure and morphology can now be fabricated with several techniques. In the present work, carbon nanotubulated fibers were grown by microwave plasma-enhanced chemical vapor deposition (MWPCVD). These carbon nanotubulated fibers were in the form of the bundles of carbon nanotubes and were aligned perpendicular to the substrate. A mixture of methane and hydrogen was used as a carbon source gas. The applied microwave power and the pressure during the growth were 400-500 W and 25-30 Torr, respectively. The growth experiments were carried out for 5 - 15 min at a substrate temperature of 600 °C or less. The vertically aligned carbon nanotubulated fibers were grown selectively on a patterned Ni thin layer as a metal catalyst prepared on the silicon (100) substrate by electron beam evaporation. The diameters of the grown nanotubulated fibers were approximately 100 nm. Raman spectra for the carbon nanotubulated fibers fabricated were recorded, and the graphitised structure was clearly confirmed from the sharp G-line peak located at 1600 cm^{-1}. The field electron emission characteristics for the vertically aligned carbon nanotubulated fibers were investigated. The onset field of the field electron emission for the carbon nanotubulated fibers was 10 V/µm.

NT-TuP2 STM Investigation of Oxygen Adsorption on Carbon Nanotubes, ***S. Santucci****, L. Lozzi, M. Simeoni, M. Passacantando,* INFM and University of L'Aquila, Italy, *L. Valentini, I. Armentani, J.M. Kenny,* University of Perugia, Italy

Carbon nanotubes, thanks to their electronic and structural properties, are studied for many important applications. One recently interesting application is the gas sensing. In fact it has been shown that the electrical conductance of single-walled carbon nanotubes (SWNTs) can be drammaticaly changed upon exposure to gaseous molecules such as NO2, NH3[1]or O2.[2] These molecules can be adsorbed both at the nanotube surface or can be accepted inside the nanotube.[3] In this work we will present STM/STS data acquired onto multi-walled carbon nanotubes (MWNTs) during the exposure to O2 molecules. The MWNT films have been deposited by plasma enhanced chemical vapor deposition (PECVD) using

Ni as catalyst particles on silicon. These samples have been exposed to O2, keeping the sample at different temperatures, in order to simulate the gas sensing processes (adsorption/desorption). The adsorption of O2 determines the variation of STS curves, showing the presence of new states, both filled and empty ones, which can be assigned to the interaction between molecules and MWNTs. These states also depend on the sample temperature, in particular the empty ones. The desorption process has been also followed, showing the missing of the oxygen-MWNT states when oxygen is removed from the STM chamber.

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NT-TuP3 Synthesis of Single-walled Carbon Nanotubes on Thin Film Catalysts via Chemical Vapor Deposition, ***Y.J. Yoon***, *J.C. Bae, H.K. Baik,* Yonsei University, Korea, *S.J. Lee,* Kyungsung University, Korea, *K.M. Song*, Konkuk University, Korea

Synthesis of single-walled carbon nanotubes (SWNTs) via chemical vapor deposition (CVD) has attracted notable attentions due to its low reaction temperature, compared to other processes. It enables SWNTs to be easily applied to electronic devices such as transistors, and chemical sensors. Recently, many researchers have been reported the synthesis of SWNTs on powder supports via CVD. However, synthetic method of SWNTs on flat Si substrates via CVD is not fully established due to the difficulty of catalyst control. The main issue of SWNT synthesis via CVD is the optimization of catalyst preparation. In this paper, to improve a yield and selectivity of SWNTs on patterned Si substrate, the optimization of catalyst was progressed by thermodynamic approaching. Catalysts were prepared by thin film deposition (Co, Ni, Fe, Mo and their alloys) on silicon substrate using D.C. magnetron sputtering system with an accurate thickness controller in angstrom scale. SWNTs were grown by catalytic decomposition of methane and hydrogen gas at the temperature range between 700 °C and 1000°C. In order to investigate the formation mechanism of SWNTs, the characterization of nanoparticles and SWNTs by SEM, TEM, and Raman was performed. The nucleation and growth step for SWNTs on various catalysts will be presented by thermodynamic approaching.

NT-TuP4 Experimental and Theoretical Studies on the Gas Adsorption of Multi Walled Carbon Nanotubes Thin Films, ***S. Picozzi***, *L. Lozzi, S. Santucci,* INFM, Univ. L'Aquila, Italy, *L. Valentini, I. Armentano, J.M. Kenny,* Univ. Perugia, Italy, *A. Pecchia, A. Di Carlo, P. Lugli,* Univ. Tor Vergata, Italy, *B. Delley*, Paul Scherrer Institut, Switzerland

The special geometry and unique properties of carbon nanotubes (CNT) offer relevant potential applications.[1] In particular, the effects of environment gases (such as O2, NO2, NH3) on the electronic and transport properties of carbon nanotubes have recently attracted great interests.[2,3] To date, the reported theoretical gas sensing studies have been based either on isolated single wall carbon nanotubes (SWNTs) or on SWNT mats. In the present work multi-wall carbon nanotubes (MWNTs) deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO2. Experimental findings revealed the chemisorption of oxidizer gas upon the surface of the MWNTs, suggesting that p-type semiconductor behavior is present. The possibility of modulating the electronic properties of nanotubes using adsorption of gas molecules is investigated using first-principles density functional calculations. Transport characteristics are calculated using non-equilibrium Green's functions. The simulations account for the reaction dynamics between the CNT and the adsorbing gas,thus allowing the determination of the preferred adsorption site as well as the calculation of the current flowing along the nanotube as a function of time. The charge transport is dominated by the hopping mechanism across a bundle of several nanotubes. For this reason the influence that the adsorbed molecules have on the hopping rate between adjacent nanotubes has been also investigated. The results elucidate the mechanisms of adsorption and doping of CNTs and its influence on their conduction properties.

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[3] P.G. Collins, K. Bradley, M. Ishigami and A. Zettl, Science 287, 1801 (2000).

NT-TuP5 Synthesis of Single-walled Carbon Nanotubes without Metal Catalysts by Arc Discharge, ***J.C. Bae***, *Y.J. Yoon, H.K. Baik,* Yonsei University, Korea

Since single-walled carbon nanotubes (SWNTs) were discovered, great effort to control the nucleation and growth of SWNTs by selecting the metal catalysts, working pressure, ambient temperature, and feeding methods of carbons. Models proposed for nucleation and growth of SWNTs usually start from the carbon-metal gas phase or carbon-metal cluster. In other words, metal catalysts were believed to be necessary for the formation of SWNTs. In recent, new the technique for the formation SWNTs was reported. This technique did not require a metal catalyst and use as precursor amorphous carbon nano-sized particles generated by laser-induced chemical vapor deposition. In other words, the proper precursors are necessary for the formation of SWNTs, and metal catalysts are not. In arc discharge method, hemispherical fullerenes, which play a role in nucleation of carbon nanotubes, were easily formed in inert ambient. In addition, in case of CVD method flux control of carbon is key factor to determine which type of carbon nanotubes are formed. It indicates that SWNTs can be synthesized without metal catalysts by flux control of carbon in arc discharge. In this work, three types carbon anode were used to control the carbon flux. One was graphite rod (6mm diameter, 70 mm length), another was graphite rod (6mm diameter, 70 mm length) in which a hole (3 mm diameter, 50 mm deep) is drilled, and third was graphite rod (6mm diameter, 70 mm length) in which a hole (3 mm diameter, 50 mm deep) is drilled and filled with pure graphite powders. SWNTs were collected from round the cathode.

NT-TuP6 Field Emission Properties of Nanostructures Based on Molybdenum Ternary Compounds versus Carbon Single Wall Nanotubes, ***M. Zumer***, *V. Nemanic, B. Zajec,* Institute of Surface Engineering and Optoelectronics (ITPO), Slovenia, *M. Remskar, A. Mrzel, D. Mihailovic*, Jozef Stefan Institute, Slovenia

As the single wall carbon nanotubes (SWCNT) were recognized as stable emitters for various electron devices, the performance of any new material is well introduced when tested in comparison to them. From several reports on field emission (FE) measurements, it is difficult to eliminate all the experimental parameters that may influence the results. On a short term time scale, the characterization may be presented by the Fowler - Nordheim plot, while the long term behavior can only be presented by real measuring results. We have investigated the FE properties of quasi one-dimensional molybdenum ternary compounds. They were synthesized by a catalytic transport reaction and characterized by conventional microscopic methods. The results of FE measurements were compared to those obtained on commercially available purified SWCNT at identical experimental conditions. All FE measurements were performed in an UHV system at 10^{-9} mbar base pressure. The samples were mounted on the top of metal pins positioned some mm from the aluminized luminescent screen biased as the anode. Current - voltage (I-V) measurements were performed under continuous bias conditions up to 4.5 kV where the resulting macroscopic field reached approx. 0.9 V μm^{-1}. The emission current from a few sites reached a value of some ten micro amps in both cases. The current variation with time was related to onset and disappearance of emission spots of various shapes. The average current initially dropped, but became relatively stable even on the time scale of a few hundred hours for both FE materials studied.

Plasma Science
Room: Exhibit Hall B2 - Session PS-TuP

Plasma Applications

PS-TuP1 Temperature Mapping in Fluorocarbon Plasmas using PLIF of CF, ***K.L. Steffens***, National Institute of Standards and Technology

During semiconductor processing, fluorocarbon plasmas are commonly used for dielectric etching. As model-based reactor design and process development become more prevalent, data is needed for model development and validation. The translational temperature in a plasma can vary spatially, leading to spatial variations in gas density and reaction rates. Spatial mapping of these temperature variations would provide useful information for modelers. In this work, 2-D temperature maps in fluorocarbon plasmas, measured using planar laser-induced fluorescence (PLIF) of the CF radical, will be presented. Measurements are made in the capacitively-coupled Gaseous Electronics Conference rf Reference Reactor in CF_4 plasmas at various power levels at 200 mTorr. PLIF has previously been used to measure spatial maps of CF_2[1] and CF radicals in fluorocarbon plasmas, by exciting the species with a laser sheet and imaging the fluorescence using an intensified CCD camera. In this variation of the PLIF technique, multiple spatial maps are imaged for the same plasma, exciting a different rotational line of the CF radical for each image. The fluorescence intensity map in each image is related to the rotational population in the probed CF ground state rotational level. Assuming a Boltzmann distribution, the ratio of image intensities can used to calculate the rotational temperature of CF, which is expected to be in equilibrium with the plasma's translational temperature under these conditions.

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PS-TuP2 A Comparison of the Performance Between Low Pressure Magnetized and Non-magnetized Microwave Discharges, *M. Perrin, T.A. Grotjohn,* ***J. Asmussen***, Michigan State University

Microwave discharges can be created and maintained at low pressures both with and without the application of static (ECR and non-ECR) magnetic fields. Thus important microwave plasma source design issues are (1) when is the application of a static magnetic field advantageous, (2) what are the differences between the output performance of similar magnetized and non-magnetized microwave discharges, (3) what microwave heating mechanisms maintain the two different microwave discharges at low pressure? This investigation attempts to answer these questions by experimentally measuring the performance of a 13cm diameter microwave plasma source operating in argon gas from 1-50 mTorr with and without a set of multipolar permanent magnets. Specifically, differences between magnetized and non-magnetized discharges are noted by comparing measured electron densities, electron distribution functions and effective electron temperatures versus pressure,i.e. 2-50 mTorr, and absorbed microwave power from 200-500W. The discharge stability of each configuration is also noted. The experimental results indicate that at pressures above 6 mTorr the non-magnetized discharge is superior in all aspects of performance to the magnetized discharge. Thus above a specific pressure ;i.e. 6 mtorr in this case, the application of static magnetic fields is not required to efficiently maintain microwave plasma processing sources. In fact the application of a magnetic field may reduce source efficiency. However at very low pressures ,i.e.below 4mtorr in this case, magnetized discharges are more efficient and stable and have lower electron temperatures and plasma potentials. The experimental measurements suggest that the non-magnetized discharge is maintained by non-collisional mechanisms at pressures below 15-20 mTorr. The similarity between discharge configurations also then suggests that similar non-collisional heating mechanisms are present in the magnetized discharge.

PS-TuP3 Ion Attachment Mass Spectrometer(IAMS) for in situ and Fragment-free Monitoring of Plasma-CVD and Dry-etching Processes, ***Y. Hirano***, *M. Nakamura, Y. Shiokawa, T. Fujii*, Anelva Corporation, Japan

We have developed and commercialized Ion Attachment Mass Spectrometer (IAMS),[1] which supplies mass spectra with no peaks due to fragment ions. Molecular ions are observed in spectra of even reactive molecules such as radicals. We demonstrated that IAMS enabled us to detect molecular ions of reactants of the Cu-CVD process and PFCs(perfluoro compounds) in an exhaust gas from a dry etching machine.[2] However, our spectrometer shows the highest sensitivity at the sample pressure of 100 Pa so far and is hardly applicable to the in situ measurements of gases for etching or CVD whose pressure is less than 10 Pa; where signal intensity for the sample at a pressure of 1 Pa was roughly estimated to be 10,000 times smaller than at the pressure of 100 Pa. In this study, we have improved the IAMS as to show the satisfactory sensitivity for the sample with the pressure of 1 to 10 Pa by (1)decelerating primary ions before collision with sample molecules, and (2)improving efficiency of transportation of ions by using a specially designed ion lens system. As a result, the peak due to molecular ion for neat cyclo-C_4F_8 was observed at a pressure of 1 Pa where the signal intensity of $2X10^{-8}$ A and S/N of 10^4 were obtained at the SEM gain of 10,000. The low-Pressure-IAMS has been found to be useful for in situ fragment-free monitoring of molecules and radicals, especially in plasma -CVD and dry etching processes. Precious discussions with Prof. Munetaka Nakata and Prof. Masao Takayanagi of Tokyo University of Agriculture and Technology are gratefully acknowledged.

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PS-TuP4 Sub-Millimeter Absorption Spectroscopy of Fluorocarbon Plasmas, ***E.C. Benck***, 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. In addition, the narrow linewidths of < 10 kHz of these continuous-wave sources are suitable for measuring rotational, vibrational and translational temperatures of radicals. Initial measurements are being conducted with a backward-wave-oscillator (BWO) source and a liquid-He-cooled bolometer detector. Radical density measurements have been made in inductively and capacitively coupled GEC Reference Reactors. The influence of wafer coatings on plasma chemistry has been measured for several different fluorocarbon (C_4F_8, C_4F_6, and C_5F_8) / oxygen etching gas mixtures.

PS-TuP5 Neutral Gas and Positive Ion Species of Ar/SF6 Inductive Plasma Discharges, ***R.R. White***, *M. Tuszewski,* Los Alamos National Laboratory, *A.M. Marakhtanov*, University of California, Berkeley

The neutral gas and positive ion species of Ar/SF6 inductive plasma discharges are studied with a Balzers PPM421 mass spectrometer. The species of two inductive plasma sources are compared: (1) a hemispherical plasma source operated at 0.46 MHz and, (2) a planar plasma source operated at 13.56 MHz. No Faraday shield is used between the coil and the quartz dielectric. The capacitive coupling of the hemispherical source is much smaller than that of the planar source. The radiofrequency (rf) power is varied between 0 and 1 kW, the gas pressure is varied between 1 and 10 mTorr, and the SF6 gas concentration is varied between 0 and 1. The main results obtained so far with the hemispherical plasma source are listed below. The SF6 gas is largely dissociated into fragments such as SF and SF2. These gas fragments have relatively low (10 - 12 eV) ionization potentials that are important for discharge sustainment. Dissociation fractions up to 95% are observed for the lowest pressures and for the highest rf powers. SF3+ is found to be the dominant positive ion species for most discharges. However, the SF5+, SF2+, and SF+ ion concentrations are significant at the lowest gas pressures and highest rf powers. Impurity gas and ion concentrations are relatively low for most discharges. Similar data acquired with the planar source will be presented and compared to those of the hemispherical source.

PS-TuP6 Introduction of a Powerful New Method of Generating Accurate Endpoint Traces Combined with Process Fault Classification for Low Dimensional Open Areas, ***D. Knobloch***, *F.H. Bell,* Infineon Technologies AG, Germany, *K. Voigtlaender, J. Zimpel,* ADP GmbH, Germany

A powerful new method of generating accurate endpoint traces based on full range optical emission spectroscopy (OES), e.g. for contact hole and VIA etch, is presented. Conventional endpoint systems derive endpoint signals by monitoring one or two discrete wavelengths. However, this technique is not accurate enough for logic and advanced memory products with low open areas and highly topographical structures. Consequently, more sophisticated and robust endpoint control of plasma processes requires the use of the full optical spectral information and powerful analysis methods. Statistical methods based on algorithms, such as evolving windows factor analysis (EWFA), principal component orientation (PCO), Hotelling's T2 and others have been used to find suitable endpoint traces. However these methods do not tend to be robust enough, because all changes in plasma emission - not only endpoint relevant changes - will be traced. To overcome these problems, a newly developed algorithm that separates endpoint information from process faults and variations is presented. The algorithm uses the complete individual weighted spectral endpoint information for a long-term robust and sensitive endpoint detection. The algorithm is based on modelling techniques constructing an optimal superposition of spectral eigenvectors to generate a spectral software filter. The application of this method in the production works like a black box for the engineer. The only requirement is the predefinition of the shape of the expected endpoint trace. Accurate and robust endpoint detection of open areas beyond 0.5% and highly topographical structures is achieved and presented.

PS-TuP7 Laser Thomson Scattering Diagnostics of Plasmas near Material Surfaces, *K. Muraoka, K. Uchino, Y. Yamagata,* ***Hassaballa Safwat***, Kyushu University, Japan

Laser Thomson scattering is a well established technique for measuring electron density and temperature of high temperature plasmas. During the last decade, the applicable range of the technique has been expanded to measurements of electron properties, not only electron temperature and density, but more generally eedf itself, of glow discharge plasmas by using data accumulation and photon counting technique.[1] It is presently being further expanded to diagnose plasmas near material surfaces of less than 100 microns. This should enable us to study plasmas of interest for barrier discharges used for plasma display panel. In addition, this will make possible to study, for example, cathode sheath phenomena, where electron drifts away from the cathode should be directly detectable. The potential of this new development is discussed.

[1] K. Muraoka et al., Plasma Sources Sci. Technol. (to be published).

PS-TuP8 Study of Process Variables and Plasma Parameters during Reactive Sputtering from a Titanium Hollow Cathode Source, ***A. Pradhan***, *S.I. Shah*, University of Delaware

Hollow Cathode Sources offer the advantages of conformal depositions and high target utilization and the ability to coat three-dimensional objects over planar sources. In addition, we have found that Hollow Cathode Sources are more suitable for reactive sputtering of compound materials as they offer stable operation and significantly higher deposition rates. These advantages have been demonstrated by using a titanium Hollow Cathode Source to reactively deposit titania thin films. The target potential and current did not exhibit the hysteresis commonly observed with planar sources. Target charging and the related arcing was not observed, even on the increasing the oxygen concentration in the sputtering gas past the metal-oxide transition point. Thin films were deposited on glass substrates and characterized by XPS and XRD. In addition, Langmuir probe measurements were carried out to determine the variation of the plasma parameters with oxygen concentration in the reactive gas and time. The spatial variation in the plasma parameters was also determined by moving the probe along the long axis of the Hollow Cathode. The electron temperature was close to 1eV, and the plasma potential varied from a few volts below to a few volts above zero. The plasma density was orders of magnitude greater than that obtained in planar sputtering, which would help explain the high deposition rate observed.

PS-TuP9 On the Limits of Operation of a Species-selective Gauge Based on the Penning Discharge Configuration[1], *C.C.* ***Klepper***, *R.C. Hazelton, F. Barakat, J. Niemel, M.D. Keitz,* HY-Tech Research Corporation, *J.P. Verboncoeur*, University of California, Berkeley

A Penning discharge tube has been used as the excitation source for optical detection of gaseous species concentrations in a neutral gas. This type of diagnostic has been primarily used in magnetic fusion energy experiments for the detection of minority species in the effluent gas (e.g. for helium detection in a deuterium background). Recent innovations[2] have allowed for extension of the operation range from <1Pa to as high as 100Pa and possibly beyond. This is done by dynamically varying the gauge parameters to keep the optical signals nearly constant (or at least away from a non-linear dependence on the pressure). However, there are limitations to this approach, because the Penning discharge can manifest itself in a number of modes, each exhibiting a different spatial emission pattern. As a result, varying the discharge parameters can cause the gauge to undergo transitions between these modes, disrupting any intended monotonic dependence of the overall emission on the varied parameter and hence any predicable impact on the emission. This paper discusses some of the modes observed experimentally. It also presents some progress made to date in using a particle-in-cell (PIC) code to predict these modes and mode transitions. The hope is that a good understanding of the physics involved in the mode transitions may allow for methods of either avoiding or suppressing such modes. This would aid in broadening the use of this plasma-based sensor technology.

[1] Research sponsored in part by the US Department of Energy under contract # DE-FG02-98ER82592-A001 (Phase II SBIR) with HY-Tech Research Corporation.

[2] C.C. Klepper et al., "Species-selective pressure gauge with extended operation", US Patent No.6351131, granted Feb. 26, 2002

PS-TuP10 A Comparison of Techniques for Measuring Plasma-induced Damage, ***P. Sakthivel***, *A. Srivastava, M. Colson, M. Tun*, Axcelis Technologies, Inc.

Plasma-induced damage is a key parameter that directly affects yield in chip manufacturing, and is even more critical for the new technology nodes that the semiconductor industry is poised to tackle. While many techniques have evolved to characterize the level of plasma damage at different stages of exposure to plasma during the manufacturing process, no single technique is considered uniquely reliable. We present, in this paper, a comparison of three of the most sensitive techniques for characterizing the performance of a second generation 300mm downstream microwave plasma strip system, the FusionES3i. The ES3i has nearly double the input microwave power for its upstream plasma source as its predecessor, and an additional RF Assist capability-a radio frequency capacitive source designed to provide low energy ions on demand. High density maps of contact potential difference were obtained on oxide coated silicon wafers to assess charging of the oxide layer on the asher using the COCOS technique (SDI), and compared with maps produced by the COS technique(KLA). NMOS and PMOS devices with several antenna ratios were also fabricated at International SEMATECH and exposed to the plasma under typical ash conditions, to compare the sensitivity of this technique to the two non-contact techniques. During some of the tests, both the upstream microwave and RF sources were operated simultaneously. The different techniques indicated that there was no evidence of charge damage for even "long" processes like post-implant strip, during which low energy ion bombardment could be used in conjunction with the microwave source. The spatially resolved data also provided a picture of the uniformity in distribution of ions over the surface of the wafer.

PS-TuP11 Electron Energy Distribution Function Measurement in Dual Frequency Very Narrow Gap Capacitively Coupled Plasma, ***B.I. Jeon***, *H.Y. Chang*, Korea Advanced Institute of Science and Technology (KAIST)

We measured Electron Energy Distribution Function(EEDF) in very narrow gap dual frequency Capacitively Coupled Plasma(CCP). 2Mhz and 27Mhz dual radio frequency is used. Electrode gap is variable bewteen 13mm and 24mm. To get the reasonable EEDF noise suppression is indispensible. We made self resonant coil with resonant frequency 2, 4, 27 and 54 Mhz to reduce rf noise. We use pulse measuring technique(double differentiation method) to get EEDF. Proper design of probe, rf noise seppression coil and low-pass filter in double differentiation circuit, we can measure EEDF in noisy plasma.

PS-TuP12 Plasma Characteristics of Magnetically Confined Linearly Extended Inductively Coupled Plasma, ***B.K. Song***, *Y.J. Lee, C.H. Jeong, G.Y. Yeom*, Sungkyunkwan University, Korea

Development of large-area high-density plasma sources is desired for a variety of next-generation plasma processing from microelectronic device fabrications to high resolution flat panel display(FPD). The plasma source developed for these application includes surface wave plasmas, inductively coupled plasmas, etc. In these plasmas, however, problems in conjunction with electron energy such as SiO_2/Si etch selectivity, etc. have been reported. These are related to the fact that the high energy portion of the electrons are prone to be exceedingly energetic in high density plasmas generated especially at low pressure and cause inadequate radical/ion ratio in the plasma. In this study, parallel-connected linear inductive antenna designs have been used to generate inductively coupled plasmas and, to improve both the plasma density and the electron temperature control, multiple-cusp magnetic fields employing permanent magnets were used and the effects of various magnet combinations and process conditions on the plasma characteristics were studied. The permanent magnets having 3000G on the magnet surface were arranged above the parallel-connected linear copper antennas by varying center-to-center distance of the magnets. Plasma characteristics such as electron temperature, ion density, and electron energy distribution functions were measured by a Langmuir probe as a function of with/without multiple-cusp magnetic confinement at low pressure Ar plasmas. The use of optimized multiple-cusp magnetic confinement in the parallel-connected linear inductive antenna designs showed improved electron temperature control in addition to the increase of plasma density. QMS(Hiden Analytical Inc., PSM 500) and OES(SC technology., PCM 402) measurement were also carried out to characterize the plasmas for the parallel-connected linear inductive antenna designs with/without the multiple-cusp magnetic confinement.

PS-TuP13 Large Area Plasmas Processing System Based on Electron-Beam Ionization, ***D. Leonhardt***, Naval Research Laboratory, *S.G. Walton, D.D. Blackwell*, SFA, Inc., *R.F. Fernsler, R.A. Meger*, Naval Research Laboratory

Electron beam (e-beam) ionization has been shown to be both efficient at producing plasma and scalable to large area (square meters). NRL has developed a 'Large Area Plasma Processing System' (LAPPS)[1] based on the e-beam ionization process, with the goals of increased control over plasma-to-surface fluxes and the modification of materials surface properties over large areas. Our system demonstrates that the beam ionization process is fairly independent gas composition and capable of producing low temperature plasma electrons in high densities. The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2-5kV, ~ 1 mA/cm^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 (100-300 Gauss) for plasma localization or without magnetic fields for a more diffuse, volumetric plasma source. Time-resolved in situ plasma diagnostics (Langmuir probes, microwave transmission and mass spectrometry) will be shown to illustrate the low electron temperature (<1eV), high electron densities (10^9-10^{13}cm^{-3}) and plasma-to-surface fluxes. Emphasis will be placed on recent surface modification tests consisting of silicon etching, anisotropic removal of polymeric material (photoresist) and organic surface activation for multi-step large-area applications. Plasma chemistry issues associated with modifying these materials using different feedstock gases in these plasma sources will be presented. In particular, the capability of high degree of dissociation and control over the incident ions will be discussed. These results come from plasma sheets in various test systems, with active areas ranging from 15cm x 20cm to areas approaching 1 square meter. Substrate uniformity in larger sources will also be discussed.

[1] Work supported by the Office of Naval Research.

PS-TuP14 Large Area Surface Modification by Atmospheric Pressure Plasma for Cleaning and Adhesion

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Plasma treatment for surface modification has been used to produce hydrophobic or hydrophilic surface on metals, plastics, glass, or polymers in industry. Especially, due to the possible low capital cost of ownership, simplicity, high throughput, etc. plasma surface treatment under atmospheric pressure is actively studied, currently. In this study, a novel large area atmospheric pressure plasma apparatus has been used to generate a large area atmospheric pressure plasma (plasmas larger than 700mm in width) and the effects of this type of plasma apparatus on the removal of organic material of large area glass substrates, ITO/glass, and Ag/ITO/glass for the large area display panel such as TFT-LCD panels and plasma display panels have been carried out. A low frequency AC power supply with a sine wave voltage (3-100kHz) was used to generate the plasmas under atmospheric pressure. He was used as the ignition and discharge gas and O_2 was used as the reactive gas. He/O_2 plasmas were generated between the two electrodes covered with a dielectric having slot shape holes and facing each other at a distance of a few mm. The sample was mounted just below the plasma region formed by these two electrodes. The size of the electrodes was 20mm(L) x 760mm(W). Using this type of atmospheric pressure plasma apparatus, dense, uniform, and very stable plasma could be obtained on the entire area of the electrode. Using this apparatus, organic materials such as photoresist were etched to estimate the cleaning rate of organic materials and cleaning uniformity. Characteristics of the plasmas were investigated by I-V characteristics using a current probe and a high voltage probe and by optical emission spectroscopy and cleaning rate was measured using a step profilometer. Characteristics of the cleaned sample surface were investigated by X-ray photoelectron spectroscopy and also by measuring contact angle of water drops.

PS-TuP15 Microwave Power Coupling Principles for Generating Small Microwave Plasmas

S. Zuo, *J.J. Narendra, A. Wijaya, D. Story, T.A. Grotjohn, J. Asmussen*, Michigan State University

The development of small high density (10^{12} -10^{13} cm^{-3}) microwave plasma sources with dimensions of 0.3 mm to several mm are under investigation. These mini plasma sources can be generated and sustained by either capacitive coupling of the microwave fields to the discharge or by a plasma resonance coupling to the discharge. Further, in some configurations plasma guided waves can be generated that power the discharge along an extended length. Various microwave field generating structures have been investigated including discharges created in the gap in the center conductor of a coaxial waveguide/cavity structure, discharges created in a quartz channel located in the dielectric layer of a microstripline, discharges created in the gap of the metal line of a microstripline, and discharges created at the end of a microwave powered electrode. The discharges generated by each of these configurations have been characterized to assess the power coupling characteristics and efficiencies of these various structures. These microwave power coupling structures have also been analyzed using electromagnetic field simulation tools. Additionally, the microwave fields in the structures that generate plasma guided waves have also been characterized using a very small sampling antenna along the plasma. The structure of these plasma guided waves have been analyzed for both long linear plasmas and for plasmas that branch into Y or T shapes using experimental measurements and electromagnetic/plasma models.

PS-TuP16 Simulation of a Micro-Plasma Reactor

D. Economou, ***S.K. Nam***, University of Houston

Recently, there has been interest in microfabricated plasma reactors with potential uses in ion thrusters, plasma displays, as integral parts of microelectromechanical systems (MEMS), etc. We have developed a self-consistent simulation model to study microfabricated inductively coupled plasma reactors. The Maxwell equations provide the power deposition profile; this is used in an electron energy equation to predict the electron temperature (assumed Maxwellian EEDF) and the rate coefficients of electron-impact reactions. These are in turn used in ion and neutral species balances to predict their 2-D density profiles. The simulation evolves until convergence. We have studied an argon plasma in a micromachined ICP, including the effect of metastables. Results will be shown and analyzed in view of the large surface-to-volume ratio of the micro-plasma reactor. Simulation results will be compared with the data of Hopwood et al (JVST B, vol. 18, p. 2446, 2000). Work supported by the NSF.

PS-TuP17 Affecting Plasma Polymerised Film Properties by the Control of Ion Energy

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By applying an RF potential onto a substrate, which is matched in phase and amplitude to these potentials in the plasma, we are able to selectively control the ion energy distribution function at a depositing surface. This technique does not perturb the bulk plasma, and therefore leaves other particles incident on the substrate, e.g. radicals, excited species, unaffected. Because of this, we are able to estimate, in-situ, the effect of ion energy upon film structure and properties. We have incorporated a suite of diagnostics including deposition rate monitor, an energy resolving mass spectrometer and an ion flux probe. Deposited films were examined ex-situ using XPS and SIMS techniques. We present data for the different monomer types triglyme and acrylic acid, and demonstrate that ion energies affect both the deposition rate, and introduces new functionalities onto the film surface.

PS-TuP18 Study of Continuous Fluorocarbon Ion Deposition on Polystyrene Surfaces using Molecular Dynamic Simulations

I. Jang, *S.B. Sinnott*, University of Florida

In this study, continuous deposition of polyatomic fluorocarbon ions ($C_3F_5^+$) on polystyrene surfaces is investigated using 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 and the incident angle is normal to surface. The results predict that 47.2 % of carbon atoms and 47.7 % fluorine atoms from incident ions are deposited on the surface. Major species remaining on the surface are the intact ion ($C_3F_5^+$) and CF_2 fragments. The average penetration depth of the ions and fragments is 1.7 nm. Some surface etching occurs during the deposition process. On average, one carbon and hydrogen atom is removed from the surface for every second ion that is deposited. Some ions or fragments combine with each other and form larger molecules. Thus, the simulations document the atomic-scale processes that ultimately lead to the growth of fluorocarbon thin films.

PS-TuP19 Ion Energy Distributions at the Substrate and Feature Charging During Plasma Etching

A.E. Wendt, *R. Silapunt, M. Patterson, R. Ding, Y.-H. Ting*, University of Wisconsin - Madison

Substrate bombardment by energetic ions is a critical element of many plasma processes, and the magnitude of the ion energy is an important process parameter. However, the conventional sinusoidal bias voltage waveform generally leads to broad bimodal ion energy distributions (IED) at the substrate, and therefore cannot be used to take full advantage of ion bombardment as a means of controlling process results. By using a non-sinusoidal bias voltage waveform, we are able to produce a narrow IED at the substrate, with dramatic results that may help in meeting future IC manufacturing requirements. Our tailored bias voltage waveform has a periodic shape at the substrate consisting of a short spike in combination with a longer period of constant voltage. Most ions cross the sheath during the period of constant sheath voltage, resulting in a narrow IED. The height of the spike sets the magnitude of the ion energy. We have previously reported measurements of the sheath voltage waveform and etch selectivity on blanket films, confirming the effectiveness of this approach. This paper addresses the influence of the IED on feature charging during the etching of patterned dielectric films. In contrast to blanket films, in high-aspect-ratio features there is a greater shadowing effect for electrons than for ions. As a result, the feature bottoms will charge positive and deflect ions, and a steady state is reached when electron and ion fluxes balance. A limitation of a narrow ion energy distribution in that case is that the feature bottom must charge to a much higher potential in order to deflect the ions compared to the case of a bimodal distribution that includes some low energy ions, drastically reducing the energy of the remaining ions that do reach the feature bottom, affecting selectivity and etch rate. Proposed modifications of the tailored voltage waveform to address these issues will be presented.

[1] Supported by SRC and NSF ECS-0078522.

PS-TuP20 Energetic CF_3^+ and F^+ Bombardments of Si Surfaces using Molecular Dynamics Simulations

J.J. Seo, *J.W. Kang, H.J. Hwang*, Chung-Ang University, Korea

Classical molecular dynamics (MD) simulations for Si etching by energetic fluorocarbon and fluorine ions have been performed to study surface ion reaction mechanisms for plasma etching. The Si-C-F potential function developed by Abrams and Graves was used to describe surface-atom interaction, which is based on the tersoff formalism. When CF_3^+ ions impacted sequentially on a Si substrate with incident energies of 50, 100 and 200 eV at normal incidence, we have observed that a mixed layer of CF_3^+ ions and Si is formed on the surface. Our results also showed that the thickness of F coverage increases and then it is saturated, as the Si surface is irradiated with F^+ ions. Etch rates and selectivities obtained from MD simulations was compared with available experimental data and another simulation result.

PS-TuP21 Simulations of Topography Defects Development (Undercut and Bowing) for Deep Silicon Etching under a SF_6/O_2 Plasma Chemistry, ***G. Marcos***, University of Orleans, France, *A. Rhallabi*, University of Nantes, France, *P. Ranson*, University of Orleans, France

New microelectronic applications such as MicroElectroMechanical Systems (MEMS) need very high aspect ratio trenches (deep/width>60) in semiconductors. Improvements in dry etching processes have been performed in obtaining deep silicon trenches by using a cryogenic method in an Inductive Coupled Plasma reactor with a SF_6/O_2 plasma discharge(see abstract of M. Boufnichel at al). The experimental research has shown that undercut and bowing formation is strongly correlated with plasma parameters, mask shape and time during processing. In order to understand the involved plasma-surface interaction mechanisms, we have developed a two dimensional etching model based on Monte-Carlo techniques. This etching model includes different surface processes due to neutral reactive species such as the fluorine and the atomic oxygen. Their flux is assumed to be isotropic. A transport model through the RF sheath is connected with the surface model to calculate angular and energetic ion function distribution. Monte-Carlo approach allows to introduce physical processes with probabilistic considerations, such as adsorption/desorption, spontaneous chemical etching, ion preferential sputtering, incident species reflexion, passivation layer formation and redeposition. Kinetic parameters are introduced as input data obtained by experimental measurements. The etched substrate is discretized by a series of uniform square cells which size defines a real number of silicon atoms. Local surface displacement is modelled by "full" cells dis/re-appearance when an etching or redeposition process occurs. This microscopic method gives an instantaneous picture of surface state during the process. In particular, it permits to follow the F/Si and O/Si surface coverage on the sidewalls versus depth and time. These information are useful to understand the transport of species in the trench. The model shows that undercut and bowing development depends on kinetic surface parameters.

PS-TuP22 Ion Trajectories in Electron-shading Damage, ***T.G. Madziwa***, *F.F. Chen, D. Arnush*, University of California, Los Angeles

In electron-shading damage, the photoresist is charged negatively, preventing electrons from entering the trench, while ions are accelerated toward the bottom of the trench. We have numerically calculated the effect of these fields on the ion trajectories. The ions are injected at acoustic speed from a sheath edge far from the substrate, and the electrons have a Maxwell-Boltzmann distribution. The photoresist and trench walls are assumed to be insulators, and the trench bottom a conductor at various potentials relative to the sheath edge. The potentials on all surfaces are given initial values, and a Poisson solver is used to compute the electric field everywhere. The ions' trajectories in this field are then computed. Setting the flux of ions to each dielectric surface equal to the Maxwellian electron flux yields a new value of the surface charge. The E-fields and trajectories are then recomputed, and the process iterated until the values converge. It is found that the E-field is concentrated near the entrance to the trench, the only place where the charges matter. The ions receive a kick there and then coast the rest of the way. Thus the trajectories are very sensitive to the exact shape of the photoresist and will change as the etch progresses.

PS-TuP23 LIF Measurement of Catalytic Species in Plasma Plume for Carbon Nanotubes Formation by PLA, ***T. Ikegami***, *M. Uchiyama, K. Ebihara*, Kumamoto University, Japan, *J. Asmussen*, Michigan State University

Single wall carbon nanotubes (SWNT) have been synthesized in an inert gas, 500 Torr, atmosphere by using pulsed laser ablation (PLA) on a graphite target containing metal catalysts such as Fe, Ni/Co. In order to clarify the mechanism of formation of carbon clusters and to understand the role of catalytic atoms in the formation of SWNT, carefully diagnostic experiments have been conducted. Specifically a carbon and Fe or Ni composite target was ablated by KrF excimer laser or YAG laser in Ar gas environment of several hundred Torr. Carbon species such as atoms, ions and molecules C_2 and C_3 in the ablation plasma plume were measured using absorption spectroscopy, ion probe, laser induced fluorescence (LIF) method, respectively. At the same time density profiles of catalytic Fe and Ni atoms were also measured using LIF method. By changing laser fluence on the target and laser wavelength (λ=248nm, 532nm, 1064nm), the relationship between carbon species and catalytic species profiles was investigated. Also the effect of magnetic and electric fields on these species was examined. Nanoparticulate soot was collected and refined to obtain nanotubes after the ablation. Properties of nanotubes were measured using AFM, XRD, FT-IR, XPS and ESR. Preliminary measurements on carbon species indicate that their density and profiles are strongly affected by laser wavelength and fluence. Species concentrations vs. the type of the catalyst will be also discussed. This research is partly supported financially by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (C), Japan.

PS-TuP24 Surface Investigation of Bone Tissue Treated with Non-thermal Plasmas, ***J.-C. Cigal***, *C.Y.M. Maurice, E. Wagenaars, L.J. van Ijzendoorn, A.H.F.M. Baede, R. Huiskes, G.M.W. Kroesen*, Eindhoven University of Technology, The Netherlands

In the last few years, much effort has been carried on the development of biocompatible plasma. Such technique directly derived from material surface processing could lead, in a long term, to a plasma-based cure for disease like restenosis, bone cancer, osteoporosis, or eczema. Our group recently developed a non-thermal plasma needle working at atmospheric pressure for this purpose. In order to be able to investigate the interaction between the plasma and living tissue, we used a low pressure plasma operating on a larger area. Because of its stability, bone tissue appeared to be the most suitable bio surface for this study. It is composed of a mineral network constituted of Calcium-hydroxy-apatite, combined with organic material (e.g. collagen). The samples have been exposed to an inductively coupled plasma, using different gases (Argon, Krypton, Helium, and Oxygen in mixture). The samples have been analysed by using infrared spectroscopic ellipsometry before and after treatment. This technique based on Fourier transform analysis presents the advantage of giving accurate information on the chemical composition of the surface of the tissue. Results have been compared with other techniques such as EDX, environmental scanning electron microscopy (ESEM), and nano-indentation. We also performed some ion beam diagnostics like RBS, PIXE, ERDA, and nuclear reaction analysis. These complementary experiments allowed us to determine the elemental of the bone tissue. These parameters are strongly connected to the above mentioned diseases.

PS-TuP25 Surface Modification of Polymers in the Development of Anti-Microbial Coatings for Medical Devices, ***G.Sh. Malkov***, *E.R. Fisher*, Colorado State University

The applying of polymers in medical devices requires strict control over material surface chemistry. Plasma-Enhanced Chemical Vapor Deposition (PE-CVD) of fluorinated monomers is a useful technique for altering the surface chemistry without affecting bulk properties and obtaining low energy surfaces. Plasma-deposited fluoropolymers demonstrate chemical inertness, lubricity, and blood compatibility. In this study, we have investigated the surface modification and characterization of polystyrene and polyvinyl chloride. Chemistry and wettability differences of modification steps were characterized using angle-resolved X-ray photoelectron spectroscopy (XPS) and static contact angle measurements. Polymer surfaces have been coated by the thin film deposition using a capacitively coupled pulsed plasma RF-discharge system with C_3F_8 and C_4F_8 as precursors. Resulting fluorocarbon films display a high hydrophobicity (water contact angle ~110°). Then the samples were activated by RF-plasma glow discharge in the presence of argon gas and coated with Pluronic F-108, which is inert to cell adhesion. The water contact angles decreased to approximately 60°. Differences in the ability to modify the fluoropolymers, depending on both monomers and plasma polymerization conditions, are observed. The composition of the surfaces will be presented as well as data from ageing studies. Preliminary XPS and contact angle measurements show a change in composition of the surfaces on time. Data from protein adhesion studies using fluorescently tagged proteins will also be presented.

PS-TuP26 Optimization of Four-component Gas He-Ne-Xe-Kr for High Efficiency Plasma Display Panel, ***T.W. Kim***, *S.U. Kwon, H.J. Hwang*, Chung-Ang University, Korea

Plasma display panel (PDP) has been spotlighted as one of the promising candidates for a flat panel display. The improvement of luminous efficiency is one of the most important issues in making a plasma display into a large flat panel device. The most fundamental element determining the discharge property is the discharging gas injected into the cell of AC PDP. Therefore, we aimed to find the optimum gas composition for maximum electric discharge. A new composition of a four-component gas, He-Ne-Xe-Kr, is proposed in order to achieve a high luminous efficiency (maximum electric discharge) in color PDP. The model utilized here is based on self-consistent simulation of the microdischarges in the PDP cell. The space and time variation of the electric field within the cell is self-consistently determined by solving the fluid equations for ions and electrons together with Poisson's equation, subject to the boundary conditions imposed by the electrode boundaries. The electrical model is coupled to a model of excited species kinetics. The density of $Xe^*(^3P_1)$ and electron, which is critical in determining the luminous efficiency, were calculated using the two-dimensional model. and The efficiency of the electrons in exciting UV emitting states of Xe was calculated. The results were then compared with measurements of luminous efficiency to identify the optimum mixing condition of He(70): Ne(27): Xe(3)-Kr gas for a color PDP.

PS-TuP27 Bond Strength Improvement of Plasma Sprayed Hydroxyapatite/Titanium Composite Coatings on Titanium: Partial Nitriding of Titanium Deposits by RF Thermal Plasma, ***M. Inagaki***, *Y. Yokogawa, T. Kameyama*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Plasma sprayed hydroxyapatite (HA) coating on titanium alloy substrates has been used for medical application to promote the osteoconductivity of implanted materials. For practical application, such as artificial joint, HA coatings with excellent adhesion to the substrate have been strongly demanded to ensure long-time fixation. However, due to the large difference in thermal expansion coefficients between coated ceramics and metal substrates, residual stress arises at the metal/ceramics interface. Such residual stress often causes cracks and reduces the bond strength of coatings. Recently, we have developed a radio frequency (RF)-TPS method that allows us to obtain strong adhesion between HA coatings and titanium (Ti) substrates by employing a HA/Ti composite coating. Here, we briefly describe a promising method to improve the adhesiveness of HA/Ti composite coatings by RF-TPS method. HA/Ti composite coatings were deposited on titanium substrates by a RF-TPS method with RF input powers of 10-30 kW. Partial nitriding of Ti deposits conducted by plasma-enhanced reaction during plasma spraying of HA/Ti composite coatings. The ratio of HA and Ti powders supplied into the plasma was precisely controlled by two microfeeders so as to change the composition from Ti-rich to HA-rich toward the upper layer of the coatings. The bond (tensile) strength of HA/Ti composite coatings was 40-65 MPa. XRD patterns of Ti coatings without HA showed that titanium nitride was formed at the surface of titanium deposits sprayed with N_2 plasma gas. Scanning electron microscopic observation showed an acicular texture on the Ti deposits prepared with N_2 added plasma gas.

PS-TuP28 Reactive Sputtering in Hollow Cathodes, ***S.I. Shah***, *A. Pradhan*, University of Delaware, *S. Berg, T. Nyberg*, Uppsala University, Sweden

Hollow cathode sputtering, due to the enclosed geometry, presents a unique opportunities that can be favorably utilized for depositing conformal coatings on complex substrates. Additional advantages related to reactive sputtering can be obtained from such enclosed sources. We have characterized a Hollow Cathode Source (HCS) for reactive sputtering from metal targets. Deposition rates close to that of metals are obtained during reactive deposition of oxides. We will present TRIM modeling to show the effect of oblique emission of the sputtered flux on the total sputtering rate. Similar effects can be seen from reflected neutrals. No hysteresis behavior in any of the sputtering parameters, typical for reactive sputtering in planar sputtering, was observed. We will present a model which will include the consideration of the relative cathode to anode areas, redeposition of the sputtered flux, pumping speed, relative flux of the metal and the reactive gas, etc., for hollow cathodes. The model shows that reactive sputtering in a circular confined geometry can be carried out at a very high deposition rate without the complexity of a hysteresis in the sputtering parameters.

PS-TuP29 Process-Induced Damage by the Low Angle Forward Reflected Neutral Beam Etching, ***D.H. Lee***, *M.J. Chung, H.K. Hwang, G.Y. Yeom*, Sungkyunkwan University, 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 particles such as positive ions and photons generated in the plasma which causes radiation damage causing physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. In the previous study, a neutral beam was formed using a low angle forward reflected neutral beam technique as a possible anisotropic etching technique without charging and its degree of neutralization and etch characteristics were investigated. When the ion beam was reflected at a reflector at the angles lower than 15 degrees, most of the ions reflected were neutralized and the lower reflector angle showed the higher degree of neutralization. In this study, process-induced damages during the etching of SiO_2 were investigated in addition to the etch rates and the etch properties of SiO_2 for fluorine-based gases using the low angle forward reflected neutral beam etching system. Surface contamination was performed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Also, possible neutral beam induced charge damage was examined through electrical characteristics such as C-V, I-V, and breakdown voltage of the gate oxide and the Si-SiO_2 interface after the etching.

PS-TuP30 Experimental Study on New Sterilization Process by using Plasma Source Ion Implantation Method with N_2 Gas, *M. Yoshida*, Mitsubishi Heavy Industries, Ltd., Japan, ***T. Tanaka***, *S. Watanabe, T. Takagi*, Hiroshima Institute of Technology, Japan, *M. Shinohara*, Kurita Seisakusho Manufacturing Co., Ltd., Japan, *S. Fujii*, Adtec Plasma Technology Co., Ltd., Japan

Plasma source ion implantation (PSII) with negative high voltage pulses has been applied to uniform sterilization process for three-dimension shaped species. This process was performed with and without external plasma source, that has been generated by inductively coupled antenna using 222 kHz RF voltage. The pulsed high negative voltage (~10 µs pulse width, 300~900 pulses/sec, 9~16 kV) was applied to the electrode in this process at the gas pressure of 2~7 Pa of N_2. This process has been found out to be capable of generating glow discharge plasma around SUS electrode, on which quartz glass plate with biological materials are placed. We have obtained a preliminary result that the PSII process has reduced log numbers of Bacillus Pumilus with N2 gas plasma generated by pulsed RF and DC voltages. This experimental result is showing a 5~6 $\log_{10}$ colony forming units reduction in Bacillus Pumilus with dried culture media by 5~10 minutes exposure. The effect of several discharge conditions such as gas pressure, pulse voltage, and RF power have been investigated experimentally. The RF discharge without negative high voltage pulses has been found to reduce colony forming units by ~3 $\log_{10}$ for 40 minutes exposure as well. However, negative high voltage pulses are necessary to achieve 5~6 $\log_{10}$ reduction of Bacillus Pumilus for ~5 minutes exposure. The state of Bacillus Pumilus on quartz glass was observed by scanning electron microscopy (SEM) with and without exposure, which is showing the surface of Bacillus Pumilus has some damage by the plasma treatment, and no damages are seen in Bacillus Pumilus by just setting in vacuum. From these experimental results, some possible effective options for the plasma sterilization systems are discussed, such as H_2O vapor mixture to generate dense OH radicals, Ar or He gas usage, and electron bombardment by the positive high voltage pulses.

PS-TuP31 Study on the Characteristics of Neutral Species in the Low Angle Forward Reflected Neutral Beam Etching System, ***M.J. Chung***, *D.H. Lee, N.G. Cho, G.Y. Yeom*, Sungkyunkwan University, Korea

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. One of the techniques fabricating a neutral beam is to use 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. Previous study showed that, by the reflection of the ion beam at 5 degree angle of incidence, most all of the ions could be neutralized. The degree of neutralization was similar to the all of the gases used in the experiment such as SF_6, NF_3 and CF_4 which can be used for the etching of SiO_2 and Si. Also, using radical beams from these gases, nearly vertical SiO_2 etching could be obtained. Even though the ions reflected at the reflector were proven to be neutralized, the energy distribution of these reflected neutrals and the possibility of cracking after reflection for reactive gases such as SF_6, NF_3, and CF_4 need to be investigated. In this study, energy and species of neutrals generated by the low angle forward reflection of reactive ions were analyzed by means of direct sampling using a quadrupole mass spectrometer (QMS) with double ion energy analyzers modified to detect neutral energy and species. Using this modified mass spectrometer, the concentration and energy distribution of each neutral species were investigated as a function of rf power, gas flow rate, and acceleration/extraction voltage of the ion gun for various reactive gases. The correlation of the etch characteristics of SiO_2 and Si with the characteristics of the measured incident neutral species were investigated to study the etch mechanism of Si and SiO_2 using the low angle reflection technique.

PS-TuP32 Improvement of Luminance and Luminous Efficiency through the Optimum Gas in AC Plasma Display Panel, ***S.J. Lee***, *H.-J. Hwang*, Chung-Ang University, Korea

The luminance and luminous efficiency improvement is a key issue for making a plasma display into a large flat panel device. We suggest a new combination of the mixture gas, in order to find the optimum mixture gas in plasma display panel. The influences of Ar, Kr addition to Ne{96%}-Xe{4%} and He{70%}-Ne{27%}-Xe{3%} mixture gases are experimentally investigated for surface discharge of alternating current plasma display panel. When rare Ar { 0.01% - 0.1% }, Kr { 0.01% - 0.1% } are added Ne-Xe and He-Ne-Xe mixture gases, the luminance increases over 20% and luminous efficiency increases over 25% at 200Torr. It is sure that luminance and efficiency are effected by penning electrons. Also, this influence of Penning effect is shown by increased wall charge { 15% - 25% } which is experimentally measured in plasma display panel.

PS-TuP33 Surface Cleaning of Organic Materials on Metal by Atmospheric Pressure Plasma, ***C.H. Yi***, *Y.H. Lee,* SungKyunKwan University, Korea, *E.S. Choi,* LG-PRC, *H.C. Woo,* Korea Vacuum Tech., *G.Y. Yeom*, SungKyunKwan University, Korea

Due to the various advantages of the use of atmospheric pressure, recent studies on the surface cleaning of organic materials are concentrated on the atmospheric pressure plasmas instead of low pressure plasmas. In this study, atmospheric pressure plasmas were generated using a capillary dielectric covered electrode and AC power supply(3-15kV) of low frequency to clean organic materials on metal surfaces such as Ag and Cu and the effects of process conditions and cleaning gases on the cleaning properties have been investigated. As the cleaning gases, He and O_2 were used as the ignition gas and cleaning gas, respectively. In addition to these gases, N_2, Ar, and SF_6 were added to improve the effect of surface treatment. The small addition of O_2 to He increased the surface cleaning rate due to the increase of oxygen radicals in the plasmas, however, the further addition of oxygen decreased the surface cleaning rate possibly due to the decrease of plasma density by the formation of oxygen negative ions between oxygen molecules and electrons in the plasma. The additional mixture of N_2 to O_2/He further increased the surface cleaning possibly due to the increased chemical reaction with surface contaminants resulting in the increased volatilization and removal from the surface. Surface characteristics after the plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS) and showed the decrease of carbon contaminants on the metal surface by the atmospheric pressure plasma treatment. Decrease of contact angles of water on the plasma cleaned surface was also observed.

PS-TuP34 A New Design in Atmospheric Plasma Generation Improves Versatility for Surface Treatment Applications in Industry, ***D. Chrysostomou***, *S. Goloviatinskii*, TePla AG, Germany

Inexpensive materials, with excellent applied bulk properties, often require surface modification to improve bondability and printability. Plasma treatment is an established industrial method for such surface modifications. Use of atmospheric plasma is more cost effective than low pressure systems and can be easily operated in continuous mode. This presentation introduces a novel design in atmospheric plasma generators that overcomes many of the disadvantages previously associated with this treatment method. A low current , 100 - 250 mA, high voltage, 1000 - 1700 V, pulsed DC arc discharge generator permits electrode construction with small dimensions. The light weight of each electrode assembly, 200 g, allows low cost operation by robotic systems. Fast point-to-point processing is possible due to very short plasma ignition times. The electrode design confines current and voltage within the discharge chamber and ensures no electrical charge transfer to the treatment surface (critical for metals and metal/dielectric hybrids in wire bond applications). Very high density equilibrium plasma, 100 W/cm^3, ensures uniform and highly effective treatments at high speed, up to 2m/sec for polycarbonate, acrylic, and silicone materials. The electrode construction produces a low temperature discharge without generating UV or ozone. NO_x levels are in the order of 100 ppm and are managed by standard filter systems. XPS analysis shows no contamination of sputtered electrode material, an essential requirement for medical, optical, and IC applications. Treatment widths of up to 40 mm are possible with a single power supply, and these systems can be further arrayed for extended treatment widths. Current electrode lifetimes exceed 1500 hours.

Surface Engineering
Room: Exhibit Hall B2 - Session SE-TuP

Poster Session

SE-TuP2 Optimum Combination of Surface Roughness for Materials with Smooth Sliding in a Vacuum, ***A. Kasahara***, *M. Goto, T. Oishi, M. Tosa*, Nanomaterial Laboratory, Japan

We used a probe of stainless steel sphere with surface roughness of 60nm, and we measured friction of stainless steel substrate which with surface roughness prepared on a submicron scale. As a result, the materials with about 100nm surface roughness showed same friction force in a vacuum as the force out as atmospheric pressure. However, frictional force is generated by relative movement between materials. Therefor we studied a difference of surface roughness of probe and form of surface roughness of a sample in order to obtain the most optimum combination condition for smooth sliding in a vacuum.We measured frictional force of stainless steel sheet surface roughness of 110nm by probes with diameter of 3.18mm and with surface roughness of 60nm,100nm and 200nm. we also used titanium and copper sheets with surface roughness polished on a submicron scall and studied relation between a direction of sliding and generated friction force. The results showed decrease in friction force under optimum combination conditions that surface roughness of substrate was smaller than that of probe with surface roughness of about 100nm and that surface grove line patterns of sliding probe and substrate cross each other at right angles.

SE-TuP3 Three-dimensional Surface Structures Created by PVD Method, ***I.G. Levchenko***, *M. Romanov*, Kharkov Aerospace University, Ukraine

We describe a new class of the plasma coatings namely the three-dimensional surface structures, as well as the technique of deposition and methods for calculating the main process parameters. These special films were produced with a view to increase a coating service life under the hard loading conditions, especially when fatigue endurance and wear resistance are the most critical factors. We created the real three-dimensional surface structures of a faceted multi-layer hard-ceramic film consisting of facets separated with the pure metal. As the hard-ceramic film, the titanium nitride and zirconium nitride composition was used. The mask technology was used for production of these structures. According to the concept proposed, the pure metal separator is used as a solid-state lubricant. Besides, the use of isolated hard-ceramic facets provides increased adhesion strength and adhesion fatigue limit; this enables deposition of relatively thick films (up to 40 micrometers) without loss of the adhesion stiffness, and prolongs the film service life before delamination. For deposition of these films, we used the molybdenum masks with various transparency factors and various facet shapes. The films were deposited using vacuum-arc deposition equipment that provides generation of the filtered ion flow free of droplets. The wear tests showed considerable increase in the wear-resistance and decrease in friction coefficient when the steel was used as the rider. For cylindrical sliding couple, the fatigue test was performed that had proved the efficiency and utility of this kind of technology.

SE-TuP4 Electron Transport Characteristics of Ultrathin Cu Films Analyzed by In-situ ac Impedance Spectroscopy, ***S.Y. Park***, *Y.H. Hyun,* Hanyang University, Korea, *J.Y. Rhee,* Hoseo University, Korea, *Y.P. Lee*, Hanyang University, Korea

The impedance and resistance are measured simultaneously by using in-situ impedance spectroscopy and I-V source during the deposition of Cu films with a thickness of 1 to 7 nm onto a glass substrate. The growth stages of films, such as the discontinuous, semicontinuous, and continuous regimes, are determined by analyzing the AC impedance spectra in addition to the rather traditional DC method. We also observed that the percolation threshold thickness is 2.5 nm by either method and that the boundary for continuous stage is 3.3 nm. The complex dielectric moduli of films thinner and thicker than 2.5 nm could be described with a parallel R-C and a series R-L equivalent circuit, respectively. It is found that the relaxation time and the inductance for the semicontinuous and continuous films are increased with increasing the film thickness, and that the changes are discussed by considering the roughness and grain-boundary scattering effects. The mechanism of growth for a variety of ultrathin films could be elucidated by applying in-situ impedance spectroscopy.

SE-TuP6 Copper Seeding on the Tantalum-insulated Silicon Oxide Film by Ion Beam Assisted Deposition for the Growth of Electroless Copper, *S. Han,* National Taichung Institute of Technology, Taiwan, R.O.C., *C.J. Yang*, National Chung Hsing University, Taiwan, R.O.C., *J.H. Lin*, National Tsing Hua University, Taiwan, R.O.C., *Z.C. Chang, C.H. Hsieh,* National Chin-Yi Institute of Technology, Taiwan, R.O.C., ***H.C. Shih***, National Tsing Hua University, Taiwan, R.O.C.

The major aim of this study is to combine the techniques of using ion beam assisted deposition (IBAD) and electroless plating to deposit Cu onto a Ta diffusion barrier layer in order to accomplish the ULSI interconnection metallization. Distribution and depth of the implanted Cu was measured by secondary ion mass spectroscopy (SIMS) profiling. The crystallinity of the electroless plated Cu was analyzed by x-ray diffraction (XRD). Cross-sectional transmission electron microscopy (XTEM) and field emission scanning electron microscopy (FESEM) were used to elucidate the growth mechanism of the electroless deposited Cu film on the Cu-seeded layer by IBAD. The surface morphology of the films was observed by atomic force microscopy (AFM). This study successfully combines the techniques of IBAD and electroless plating for Cu to provide an appropriate quality for the gap-filling submicron trenches and vias with excellent step coverage.

Surface Science
Room: Exhibit Hall B2 - Session SS-TuP

Surface Science Poster Session

SS-TuP1 In-situ Observation of Chemical State of a Si Electrode Surface during a Galvanostatic Oscillation in Fluoride Electrolytes Using Infrared Absorption Spectroscopy, ***Y. Kimura***, *J. Nemoto, M. Niwano*, Tohoku University, Japan

Electrochemical etching of silicon (Si) is an important technique for the fabrication of micro- and nano-structures on Si, and therefore, it has been extensively investigated theoretically and experimentally. It is well known that when an anodic potential below about 1 V is applied to a Si electrode, porous silicon (PS) forms in the vicinity of the surface. Interestingly, when a higher anodic potential, several volts or more, is applied to a Si electrode, an oscillation in the anodic potential or the anodic current density takes place. Previously, the oscillation has been interpreted as being due to alternative formation and removal of silicon oxide on the Si electrode surface. However, the chemistry of a Si electrode surface during galvanostatic oscillation has not been fully understood. In this study, we have investigated a galvanostatic oscillation phenomenon during anodization of a silicon (Si) crystal electrode in fluoride electrolytes using infrared absorption spectroscopy in multiple internal reflection geometry (MIR-IRAS). We confirm that the electrode surface is covered with a thin oxide layer during the course of galvanostatic oscillation. We observe a weak oscillation of the oxide thickness that synchronizes with the oscillation of an anodic potential. We also find that when the anodic potential falls to its minimum, hydrogen-substituted oxide (suboxide, $Si(O_3)$-H) forms on the electrode surface. We propose a model of galvanostatic oscillation in which it is assumed that an decrease in the anodic potential is due to the formation of pits in the oxide over layer and low-quality oxides containing $Si(O_3)$-H species are preferentially formed at the pit sites. We suggest that formation of an inhomogeneous oxide layer plays a crucial role for the galvanostatic oscillation phenomenon.

SS-TuP2 What Governs the Si(100) Low Temperature Phase ? - Study by STM and LEED, ***S. Yoshida***, *O. Takeuchi, K. Hata, H. Shigekawa*, University of Tsukuba, CREST, Japan

Through the recent intensive study on the low temperature phase of Si(100) by Scanning Tunneling Microscopy (STM) and Non-Contact Atomic Force Microscopy, symmetric dimmer, c(4x2)/p(2x2), and c(4x2) phases have been confirmed to exist below 30K, giving rise to the controversy on the ground state of Si(100). In addition to these structures, we recently succeeded in observing a single p(2x2) phase by STM at 10K for the first time, and have studied the conditions for the appearance of all these phases. For example, although c(4x2) phase easily appears in the case of p-type Si(100), particular sample conditions are necessary for the observation of the p(2x2) single phase; (1) n-type, (2) high dope, and (3) very low defect density. Furthermore, for the n-type Si(100) surface, we have succeeded in the direct observation of the phase transition between p(2x2) phase (lower temperature side) and c(4x2) phase (higher temperature side) by STM and LEED measurements. These obtained results suggest the great importance of the dopant and defect influences on the Si(100) surface phase transitions. Tip induced effect will also be discussed.

SS-TuP3 Stability Studies of Monolayers on Scribed Silicon to Water, Air, and X-ray, ***G. Jiang***, *T.L. Niederhauser, S.D. Davis, M.R. Linford*, Brigham Young University

The stability of alkyl monolayers on scribed silicon to air, water, and/or X-rays was investigated. Monolayers were prepared by scribing silicon surfaces in the presence of reactive liquids (1-pentene, 1-decene, 1-hexadecene, methyl iodide, 1-iodopetane, 1-iodododecane, 1-butanol, 1-bromopentane, and 1,4-dibromobutane) with a computer-controlled diamond-tipped instrument. In all cases some initial oxidation of the underlying silicon surface was observed by X-ray photoelectron spectroscopy (XPS), which increased with time until the O1s/Si2p XPS ratio reached a stable level (after 100 - 200 hours). In the case of silicon scribed under the iodoalkanes, the iodine to silicon ratio by XPS decreased with time until it also reached a stable value. The C1s/Si2p XPS ratios for all surfaces remain essentially constant after all exposures to air and water, which indicates that monolayers of 1-alkenes and 1-haloalkanes on scribed silicon are quite stable. Kinetics measurements using water contact angles on scribed patches and water capacity measurements of hydrophobic corrals on silicon show trends similar to the XPS results. In general, hydrophobic corrals retained much of their capacity to hold water. Surface oxidation is shown to take place at the silicon surface. It is suggested that iodine is lost by hydrolysis of surface Si-I bonds. Finally, no change in the amount of C, O, or Br at the surfaces was observed by XPS after 3 - 4 hr of illumination with monochromatic Al Ka X-rays, indicating that XPS analyses can be performed on monolayers on scribed silicon without substantially damaging them.

SS-TuP4 Bevel Crater SIMS for Auger Analysis of Laterally Oxidized AlGaAs/GaAs Multilayers, ***S.A. Wight***, *G. Gillen, P. Chi, A. Fahey, A. Roshko, K. Bertness*, National Institute of Standards and Technology

Recently, in support of a project to engineer strain in compound photonic semiconductors, we employed a combination of Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES), and Scanning Electron Microscopy (SEM) to characterize MBE grown, laterally wet-thermal oxidized, $Al_{.98}Ga_{.02}As$ layers in an attempt to determine compositional uniformity through the oxide layers. Typical samples for this study consist of alternating layers of $Al_xGa_{1-x}As$ (where x is between 0.90 and 1.0) and GaAs. Each AlGaAs layer is 80.0 nm thick and is separated from adjacent layers by 150 nm of GaAs. The surface is capped with 200 nm of GaAs. Each sample has a series of trenches (spaced 100 µm apart) etched through the multilayer to expose the buried AlGaAs layers. The lateral extent of oxidation was designed to be 25 µm from the trench edge. An external raster waveform was used in place of the standard digital raster to produce bevel craters on a commercial SIMS instrument. Beveled samples were analyzed using O2+ and Cs+ microbeam imaging in the SIMS and by AES/SEM in a commercial scanning Auger instrument. Bevels were cut in AlGaAs samples using Cs, O and Ga + primary ion beams at several different energies. Both Cs+ and Ga+ beveling produced very distorted bevels resulting from the large sputter rate differences between oxidized and unoxidized regions and a high degree of surface topography as determined by SEM imaging. Best results were obtained by using O2+ bombardment for bevel production. Currently, we are using Ar+ sputtering at a few keV impact in the Auger instrument to remove the primary beam oxygen before analysis.

SS-TuP5 Oxygen Reactivity of Clean and Au-induced High-Index Si Surfaces, *J.C. Moore,* ***J.L. Skrobiszewski***, *A.A. Baski*, Virginia Commonwealth University

We have studied the oxygen reactivity of the clean high-index Si(5 5 12) surface, as well as nearby Au-induced facet planes. The (5 5 12) surface is oriented approximately midway between the (001) and (111) planes and forms a single-domain, row-like reconstruction. When submonolayer coverages of Au are deposited and annealed on Si(5 5 12), the surface undergoes significant restructuring to form a variety of nearby facet planes. In this work, we use scanning tunneling microscopy to investigate the O_2 reactivity of these various surfaces for a range of temperatures (600 to 800 °C), pressures (10^{-7} to 10^{-6} Torr), and exposures (50 to 200 Langmuirs). At lower temperatures (<700 °C), O_2 exposure of the clean (5 5 12) surface results in disordered oxide growth, similar to that previously observed for the low-index Si surfaces. At higher temperatures (>700 °C), etching is observed via step retraction and subsequent pinning by small islands, presumably due to oxide growth. The density of these islands decreases at higher temperatures (800 °C), indicating that oxide etching dominates in this temperature regime. With regard to the Au:Si(5 5 12) system, for oxygen exposures of ~100 L and moderate temperatures (700 to 750 °C), oxide island formation is seen on the lower Au coverage (337) facets, but no etching or oxidation is observed on higher coverage facets such as (5 5 11). This behavior indicates enhanced stability of the higher coverage Au-induced surfaces, which is consistent with the passivating nature of this adsorbate.

SS-TuP6 The Origin of the Metallic States on Ge(100) Surface, ***C. Jeon***, Sungkyunkwan University, Korea, *C.C. Hwang, K.-J. Kim, T.-H. Kang, B. Kim,* PAL, POSTECH, Korea, *C.-Y. Park*, Sungkyunkwan University, Korea

Semiconductor surfaces exhibit a temperature-induced metallization upon raising temperature. Photoemission spectroscopy (PES) and low-energy electron diffraction (LEED) studies on Ge (100) surface, Kevan and Stoffel, observed a metallic state above 130K whose intensity increases as temperature rises.[1] At the same time, a c(4x2) LEED pattern was observed to convert to a 2x1. A similar increase in metallicity with temperature (up to about 900K) on the Si(100) was reported in a recent study.[2] In this work, angle resolved ultra-violet PES was utilized to investigate the metallization on the Ge(100) surface from room temperature up to 900K. The metallic state was observed at about 580 K around two symmetric points without any change in LEED pattern. Based on these results, we'll discuss the difference and similarity between the origin of the metallic surface states of the Ge and Si(100) surfaces.

[1] S. D. Kevan, N. G. Stoffel, Phys. Rev. Lett. 53, 702, 1984

[2] C. C. Hwang et al., Phys. Rev. B 64, R201304, 2001

SS-TuP7 Two-dimensional Electronic Excitations in a Metallic Monolayer on a Semiconductor Surface, ***T. Inaoka***, Iwate University, Japan, *T. Nagao*, Tohoku University, Japan, *S. Hasegawa*, University of Tokyo, Japan, *T. Hildebrandt, M. Henzler*, University of Hannover, Germany

There exists a surface-state band at the Si(111)-(√3x√3)-Ag surface created by depositing a monolayer of Ag on the Si(111) surface. An electron system in this band forms a realistic two-dimensional (2D) conduction-electron system. Recently, 2D plasmons (PLs) in this electron system have been clearly observed by high-resolution electron energy-loss spectroscopy in a broad wave-number range including PL decay due to electron-hole pair (EHP) excitations. In the present work, by means of the local-field-correction (LFC) theory, we evaluate the exchange-correlation (X-C) effects on the above electronic excitations. We compare three cases, namely, (i) random-phase approximation, (ii) Hartree-Fock approximation, and (iii) STLS approximation formulated by Singwi, Tosi, Land, and Sjölander. The X-C effects are neglected in (i), only the X effect is considered in (ii), and both the X and C effects are taken into account in (iii). We determine the electron density and the electron effective mass so that the calculated results in (iii) accord with the experimental ones. Our calculations give a good description of the experimental results of the energy dispersion and the energy-loss intensity of the 2DPL. When the X or both the X and C are switched on, with increase in wave number q, the dispersion curve begins to shift downward, and decays away due to EHP excitations at a smaller q value. Simultaneously, the integrated resonance intensity of the 2DPL in the energy dependence of the energy-loss function declines more quickly at smaller q values. This effect is more conspicuous in (iii) than in (ii). Our electron system has a large effective Bohr radius, and consequently a high effective density, because our electron system lies on a semi-infinite dielectric medium. However, owing to low dimensionality, the X-C effects appear remarkably in the 2DPL with increase in q.

SS-TuP8 Formation pf Platinum Silicides on Si as followed by AES and XRD, ***J. Liday***, Slovak University of Technology Bratislava, Slovakia, *M. Jergel*, CINVESTAV-IPN, Mexico, *P. Vogrincic, I. Hotovy, R. Kosiba*, Slovak University of Technology Bratislava, Slovakia, *G. Ecke*, Technical University of Ilmenau, Germany

Auger electron spectroscopy was used for depth profiling of platinum silicide thin layer formed as a result of annealing of 43 nm platinum layers deposited on Si (111). The factor analysis was utilized for interpretation of Auger spectra. The stoichiometry of silicide layers was determined by X-ray diffraction in both Bragg-Brentano and grazing incidence (at angles 0,5°, 1°, 1.5° and 2°) geometries in order to distinguish the depth distribution of intermediate platinum silicide phases (Pt_3Si, Pt_2Si, PtSi).

SS-TuP9 Experimental and Computational Studies of the Adsorption of Allyl Alcohol on the Si(100) Surface, ***L. Zhang***, *A.J. Carman, S.M. Casey*, University of Nevada

In order to determine which mechanism, oxygen-addition or cycloaddition, plays a dominant role in governing the adsorption of organic molecules on silicon surfaces, the adsorption of a bi-functional molecule, allyl alcohol, on the Si(100)-(2x1) surface was investigated experimentally using Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and low-energy electron diffraction. The AES studies show that the surface adsorption of allyl alcohol is similar to the adsorption of the mono-functional molecule n-propanol, and is different from the adsorption of propene, based on final coverage comparisons. TDS results show that both allyl alcohol and n-propanol have no desorbing parent molecular species, while propene desorbs molecularly from this surface. Both allyl alcohol and propanol display desorption products consistent with the loss of water during decomposition. Computational studies were also performed using density functional theory and cluster models of the surface, in order to compare with the results from the experimental studies. Both the computational and experimental studies indicate that the oxygen-addition mechanism is most likely the favored path over [2+2] cycloaddition-type reactions with the Si(100) surface.

SS-TuP10 Stochastic Motion of 7x7 Kinks at Monoatomic Step Edges, ***T. Fukuda***, *S. Maeda, H. Nakayama*, Osaka City University, Japan

Control of steps on the surface have been regarded as one of the promising technique for future electronic devices.[1] Synthesis of artificial step arrangement can be achieved by photolithographically patterned substrates followed by thermal treatment. Because an individual step movement is governed by the detail balance between attachment and detachment of surface adatoms at step edges, the study of adatom kinetics is a crucial issue for understanding and controlling of step configuration. Here we propose a method for measuring migrating adatoms and step movements below the 7x7-"1x1" transition temperature.. Microscopically, meandering steps consist of long straight segments with well defined orientations and short segments called kinks. On the Si(111) surface, these kinks are expected to be quantized by the 7x7 reconstruction and their widths and strides are limited within the 7x7 period. Even in thermal equilibrium, these kinks will stochastically fluctuate by attaching or detaching adatoms. So, the individual kink can be regarded as one dimensional "Brownian particle". In this study, we made an in situ measurement of the kink motion by the high-temp. STM and found the kink is really Brownian particle. Because the chemical potential around the kink is uniform in thermal equilibrium, there is no net mass transport between the surface adatoms and the kink site. The Brownian kink, therefore, will not diffuse but restore its position. The kink velocity follows gaussian distribution and its standard deviation is a measure of the diffusion constant of the kink, which is closely connected to the adatom diffusion constant. The temperature dependence of the standard deviation showed an activation type behavior with an energy of ~0.87 eV, compared with the adatom diffusion energy of 0.75±0.2 eV on the Si(111) 7x7 surface.[2]

[1] T.Ogino et al., Appl. Surf. Sci. 107 (1996) 1.

[2] Voigtlander et al., Phys. Rev. B51 (1995) 7583.

SS-TuP11 Atomic Structure of Bare Si Dimer on H/Si(100) Surface, ***C.C. Hwang***, POSTECH, Korea, *C. Jeon*, Sung Kyun Kwan University, Korea, *K.-J. Kim, T.-H. Kang, K.W. Ihm, B. Kim*, POSTECH, Korea, *C.-Y. Park*, Sung Kyun Kwan University, Korea

When H adsorbs on the Si(100) surface, H bonds preferentially to Si dangling bonds and can form monohydride, Si-H. The structural, electronic, and chemical properties of the Si(100) surface are considerably modified by H adsorption. Recently, partially H-desorbed Si(100)2x1-H surfaces by thermal annealing or photon irradiation have received much attention, for example, due to its increasing chemical reactivity to H_2.[1] The modified chemical property could be strongly related to the atomic structure of bare Si dimer. It has been reported from scanning tunneling microscopy experiments that untilted dimers, which are different from those on the clean 2x1, are responsible for the exotic phenomenon. Contrary to this assertion, our synchrotron radiation photoemission spectroscopy results obtained at PAL in Korea[2] show that bare Si dimers are tilted and similar to those on the clean Si(100)2x1 surface. In this presentation, we will provide Si 2p core level and valence band spectra from partially H-desorbed surfaces and discuss possible origins of the chemical reactivity.

[1] E. J. Buehler and J. J. Boland, Science 290, 506 (2000).

[2] C. C. Hwang et al., Phys. Rev. B 64, R201304 (2001).

SS-TuP12 Shape Transformation of Silicon Trenches during Hydrogen Annealing, ***H. Kuribayashi***, *R. Hiruta, R. Shimizu*, Fuji Electric Corporate Research and Development, Ltd., Japan, *K. Sudoh, H. Iwasaki*, Osaka University, Japan

In trench gate MOSFETs, trench corner rounding, which is caused by surface self-diffusion during heat treatments, is significant for the gate oxide reliability. Though the evolution of a crystal shape through surface self-diffusion during heating in vacuum has been extensively investigated, it has not been sufficiently studied in specific ambient, which is applicable to semiconductor process. In this work, we have studied the shape transformations of silicon trenches through surface self-diffusion during annealing in hydrogen ambient. The trench stripes on Si(001) with a depth of 3µm were fabricated by RIE technique with HBr contained gas plasma, where the trench sidewall surface orientation was chosen to be (110) and (-110). Then the samples were annealed at 1000°C in hydrogen ambient at various hydrogen pressures. The cross-sectional profiles of the trenches were observed by SEM after cleaving the substrates along the trench stripes. The observed time evolution of trench shapes was well reproduced by numerical simulation based on Mullins' continuum theory.[1] Thus we confirmed that the evolution of the trench-shape was due to Si surface self-diffusion. From comparison between the time scales in the experiment and the simulation, the diffusion coefficient was estimated to be about $2x10^6 nm^2/sec$ at 5.3kPa, which is smaller than that at vacuum ambient.[2] It was found that the rate of shape transformation decreased with increasing hydrogen pressure, showing strong pressure dependence of the diffusion coefficient. In the symposium, we are going to discuss the dependence of silicon surface on hydrogen pressure in detail. In addition, the behavior of atomic steps on the trench sidewall surfaces, which was observed by AFM, will be also discussed.

[1] W.W.Mullins, J.Appl.Phys.28,333(1957)

[2] Yang et al., Surf.Sci.356,101(1996).

SS-TuP13 Adsorption and Photodissociation of 4-Haloanilines on GaN(0001)-(1x1), ***V.M. Bermudez***, Naval Research Laboratory

Photochemical reactions of organic molecules on semiconductor surfaces are of interest as a means of synthesizing patterned structures with specific chemical functionalities. The adsorption of 4-chloro- and 4-iodoaniline on the GaN(0001)-(1x1) surface, and the effects of subsequent exposure to near-UV or vacuum-UV radiation, have been studied using primarily UV photoemission and electron energy loss spectroscopies, supported by ab initio quantum-chemical modeling. Both 4-haloanilines adsorb via the molecular NH_2 group, with the phenyl ring intact, as does aniline itself.[1] Like aniline, both are very reactive with the clean GaN(0001)-(1x1) surface, requiring only a small dose to achieve saturation coverage (ca. 0.29 molecules/surface site). 4-Iodoaniline is photochemically active as an adsorbate on GaN, as expected from its apparent behavior in non-polar solvents. UV radiation promotes dissociation of the molecular C-I bond, leading to the transfer of I to available sites on the GaN surface. The molecular C-I bond is intact prior to irradiation, as suggested by the changes in ELS and UPS data seen to result from UV exposure. The photochemical activity of 4-chloroaniline adsorbed on GaN is at present uncertain, but it appears to be relatively inert, again consistent with its behavior in non-polar solvents. Similar results were obtained for both n- and p-type GaN, suggesting that the photochemistry is not mediated by excited carriers from the GaN substrate.

[1] V.M. Bermudez, Surf. Sci. 499 (2002) 109, 124.

SS-TuP14 RHEED and STM Study of Initial-stage Structural Change of Si(100) Surface Induced by Exposure to Ethylene Gas and Annealing, ***T. Takami***, Visionarts Inc., Japan, *I. Kusunoki*, Tohoku University, Japan

The initial stage of the structural change in clean Si(100) - 2 X 1 surface induced by annealing at 913 K and exposure to ethylene gas has been studied by reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). Transmitted bulk Si and particle SiC spots appeared on the RHEED patterns of the ethylene-exposed Si(100) surface. The obtained STM images were in accordance with the respective RHEED patterns. At the flat area of the exposed surface where the RHEED pattern showed twice the periodicity of surface spots and transmitted bulk Si spots, the STM image showed 2 X n (n=6,7,8,9,10,11,12) reconstruction. The obtained 2 X n STM image depended on the bias voltage.

SS-TuP15 Structure of Stable Si(6 9 17) Facet on Si(5 5 12), *Y.Z. Zhu, S.H. Cho, W.X. Quan,* ***J.M. Seo***, Chonbuk National University, Korea

Up to now, it has been known that the stable facet parallel to the atomic row of Si(5 5 12) is Si(113). In the recent structural studies on Si(5 5 12) using STM, it has been found that there exists another stable facet, Si(6 9 17), whose azimuthal angle is 97 degree-off from the atomic row and polar angle is 6.2 degree-off from Si(5 5 12). As this (6 9 17) facet appears at differently inclined surfaces, it is not simply due to miscutting. Although Si(6 9 17) facet is nearly vertical to the atomic row, it consist of 1.92 nm wide (337) terraces and single (011) steps, of 0.195 nm height, connecting such narrow (337) terraces. The unit cell of (6 9 17) contains a pair of tetramers and π-7 chain which is quite similar to those of (337) subsections composing of Si(5 5 12). As the (6 9 17) facet is always accompanied by defects like grain boundaries, it can adapt smoothly-bending facets as well as straight facets. It can be concluded that it is essential to form such flexible (6 9 17) facets in combination with straight (113) facets in order to relieve the local strain with various directions.

SS-TuP16 Interfactant-mediated Growth of Ultrathin Bismuth Films on Si(111), ***J.T. Sadowski****, T. Nagao, Y. Fujikawa, S. Kuwano, T. Sakurai*, Tohoku University, Japan

Semimetal bismuth (Bi) has quite distinctive electronic properties due to its covalent-like bonds, highly anisotropic Fermi surface and low carrier concentrations. The small carrier effective masses and the very long mean free path result in large MR effects observed in bulk single crystals of Bi. However, fabrication of high quality bismuth films with nanometer thickness, required for the technological applications, still appears to be difficult. Recently, we have found that ultrathin Bi layers deposited at room temperature on the Si(111)-7x7 surface exhibit 2D growth after forming initial rough transition layer, and self-organizes into a single crystal ultrathin film nearly perfectly aligned to the Si substrate. In this paper we report the scanning tunneling microscopy studies of the role of the interfactants of Au-induced surface superstructures in the growth of flat, very well ordered, ultrathin Bi films on Si(111) surface. The morphology of the Bi ultrathin film was found to be modified by the presence of interfactant surface superstructures since the growth kinetics is modified by the change in the diffusion length, nucleation density, and the interface free energy due to the modification in the atomic as well as domain-wall configuration. In the systematic study, the morphology and detailed atomic structure of the Bi layer grown on the various Au-induced surface superstructures such as 5x2, α-root3xroot3, and β-root3xroot3-Au will be discussed and compared with the results of the direct Bi growth on the Si(111)-7x7 surface, as well as with growth on otherwise modified interfaces such as α-root3xroot3 and β-root3xroot3-Bi superstructure.

SS-TuP17 Measurement of the Dependence of Bulk Defects on the Reactivity of the TiO_2(110) Surface, ***S.N. Thornburg****, J.M. Burst, C.A. Ventrice, Jr.,* University of New Orleans, *U. Diebold*, Tulane University

Missing-atom point defects at metal oxide surfaces often enhance the reactivity of these surfaces towards the adsorption of simple molecules. A previous study of the adsorption of S on the TiO_2(110) surface found that the reactivity of this surface at temperatures >120°C was enhanced by the presence of bulk missing-oxygen defects.[1] This was determined by measuring the S 2p uptake with x-ray photoelectron spectroscopy as a function of reduction time. However, this was performed on a new TiO_2 crystal, so the influence of bulk impurities on the uptake of S was difficult to determine. A technique for reoxidizing dark blue, bulk-reduced, TiO_2 crystals has been developed that allows us to return these crystals to a defect free clear state. The degree of bulk reduction is monitored using optical spectroscopy and temperature dependent resistivity measurements with a four point probe. Optical spectroscopy measurements for both the dark blue and clear crystals show the same absorption edge at 3.0 eV, which corresponds to the bulk band gap of TiO_2. However, the dark blue crystals also show a strong absorption below 2.6 eV. Photoemission measurements of the S uptake, O reduction, and S peak shift at 250°C and room temperature have been performed on both dark blue and clear crystals. At room temperature, the S saturates at approximately one monolayer coverage for both clear and bulk reduced crystals. At 250°C, the adsorbed S replaces the first few layers of oxygen atoms. The rate of S adsorption is found to depend on bulk reduction, but at a reduced rate as compared to the measurements on a new crystal. This indicates that bulk contaminants in new crystals are also influencing the S adsorption rate.

[1] E. L. D. Hebenstreit et al., Surf. Sci. 486, L467 (2001).

SS-TuP18 FT-IR Investigation of Water Adsorbed on a -Al_2O_3 and MgO at 296 K, ***H.A. Al-Abadleh****, V.H. Grassian*, University of Iowa

Fundamental studies of water adsorption on oxide surfaces are of great interest as the water/oxide interface plays an important role in many if not all environmental chemical processes. In these studies, transmission FT-IR spectroscopy is used to investigate the adsorption of water on α-Al_2O_3 (0001) and MgO (001) surfaces. The FT-IR spectra of the (0001) surface of α-Al_2O_3 and (001) surface of MgO single crystals are measured in the presence of 0.2 to 20 Torr H_2O vapor pressure corresponding to 1 to 95% relative humidity (RH) at 296 K. The adsorption of D_2O on the single crystal surfaces of on α-Al_2O_3 and MgO is also carried out in order to obtain additional insight into the behavior of adsorbed water. Water adsorption on nitrate-coated oxide single crystal surfaces are also carried out to investigate the effect of adsorbed ions on the hydrogen bonding network of water on oxide surfaces. The FT-IR spectra are analyzed so as to quantify the amount of water adsorbed on these oxide surfaces under ambient conditions and to determine more about the nature of the adsorbed water layer.

SS-TuP19 Ozone Reactivity on Processed Mineral Oxide Particles, ***C.R. Usher****, A.E. Michel, V.H. Grassian*, University of Iowa

Wind-blown mineral dust from arid and semi-arid regions can be transported over large distances in the troposphere. The reaction of dust with trace atmospheric gases can result in the presence of organic and inorganic surface coatings. These coatings will alter the surface chemistry of mineral dust with other tropospheric species. In this study the reactivity of ozone on mineral oxides (e.g. α-Al_2O_3 and SiO_2) that had been previously reacted with nitric acid, sulfur dioxide and organics has been measured. Comparison of the kinetics of ozone decomposition on previously reacted particles to particles that have not been reacted shows that the reactivity can either increase or decrease depending on the nature of the coating. Insight into these reactions is obtained by FT-IR spectroscopy of the coated oxide particle surface before and after exposure to ozone.

SS-TuP20 Adsorption of Vesicles to Titanium Dioxide: Effect of Vesicle Size and Lipid Composition, ***I. Reviakine***, University of Houston, *F. Rossetti*, ETH Zurich, Switzerland, *A.N. Morozov*, University of Leiden, The Netherlands

Adsorption of intact vesicles has been shown to be the first step in the formation of supported phospholipid bilayers.[1,2] While the process of supported bilayer formation has been investigated in significant detail, that of vesicle adsorption has received much less attention. Experimental[2] and theoretical[3] studies indicate that the extent of deformation of the adsorbed vesicles determines whether they will form a Supported Vesicular Layer (SVL) or a Supported Phospholipid Bilayer (SPB). Bending rigidity of the bilayer and vesicle size control the extent of vesicle deformation on a given surface. This study has therefore focused on investigating the effect of these two parameters on the properties of an SVL formed on the surface of TiO_2, where vesicles used in this study adsorbed but did not form SPBs. A combination of spectroscopic (Quartz Crystal Microbalance with

Dissipation measurement, QCM-D) and microscopic (Atomic Force Microscopy) techniques was used to follow the adsorption process. Voight model was used to interpret QCM-D response [4] and the results were compared with the Random Sequential Adsorption model.

[1] Keller and Kasemo, Biophys J. 1998, 75, 1397.
[2] Reviakine and Brisson, Langmuir 2000, 16, 1806.
[3] Seifert U., Adv. Phys. 1997, 46, 13.
[4] Voinova et al., Physica Scripta 1999, 59, 391.

SS-TuP21 Perchlorate Reduction on Irradiated Titania Studied by LITD-FTMS, XPS, and IC

K.D. Lormand, *D.P. Land, E.L. Pyatt-Rudolph*, University of California-Davis

Inorganic contaminants in water supplies have been a concern for decades, due to possible deadly health effects. Perchlorates, in particular, have posed a major concern as of late due to their irreversible and damaging effects on the human thyroid, long residence time in water sheds, and resistance to existing catalysts used in water treatment. However, preliminary studies have shown that oxidized surfaces of titanium exposed to ultraviolet radiation reduce perchlorates in aqueous solutions effectively. The reaction mechanism of this reduction has been studied using laser induced thermal desorption- Fourier transform mass spectroscopy, x-ray photoelectron spectroscopy, and ion chromatography. A new chamber that allows for the rapid introduction of samples reacted in aqueous solution into UHV for analysis was used for the LITD-FTMS studies. Reacting the perchlorate solutions with the titania catalyst at atmospheric pressures allows for a more inclusive reaction mechanism due to the incorporation of atmospheric water, carbon dioxide, nitrogen, and oxygen. Surface species are seen both in the LITD-FTMS experiments as well as in the XPS studies, while species that do not adhere to the catalyst surface can be seen in the IC solution studies. Studies show that LITD-FTMS of perchlorate and its oxy-chloride derivatives do not have distinct enough fragmentation patterns to be studied by LITD-FTMS. XPS and IC studies have indicated that titania, in a thin film form, is a slow, but effective catalyst for the reduction of perchlorate. Higher surface area titania, like nano-particulate titania, may prove faster in the reduction of perchlorate to chloride.

SS-TuP22 Electron- and Photon-stimulated Desorption of Alkali Atoms from a Lunar Sample and a Model Mineral Surface[1]

B.V. Yakshinskiy, *T.E. Madey*, Rutgers, The State University of New Jersey

To investigate mechanisms for the origin of alkali atoms in the atmosphere of the Moon, we are studying the electron- and photon-stimulated desorption (ESD and PSD) of K atoms from a model mineral surface (SiO_2 film), and ESD and PSD of Na atoms from a piece of lunar basalt. X-ray photoelectron spectroscopy demonstrates the existence of traces of Na in the lunar sample. To permit increased signal for detailed measurements of desorption parameters (appearance thresholds, yields, energy distributions), a fractional monolayer of Na is predeposited onto the lunar sample surface. An alkali atom detector based on surface ionization and a time-of-flight technique are used for ESD/PSD measurements, together with a pulsed electron gun, and a mechanically-chopped and filtered mercury arc light source. We find that bombardment of the alkali covered surfaces by UV photons or by electrons with energy E>4 eV causes desorption of "hot" alkali atoms. The results are consistent with the model developed to explain our previous measurements of sodium desorption from a silica surface[2] and desorption of K atoms from water ice:[3] charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. The data support the suggestion that PSD by UV solar photons is a dominant source process for alkalis in the tenuous lunar atmosphere.

[1] supported in part by NASA
[2] B. V. Yakshinskiy and T. E. Madey, Surf. Sci. 451(2000) 160
[3] B. V. Yakshinskiy and T. E. Madey, J. Geophys. Res. 106, E12(2001) 33303.

SS-TuP23 The Periodically-Stepped NiO(100) Surface and the Adsorption of Bromobenzene

S. Chapman, *M.A. Langell*, University of Nebraska-Lincoln

Periodically-stepped NiO(100) was prepared and characterized the surface with Low Energy Electron Diffraction, (LEED), Auger Electron Spectroscopy, (AES), and X-Ray Photoelectron Spectroscopy, (XPS) to model surface defects relevant to heterogeneous chemical processes. All solid materials, including single crystal surfaces, possess irregular steps and other defects. These step defects, model undercoordinated sites that initialize catalytic and other chemical behavior. The NiO(100) single crystal was cut, polished, and oriented with regular repeating steps of seven-atom terrace width. LEED diffraction patterns are characteristic of an ordered step array with appropriate terrace and step height dimensions. Preliminary results show bromobenzene adsorbs onto stepped NiO(100) surface at 133K. The XP spectra of 515L of the adsorbate give two distinct carbon peaks separated by 4.5eV and the Ni 2p region peaks exhibit minimal structure loss. Thermal Desorption Spectrometry, (TDS), shows the majority of physisorbed bromobenzene desorbing molecularly by 190K and smaller adsorbed ring fragments around 280K. Studying a surface of characterizable defects of known density helps further the understanding of the first initial steps occurring in a chemical reaction and in the fabrication of nanostructure materials.

SS-TuP24 MCS and KMCS of Adsorption Probabilities: The Auto-catalytic Adsorption Phenomenon

J. Stephan, University of Potsdam, Germany, ***U. Burghaus***, Ruhr-University of Bochum, Germany

An increase in the coverage, Θ, dependent adsorption probability, $S(\Theta)$, with increasing coverage, i.e. an auto-catalytic adsorption phenomenon which is called for now adsorbate-assisted adsorption, has frequently been observed for the adsorption of prototype molecules on quite different surfaces. However, the effect has rarely been addressed theoretically. We present a steady-state Monte Carlo (MCS) version of the modified Kisliuk model which is consistent with the energy, E_i, dependence of the phenomenon and includes the effect of surface defects on $S(\Theta)$. Although steady-state MCS lead already to a better understanding of the microscopic scenario than analytical models, the influence of the adsorption temperature, T_s, on $S(\Theta)$ can in principle not be studied. We therefore present additionally first results of a time-dependent (kinetic) Monte Carlo simulation scheme (KMCS) which can account in principle also for the T_s dependence of $S(\Theta)$. The MCS schemes are tested for different adsorption scenarios (such as the Kisliuk and Langmuirian dynamics) and especially for the auto-catalytic adsorption. Furthermore, a comparison of the simulations with experimental data for CO adsorption on both polar (O- or Zn-terminated) ZnO surfaces [Th. Becker, et al., JCP 113 (2000) 6334] will be shown. Although the scheme can be applied to other adsorption systems, the polar surfaces of ZnO are a perfect test system for the algorithm which is mainly based on the differences in the mass-mismatch of the adsorbate (CO) and the surface atoms (O or Zn).

SS-TuP25 Synchrotron Radiation X-ray Photoelectron Spectroscopy Study of Thermal Effects on Nb Surface Oxides[1]

Q. Ma, *P. Ryan, J. Freeland, R.A. Rosenberg*, Argonne National Laboratory

We report a recent x-ray photoelectron spectroscopy study of thermal effects on the oxides grown in air on crystalline Nb surfaces. Both angle-resolved and glancing-incidence x-ray photoelectron spectroscopy techniques were used in this study. The samples were annealed at 430 °K and 540 ° K for various lengths of time. We will demonstrate that the reduction of the insulating Nb_2O_5 layer to lower oxidation states is primarily an interface-mediated reaction. Annealing at 430 °K produces a semiconducting, layered oxide with a composition of NbO_x that changes from x = 2.5, 2.0, 1.5, 1.0, to 0.5 across the oxide. Annealing at 540 °K produces a metallic oxide layer with a composition that is mainly $NbO_{0.5}$, but changes continuously and rapidly near the oxide surface. A photoelectron diffraction effect is observed on the 540-K annealed surface, which possibly indicates the formation of an ordered, but faceted, oxide layer. Oxygen readily diffuses into the Nb substrate by annealing at 540 °K. However, oxygen diffusion proceeds predominantly within the oxide in the case of annealing at 430 °K.

[1] This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

SS-TuP26 Active Sites of Photocatalyst for Water Decomposition of RuO_2-dispersed p-block Metal Oxides Involving In^{3+}, Ga^{3+}, Sn^{4+} and Ge^{4+} with d^{10} Configuration

J. Sato, *H. Nishiyama, N. Saito, K. Ikarashi, Y. Inoue*, Nagaoka University of Technology, Japan

The development of solid photocatalysts to produce hydrogen from water has been among important issues. The photocatalysts discovered so far have been the transition metal oxides with d^0 configuration. In aiming at finding a new photocatalyst group, we have focused on the p-block metal oxides with d^{10} configuration.[1] In the present study, MIn_2O_4, MGa_2O_4, M_2SnO_4 (M = Mg, Ca, Sr, Ba), and Zn_2GeO_4 were employed, and the effects of M on the photocatalytic activities were examined. For photocatalytic decomposition of water, RuO_2 were loaded on p-block metal oxides by an impregnation method. MIn_2O_4 (M= Ca,Sr) have pentagonal-prism-like tunnel structures with two distorted InO_6 octahedra each. For M = Ca and Sr, hydrogen and oxygen were stably evolved in repeated run under Xe lamp light illumination, whereas little activity was observed for M= Ba. The activity of M_2SnO_4 (M= Ca, Sr, Ba) was remarkably large for M= Ca and M= Sr, but negligible for M= Ba. The SnO_6 octahedra of M= Ca and M=Sr were distorted, whereas those of M= Ba were normal, indicating the contribution of the deformed octahedra to photocatalysis. In MGa_2O_4 (M=Mg, Sr, Ba), the activity was observed for M=Sr and M=Ba, but not for M=Mg, for which there existed correlation between photocatalytic activity and distorted metal-oxygen units. The present study clearly demonstrates that the distorted metal-oxygen units play an important role in the photocatalysis, which is possibly related to the efficiency of photoexcited charge formation. The p-block metal oxides with d^{10} configuration is concluded to form a new photocatalyst group for water decomposition.

[1] J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, J. Phys. Chem., 105, 6061 (2001).

SS-TuP27 How Thick is my Oxide?, ***D.D. Allred***, *S. Lunt*, Brigham Young University

"How thick is the oxide on this sample?" is a question is frequently heard in the lab. After a thin film is removed from the deposition system, exposing it to air on its top surface, it can begin to tarnish. I will review our work in determining the kinetic constants required to answer the question posed, to estimate the thickness of the tarnish layer as a function of time and temperature for several thin film metal exposed to laboratory air at temperatures near ambient for times up to several thousand hours. The thickness and composition of the tarnish layer is important, particularly when it is to be used in an application, such as for gate oxides for ULSI devices, for which understanding and controlling the thickness of ultrathin oxide layers is important. Our EUV optics deposition group also labors in an area where the thickness of ultrathin post deposition films is extremely important. We have looked for a single, or set of, papers which would help us answer this question for materials of interest for the extreme ultraviolet optics (EUV) community. Since the data could not be found in the literature, we resolved to measure and report them. We have studied the tarnishing of a variety of very thin metal films (typically 3-30 nm) including: Al, several of the 3-d metals (e.g. Sc, V, Cr, Fe), one each of the 4d (Ru) and 5d (W) metals and U, and UO2 in laboratory air at temperatures near ambient for several months. We have used spectroscopic ellipsometry, AFM, XPS, and low-angle x-ray diffraction in this work. The tarnish formed is not the familiar bulk oxide for Al and some other cases. We will focus particularly our progress in understanding the stages of oxidation in the 2-6 nm range, thicker than is usual for surface studies but thinner than most corrosion work. We will also show that EUV reflectance is itself a sensitive tool for measuring the thickness of ultrathin oxide films such as SiO2 and UO2.

SS-TuP28 New Insights into Self-Assembled Monolayer Structure and Dynamics, ***S.B. Darling****, *S.J. Sibener*, The James Franck Institute at The University of Chicago

We have studied the effect of adsorption of a low-density alkanethiol monolayer on the state of the Au(111) reconstruction. It is commonly believed that the substrate deconstructs following formation of a thiolate self-assembled monolayer, but our results suggest this is not always the case. Helium diffraction from 1-decanethiol (C10) and 1-octanethiol striped phase monolayers is exploited to establish the surface nearest-neighbor spacing and to illustrate a unit cell corresponding to the long dimension of the (23x√3) reconstruction. Complementary scanning tunneling microscopy data are also presented that show persistence of the reconstruction during growth of a decanethiol striped phase monolayer and no evidence for vacancy islands typically associated with deconstruction. Our model involving a still-reconstructed substrate is consistent with all of the available data. Furthermore, the low-energy surface vibrational structure of the (11.5x√3) striped phase of C10 has also been studied. Energy-transfer spectra for this system exhibit a dispersionless inelastic feature at 8 meV. We assign this to the frustrated translation of the entire molecule vibrating with polarization perpendicular to the surface. These results further the understanding of the forces that govern nanoscale self organization.

SS-TuP29 Oxygen Induced Reconstructions and Epitaxial Growth of MoO2(100) on Mo(112) : A Combined STM and LEED Study, ***B.K. Min****, *A.K. Santra, D.W. Goodman*, Texas A&M University

Oxygen chemisorption followed by oxidation of Mo(112) has been investigated in detail by the use of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Oxygen-induced p(2x3)-O, p(1x2)-O and p(1x3)-O missing row reconstructed surface structures are observed using STM and are shown to be dependent on the substrate temperature during oxygen adsorption. Atomically resolved STM data explain the undulated LEED pattern observed for the p(1x3)-O surface. This is the first direct demonstration of the epitaxial growth of MoO2(100) on a Mo(112) surface where the p(1x3)-O reconstructed surface is shown to be the precursor. A new oxide surface has been observed that corresponds to the c(2x2) reconstruction of MoO2(100) and correlates with the onset of oxide formation. Oxidation at 1250K produces a mixture of MoO2 and MoO3 (3:1) as determined by XPS and AES.

Thin Films
Room: Exhibit Hall B2 - Session TF-TuP

Poster Session

TF-TuP1 Origin of Crystalline Quality Deterioration in Epitaxial Growth of CeO$_2$ Layers on Si Substrates, ***T. Inoue***, *S. Shida, H. Takakura, K. Takahashi, A. Horikawa, N. Sakamoto, M. Ohashi*, Iwaki Meisei University, Japan

Cerium dioxide (CeO$_2$) is a promising high K insulating material for microelecronic applications with chemical and mechanical stability. It is known that epitaxial CeO$_2$(110) layers grow on Si(100) substrates with a long range lattice ordering. It is reported that crystalline quality of the epitaxial layers varies from poly-crystalline to single-crystalline, in the vicinity of the critical temperature of the epitaxial growth. This is thought to be due to nucleus generation mode variation depending on surface asperity, contamination from the growth atmosphere and so on. In order to clarify the origin of the crystalline quality deterioration, it is strongly desired that the direct observation and structural analysis of the surface of epitaxial layers and the interface between the epitaxial layer and the substrate. This paper describes the results of microscopic analyses. AFM analyses indicate that there are three kinds of facets at the CeO$_2$ layer surfaces: gable roof shaped CeO$_2$(110) facets having excellent crystallinity, irregular shaped CeO$_2$(110) hillocks having poor crystallinity and tetrahedral hillocks with (111)-orientation. Cross-sectional TEM observations clarify that the shape and crystallographic structure of the irregular hillocks, whose increase in surface density leads to the deterioration of the epitaxial layer.

TF-TuP2 Structural and Electrical Characteristics of ZrO$_2$ as a Gate Dielectric and Buffer Layer Grown by RF Magnetron Sputtering, ***G.S. Lim***, *H.S. Choi, J.H. Lee,* Korea University, *Y.T. Kim, S.I. Kim,* Korea Institute of Science and Technology, *I.H. Choi*, Korea University

The zirconium oxide (ZrO$_2$) layer has been reported to have a relatively high dielectric constant and a strong barrier property against diffusion. Therefore, the buffer layer combined with SiO$_2$ is expected to have a good interface with silicon and a strong barrier property against interdiffusion. The emphasis of the results is twofold: the first is the high quality of the investigated films as evidenced by the small measured values of loss factor, flatband voltages, and surface states density as well as the low dispersion of the relative dielectric constants. This work examines the structural and electrical properties of ZrO$_2$ thin films deposited by rf magnetron sputtering using a Zr target. The ZrO$_2$ /ZrSi$_x$O$_y$ /SiO$_2$ layer is stoichiometric, uniform, amorphous, and has an equivalent oxide thickness of ~1 nm and a dielectric constant range from 15 to 18 depending upon process conditions and very small C-V hysteresis and low leakage current. The second is that Metal-ferroelectric-insulator-semiconductor (MFIS) structures using zirconium oxide (ZrO$_2$) layers as an insulating barrier against interdiffusion have been investigated. Strong barrier effect of ZrO$_2$ layer is demonstrated by both High-resolution transmission electron microscopy (HRTEM) and analysis of Auger Electron Spectroscopy (AES). Coercive field that decisively affects the memory window becomes greater by inserting the ZrO$_2$ buffer layer between ferroelectric thin film and silicon substrate and thus the memory window also increases with an electric field to the SrBi$_2$Nb$_2$O$_9$ (SBN). The memory windows of the MFIS structure were in the range of 0.7 ~ 3.6 V for gate voltages form 3 to 9 V. The maximum memory window was observed in the MFIS with a 12-nm-thick ZrO$_2$ layer. And the leakage current density was 4.74x10^{-8} A/cm^2 at an applied voltage of 3 V.

TF-TuP3 Structural Dependence of Magneto-optical and Optical Properties of Mn-Fe Alloys Films, ***J.B. Kim***, Hanyang University, Korea, *Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine, *R. Gontarz*, Hanyang University, Korea, *J.Y. Rhee*, Hoseo University, Korea, *Y.P. Lee*, Hanyang University, Korea

The structural dependence of the magneto-optical [equatorial Kerr effect (EKE)] and optical [optical conductivity (OC)] properties of the Mn$_{1-x}$Fe$_x$ alloy films have been investigated. Mn$_{1-x}$Fe$_x$ ($0 < x < 1$) alloy films were prepared by face-to-face DC sputtering onto glass substrates kept at 293 K. The x-ray diffraction study shows a bcc structure for the Mn$_{1-x}$Fe$_x$ alloy films with $x > 0.9$, a mixture of the fcc (γ-phase) and bcc (α-Fe phase) structure for $0.65 < x < 0.8$, and a fcc-like structure (γ-phase and α-Mn) for $x < 0.65$. It was shown that the EKE signal at 293 K for the Mn$_{1-x}$Fe$_x$ alloy films can be observed only for $x > 0.50$. All the EKE spectra have nearly the same spectral shape (Fe-like) and differ from each other only in the intensity. The observed experimental EKE spectra for the Fe-rich Mn$_{1-x}$Fe$_x$ alloys can be nicely described by the simulated ones made in the framework of the effective medium approximation on the suppositions of nonmagnetic γ-phase and that the boundary between pure γ-Fe phase and a mixture of γ- + α-Fe phases follows the phase diagram for bulk Mn-Fe alloys. The optical

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* Morton S. Traum Award Finalist

properties of all the investigated alloys can be separated into three groups which are related to the different crystalline structures of alloys: the OC spectra for the $Mn_{1-x}Fe_x$ alloys which contains α-Fe phase (x > 0.65-0.70) exhibit a noticeable interband absorption peak located at about 2.4 eV; such a peak is completely absent in the γ-phase based alloys; and the α-Mn based alloys reveal a significant interband absorption peak near 1.4-1.5 eV.

TF-TuP4 Effects of Deposition Parameters and Physical Properties of Thin Films on Gas Sensing Characteristics, ***I. Hotovy***, Slovak University of Technology Bratislava, Slovakia, *J. Huran*, Slovak Academy of Sciences Bratislava, Slovakia, *J. Liday*, Slovak University of Technology Bratislava, Slovakia, *L. Spiess*, Technical University of Ilmenau, Germany, *P. Siciliano*, IME-CNR Lecce, Italy

Our research has been focused on the preparation and characterization of NiO thin films deposited by reactive magnetron sputtering. Small gas sensors on alumina substrate with different NiO thin films were fabricated and then were investigated their physical and sensing properties for application to nitrogen oxide. In order to apply NiO thin films to the nitrogen oxide gas sensor, NiO thin films (2000 Å) were prepared by dc reactive magnetron sputtering from a nickel metal target in an Ar@+@O_2 mixed atmosphere in two sputtering modes. Details about the deposition of NiO have been reported in previous papers.[1] The oxygen content in the gas mixture varied from 20 to 60 %. The films deposited in the metal-sputtering mode resulted in a polycrystalline (fcc) NiO phase with nearly stoichiometric composition. On the contrary, the films prepared in the oxide-sputtering mode were amorphous and oxygen rich. The post-annealing (500°C) of as-deposited NiO thin films changes amorphous to the (fcc) NiO phase for samples prepared in oxide-sputtering mode. TEM observations revealed a dense fine-grained structure with the grain size in the range 40-100 Å. AFM showed that the surface morphology NiO films could be modified by the process parameters as the oxygen content and the pumping speed. SEM observation and EDX analyses revealed uniform morphology and homogenous dispersion of NiO, Pt and Al_2O_3 phases. The depth distribution of elements (Ni and O) in the NiO thin films was measured by AES. We have investigated the sensitivity (I_g/I_0) versus operating temperature of NiO films when a concentration varied from 1 to 10 ppm of NO_2.

[1] Hotovy, I., Huran, J., Spiess, L., Hascik, S.: Sensors & Actuators B 57 (1999) 147-152.

TF-TuP5 Control of Epitaxial Film Growth of CuO and Cu_2O by Reactive-dc Magnetron Sputtering on Cu Target Kept in UHV Prior to Each Sputtering, ***I. Takahiro***, *M. Kunisuke*, Yokohama City University, Japan

The CuO and Cu_2O films were deposited on air-cleaved MgO(001) substrate by reactive dc-magnetron sputtering. The metallic Cu target was kept in UHV prior to each sputtering to avoid it's target poisoning. We determined the films structure and their orientation by reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD). Before film deposition, it took 10 minutes for presputtering to clean the target surface. When presputtering was carried out in the Ar plasma at 10 mTorr, the CuO(111) // MgO(001) film was grown by sputtering in Ar (7 mTorr) and O_2 (3 mTorr) mixture plasma. On the other hand, the Cu_2O film was grown at the presputtering with Ar (7 mTorr) and O_2 (3mTorr) mixture plasma, where a few Cu regions were coexisted in it. The Cu_2O film had the following orientations: Cu_2O(001) // MgO(001), Cu_2O(110) // MgO(001) and Cu_2O(111) // MgO(001). These results indicate that the presputtering process is also an important factor in our system, which is probably associated with the shutter position inserted between substrate and target in presuputtering in our study. Then we have to consider about the shutter positioning effect for the presputtering. We also confirmed that the CuO and Cu_2O films are easily grown by exposing Cu film to O_2 gas at 10 mTorr. Therefore we have to discuss the thin film growth of CuO and Cu_2O from the viewpoint of the structure formation due to the condensation of the sputtered species and the oxidation of Cu film. We will make clear these effects on CuO and Cu_2O growth.

TF-TuP6 Preparation of Fe and Fe-N Thin Films using RF Magnetron Sputtering with Multipolar Magnetic Plasma Confinement, ***K. Kawai***, *H. Harada, K. Kawabata*, Hiroshima Institute of Technology, Japan

Thin films of αFe or alloys are suitable and widely used as media materials. Among them, Fe and Fe-N thin films are promising candidates as materials for thin film heads used in magnetic recording devices because of their saturation magnetization characteristics. However, the efficient preparation of ferromagnetic thin films at a low gas pressure for a conventional planar magnetron sputtering with a thick target of magnetic materials is difficult because of the lower magnetic field above the target. We previously developed an unbalanced magnetron sputtering with a multipolar magnetic plasma confinement(MMPC) to prepare ferromagnetic thin films. The thin films of Fe and Fe-N were prepared on 7059glass substrates by the RF (13.56MHz) magnetron sputtering technique with MMPC, employing an Fe target(100mmϕ,5mm thick). Fe films were prepared at the RF powers of 100-200W and argon pressure down to $6.7x10^{-1}$Pa. It is shown that the deposition rate of Fe films linearly increases from about 4 to 12 nm/min, whose values are three times that of a conventional magnetron sputtering system. Fe-N films were also deposited by the same sputtering system in an Ar-N_2 gas mixture at different total gas pressures of $6.7x10^{-1}$-$8.0x10^{-2}$Pa and the gas flow ratio(N_2/Ar+N_2) of 0.1-0.6,where an RF power was kept at 150W. The electrical resistivity for reactively sputtered Fe-N films was significantly decreased from 300 to 90μmΩcm by lowering the total gas pressure to $8.0x10^{-2}$Pa. Compositional ratios were obtained in the range of 0-0.3 with increasing gas flow ratio of N_2 by XPS. The intensity of the Fe_3N line is observed by an XRD pattern of the Fe-N films deposited at $8x10^{-2}$Pa. These results demonstrated that this method is useful for fabricating high quality Fe-N thin films. Thus, this sputtering system is expected to greatly improve the efficient fabrication of high quality Fe and Fe-N thin films.

TF-TuP7 Mass and Optical Spectroscopy during Super-high Rate Ni Deposition by an rf-dc Coupled Magnetron Sputtering System with Multipolar Magnetic Plasma Confinement, ***M. Ohnishi***, *K. Kumabuchi, Y. Yamagata, K. Kawabata*, Hiroshima Institute of Technology, Japan, *H. Kajioka*, Industrial Research Institute Hiroshima Prefecture West, Japan

Magnetron sputtering systems offer an attractive alternative to electroplating fabricating techniques for films. Unfortunately, a high rate sputtering system for ferromagnetic films by conventional magnetron sputtering with a thick target of magnetic materials is difficult, because of the lower magnetic field above the target. An rf-dc coupled magnetron sputtering system with multipolar magnets around a Ni target (200mmϕ, 8mm thick) has been designed and tested for super-high rate Ni deposition. The deposition rate of the Ni films linearly increases with increasing dc power at an rf power of 50W and an Ar gas pressure of 0.5Pa and reaches the highest value of about 1.1μmm/min at a dc power of 20kW and at a distance of 120mm from the target surface. We measured simultaneously the ion energy distribution and optical emission spectra during high rate deposition for Ni films by an energy-resolved mass spectrometer PPM-422 (Balzers) whose orifice was set in front of the sputtering target at a distance of 260mm and by an optical emission spectrometer (OES), respectively. As the dc power increases, the peak energy of Ar^+ ion spectra shifts to a lower energy of a few eV from about 22eV and also that of Ni^+ ion spectra shifts to a lower energy of a few eV from about 12eV. The behavior in the energy of Ar^+ and Ni^+ ions in this experiment may be attributed to the plasma quenching induced by the increase in the number of sputtered Ni atoms in the plasma region. The experimental results show that the intensity of both the Ni^+ and Ar^+ ion spectra increases with increasing dc power, and the intensity ratio of Ni^+ to Ar^+ ions is more than 0.1 during high rate deposition. It is also observed from the OES results that the intensity of Ni^+ ion lines and Ni-neutral atom lines increases with increasing dc power, and is significantly higher than that of Ar^+ ion lines and Ar-neutral atom lines.

TF-TuP8 Large Remanent Polarization of Cerium-modified Bismuth Titanate Thin Films for Nonvolatile Ferroelectric Random Access Memory, ***K.T. Kim***, *C.I. Kim, D.H. Kang, I.W. Shim*, Chung-Ang University, Korea

The bismuth layer-structured ferroelectrics (BLSFs) are attractive lead-free material for ferroelectric random access memory (FeRAM) application because of its relative fatigue free character. However, BLSFs thin films have a disadvantage for high density integration in FeRAM in that they have a low remanent polarization. The ferroelectric properties, the crystal structure, and the microstructure of $Bi_4Ti_3O_{12}$ (BIT) thin films are influenced by the substitution of different sized ions in these bismuth layer-structured compounds. We investigated on the fabrication of cerium - substitution in BIT thin films using the MOD method, and on the effect of Ce-substitution in BIT thin films on the ferroelectric properties, such as the remanent polarization, fatigue, and retention characteristics. The incorporation of Ce into BIT results in a large 2Pr value, which is much larger than that of $SrBi_2Ta_2O_9$ (SBT) and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films at an applied voltage of 10 V.

TF-TuP9 Analysis of Stresses in Ru Thin Films Deposited by MOCVD, ***H.J. Lim***, *S.Y. Kang, C.S. Hwang, H.J. Kim*, Seoul National University, Korea

Ru is the most promising material for the capacitor electrode in the next generation DRAMs. Ru thin films, however, which are deposited by chemical vapor deposition have high tensile stresses. So many problems in respect of device reliability such as peeling or thermal deformation have been reported. In this study, we investigated the effects of the various deposition parameters on the stress behavior. Ru thin films were prepared by MOCVD on Si substrate using RuCp(i-PrCp) precursor and O_2 reaction gas. The stresses of films were measured using laser scanning method. The tensile stress increased with reduction of substrate temperature. And in thicker films, larger tensile stress appeared. These tendencies are attributed to low atomic mobility of the Ru material(T_m=2523K). Also tensile stress increased after annealing. It can be explained by volume shrinkage through rearrangement of grain boundary having less density during annealing. Based on these results, we propose the mechanism of this stress behavior with quantitative analysis. Then the experiments to reduce these stresses were performed by control of oxygen gas flow rate. The addition of the excess oxygen suppressed the grain growth, leading to reduction of tensile stress effectively.

TF-TuP10 Phase Changes of Chromium Nitride Films Annealed in Vacuum, ***H.-Y. Chen***, *F.-H. Lu*, National Chung Hsing University, Taiwan

CrN films were deposited onto (100) Si substrates by a cathodic arc plasma deposition technique. The films were encapsulated in vacuum (~10^{-4} torr) and then annealed over the temperature range of 500°C to 1200°C for 2 hr. X-ray diffraction results showed that Cr_2N phase appeared over the whole temperature range. The relative integrated intensity of Cr_2N phase increased rapidly with temperature. Additional $CrSi_2$ phase was formed above 900°C, which was resulted from the reaction between CrN films and Si substrates. The formation energy of $CrSi_2$ was also discussed. The formation of Cr_2N phase above 900°C would be enhanced by the formation of $CrSi_2$. The CrN films were detached from Si substrates at relatively high temperature, which might be mainly due to the thermal stress stemmed from a large thermal mismatch between Si (α=2.5x10^{-6} K^{-1}) and $CrSi_2$ (α=9.0x10^{-6} K^{-1}).

TF-TuP11 Effect of Graphite Content on Carbon Nitride Films Prepared by Hot Carbon Filament CVD, *S. Aizawa, M. Aono, N. Kitazawa*, ***Y. Watanabe***, National Defense Academy, Japan, *O. Shimizu, Y. Suda*, Mitsubishi Pencil Co. Ltd., Japan

Carbon nitride (CNx) films were prepared on silicon single crystal substrates by hot filament chemical vapor deposition (HFCVD). Several kinds of carbon coils with different graphite contents, up to 90 %, were applied for the filament. The carbon coil was heated at about 2073 K in a nitrogen atmosphere of 100 Pa. The effects of the graphite content on the surface morphology and the nitrogen content in the CNx films were studied by using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Contamination free CNx films were prepared successfully and the nitrogen content in the films is evaluated from the photoelectron peaks of carbon and nitrogen and the sensitivity factor of the XPS. AFM observations reveal that the surface roughness of the CNx films increases with the graphite content. It is found from the XPS analysis that the nitrogen content does not depend strongly on the graphite content. SEM observations of the carbon filament after deposition show that morphologies of the filament surface have changed with the graphite content. This suggests that emitting behavior of carbon clusters varies in accordance with the graphite content.

TF-TuP13 Influence of Nitrogen Concentration on Conductivity of N-doped a-SiC:H Films Deposited by PE CVD, ***J. Huran***, Slovak Academy of Sciences Bratislava, Slovakia, *I. Hotovy, J. Liday*, Slovak University of Technology Bratislava, Slovakia

The application of SiC in semiconductor device technology requires controlled and selective doping. Standard technologies for silicon device production, such as ion implantation at room temperature and the subsequent thermal annealing of radiation damage at moderate temperatures cannot be adopted because the radiation damage in SiC is extremely stable. Very high temperatures are necessary for its annealing and to activate dopants. One way to overcome this problem is to perform high current pulse electron or ion beam irradiation instead of high temperature annealing. Nitrogen-doped amorphous SiC films were grown by a PE CVD technique. Samples with different amounts of N were achieved by a small addition of ammonia into the gas mixture of silane and methane, which were directly introduced into the reaction chamber. The actual amount of nitrogen in the SiC films was determined by AES. The hydrogen concentration was determined by an elastic recoil detection method. For irradiation experiments we used electron beams with a kinetic energy 200 keV, a pulse duration of 300 ns, and a beam current of 150 A/cm^2. For the electrical characterization of the SiC films vertical diode structures were formed on the prepared SiC/Si samples. A quantitative analysis of the AES spectra was used to determine the concentration of carbon, silicon and nitrogen. It was found that with increased nitrogen doping and following activation of dopants the resistivity of the amorphous SiC films was substantially reduced.

TF-TuP14 Nitride -based Tipless Cold Cathodes for Microdevice Applications, ***N. Badi***, *K. He, N. Medelci, A. Bensaoula*, University of Houston

This paper reports on the electron field emission from sulfur doped boron nitride thin films deposited on Si, TiN/Si, and hydrogen plasma roughened silicon (Si: H_2) substrates by a filamentless End Hall ion source -assisted physical vapor deposition technique. Patterned S-BN/TiN/Si and TiN/SiO_2/S-BN/TiN/Si arrays were also fabricated by using a combination of selective wet etching and photo-assisted reactive ion etching (PA-RIE) processes. The TiN interfacial layer and the substrate morphology influence considerably the emission properties of sulfur-BN layers. Preliminary results show an enhancement in emitted current density and a reduction in threshold voltage. To investigate the effects of heat treatment and pressure on field emission, in-situ thermal annealing up to 250 °C was carried in vacuum and in a controlled air ambient. The I-V characteristics of our samples did not significantly change in a pressure range from 8 x 10^{-8} to 3 x 10^{-5} Torr. Temporal stability measurements at different pressures show only a small current density fluctuation. These results are encouraging as far as device operation in harsh environments.

TF-TuP15 Electrical and Optical Properties of a-C:H:Si Films Deposited by r.f. Plasma Chemical Vapor Deposition, ***I.J. Kim***, *Y.T. Kim, W.S. Choi, D.H. Yoon, B. Hong*, Sungkyunkwan University, Korea

Research in recent years has been made to study the incorporation of silicon atoms into hydrogenated amorphous carbon(a-C:H:Si) films with interesting results. Films with very low friction coefficients, improved adhesion and increased sp^3 character have been reported. However, an investigation of the electrical and optical properties of silicon incorporated hydrogenated amorphous carbon(a-C:H:Si) films is still lacking. In this study, we present the results obtained for electrical and optical properties of silicon incorporated hydrogenated amorphous carbon(a-C:H:Si) films deposited on Si(100) wafers and corning 7059 glass from radio-frequency glow discharge of mixtures of methane and silane gas. The flow rates of CH_4 and H_2 were fixed at 10 Sccm and 90 Sccm, respectively, and the SiH_4 flow rate was varied from 0 to 2.0 Sccm. We have used Raman spectrophotometer, ultra violet-visible(UV-VIS) spectrometer and Fourier transform IR(FT-IR) for determining optical properties and current-voltage(I-V) measurement for electrical proprties.

TF-TuP16 Pulsed Laser Deposited Zn_2GeO_4: Mn Thin Films for Field Emission Displays, ***L.C. Williams***, *D.P. Norton, P.H. Holloway*, University of Florida

Field emission displays (FEDs) are among several technologies competing to become the principal device in the flat panel display market. Thus, the development of low voltage phosphors are critical. Thin film phosphors offer the following advantages over powder phosphors: better mechanical integrity, more efficient use of material, and better heat sinking. Thin film Zn_2GeO_4: Mn has been pulsed laser deposited in this study and its cathodoluminescent properties were characterized. The Zn_2GeO_4: Mn thin films were deposited onto MgO, yttria stabilized zirconia (YSZ), and Si substrates. In addition, the deposition temperature was varied from 600 to 750 °C. The best cathodoluminescent brightness was observed from YSZ substrates. A green cathodoluminescent emission peak at 540 nm was observed for depositions at temperatures $\geq$ 650 °C. At a deposition temperature of 600 °C, a red shifted emission peak was observed at 650 nm. Observation of the red shifted peak correlated with the lack of crystallinity in the films deposited at 600 °C. The shift in emission will be discussed in view of reports that the emission from Mn is sensitive to the symmetry (octahedral versus tetrahedral) in a host lattice.

TF-TuP17 Study of GaPN Epilayers Grown by Molecular Beam Epitaxy, ***M.A. Santana-Aranda***, CINVESTAV-IPN, Mexico, *C. Mejía-García*, IPN, Mexico, *M. Meléndez-Lira*, CINVESTAV-IPN, Mexico, *G. Contreras-Puente*, IPN, Mexico, *M. López-López*, CINVESTAV-IPN, Mexico, *K. Momose, A. Utsumi, H. Yonezu, Y. Furukawa*, Toyohashi University of Technology, Japan

III-V-Nitrogen compounds open the possibility of monolithic integration on III-V based light emitting devices and Si based microelectronics. Small amounts of nitrogen in the GaPN alloy increase the light emitting efficiency of GaP. While, according to Vegard's rule, lattice matching of GaPN to Si is accomplished with around 2.1% nitrogen. In this work, we present the characterization of GaPN layers with up to 2.41% nitrogen content grown on GaP substrates by molecular beam epitaxy. Photoluminescence, contact-less electro-reflectance and Raman scattering measurements are performed in order to characterize the quality of the layers, and compared to results obtained with high-resolution x-ray diffraction, atomic force microscopy and transmission electron microscopy. The photoluminescence spectra are red shifted with increase of nitrogen content. The behavior of the energy band gap determined with the electro-reflectance measurements is compared to previously published calculations and experimental determinations. GaP-like LO mode, as observed by Raman scattering, is shifted toward lower frequencies because of two contributions; alloying and strain. Furthermore, high-resolution x-ray diffraction reveals that GaPN layers are partially relaxed, which is supported by transmission electron microscopy and atomic force microscopy. Transmission electron microscopy shows dislocations and micro-cracks for the samples with higher nitrogen content. Atomic force micrograph of the sample with 2.41% of Nitrogen show the presence of some grooves parallel to the direction, that are related to the process of strain relaxation.

TF-TuP18 Ultraviolet Emitting SrS:Te Thin Films, *P.D. Rack*, University of Tennessee, ***J.M. Fitz-Gerald***, University of Virginia

The development of semiconductor based ultraviolet (UV) light sources is of critical importance for miniaturized ultraviolet light sources which have application in biological agent detection, non-line-of-sight covert communications, water purification, equipment/personnel decontamination, and white light generation. To this end, a significant amount of research is currently being performed to extend the III-V nitride blue lasers and light emitting diodes into the ultraviolet region. In this paper we will discuss the ultraviolet emission of pulsed laser evaporated thin film SrS:Te. SrS has an indirect bandgap of ~ 4.32 eV and when doped tellurium ultraviolet emission occurs from bound excitons. Un-doped SrS thin film properties (crystallinity and composition) as a function of the growth conditions will be presented and the effect that the tellurium concentration has on the ultraviolet emission will be discussed. The nature of the bound excitons will be discussed along and thermal quenching data will be presented.

TF-TuP19 Growth and Characterization of Single Crystal Multi Layer Nano Structures for Fast Ion Conduction, *S. Azad, S. Thevuthasan, V. Shutthanandan, C.M. Wang, D.E. McCready, J.W. Stevenson, S. Baskaran,* ***C.H.F. Peden***, Pacific Northwest National Laboratory

Recently, considerable interest has been shown in the growth and characterization of nanoscale materials since they often have very different properties from the bulk material. It has been demonstrated that restructuring simple ionic crystals at the nano scale can alter the electrical properties of ion conducting materials. Such materials have potential applications in solid electrolyte-based devices such as high-temperature batteries and fuel cells.[1] Recently, we successfully grew epitaxial single-crystal multi layer thin films of pure and mixed ceria and zirconia on single-crystal yttria-stabilized zirconia (YSZ) substrates at the Molecular Beam Epitaxy facility of the Environmental Molecular Sciences Laboratory (EMSL). The films, with different thickness, were grown at various substrate temperatures in order to investigate the role of substrate temperature and film thickness on ionic conductivity. The interface between pure and mixed ceria films and YSZ substrates showed misfit dislocations, and the defect density at the interface affected the ionic conduction. These films were characterized using in-situ reflection high-energy electron diffraction (RHEED), ex-situ x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS) along with ion channeling. These results will be discussed along with the ionic conductivity measurements from these films and substrates.

Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research.

[1] N. Sata, K. Eberman, K. Eberl and J. Maier, Nature 408 (2000) 946.

TF-TuP20 Molecular Beam Deposition of Yttrium Oxide as a Host Material of Er Doping for an Optoelectronic Amplifier Application, *B. Cho,* ***T. Van****, J.P. Chang*, University of California, Los Angeles

Erbium has been extensively used as a doping material for silicon-based optoelectronic amplifiers due to the 1.54 µm light emission from its trivalent ion, which is one of the standard wavelengths in optic communication. We deposited yttrium oxide as a host material for erbium doping using molecular beams from metal-organic precursor with bera diketonate structures, Y(TMHD)$_3$ [TMHD; tris (2,2,6,6-tetramethyl-3,5-heptanedionato)] as well as H, N, and O atom beams and Ar$^+$ ion beam. We chose Y$_2$O$_3$ as a waveguide core material because it has higher Er solubility and refractive index than silicon or silica, enabling higher signal gain on smaller dimension devices. However, the Er dopants should be evenly distributed to reduce the cooperative upconversion effects leading to the decrease in quantum yield. We could achieve high quality epitaxial films at lower temperatures than required in prevailing sputtering or ion implantation methods by controlling the beam fluxes and energies. During the deposition we monitored the in-situ deposition/etching rates using a quartz crystal microbalance. This low temperature process could reduce the Er diffusion, segreagation, and precipitation resulting in deleterious effects on Er luminescence. Optically-active Er complexes can be easily incorporated into the growing Y$_2$O$_3$ film without causing defects in the host material since the coordinations are preserved in the precursor molecules as well as Er-O has a lattice constant very similar to Y$_2$O$_3$ film. We investigated the effects of substrate and doser temperatures, fluxes and energies of the beams on the dopant concentration, its spatial distribution, and the film structure and composition. To this end, we characterized the deposited samples using SIMS, LEED, XRD, and XPS.

TF-TuP21 Infrared Emission from Electroluminescent Thin Film ZnS Doped with Rare Earth Fluorides, ***W. Glass****, A.S. Kale, M. Davidson, P.H. Holloway*, University of Florida

Alternating current thin film electroluminescent devices (ACTFELDs) are well-known thin film structures used for flat panel displays. A well-known phosphor for such displays is ZnS doped with either transition or rare earth elements. The infrared emission from these types of materials is often overlooked except in the case of ZnS:ErF$_3$, which has been of interest for fiber optic communications. The infrared intensity of these phosphors is dependent on the environment of the luminescent centers and can be improved by modification of deposition and processing. In this study, rare earth fluoride doped ZnS films were deposited by RF planar magnetron sputter deposition. Deposition temperature was varied to determine temperature effects on brightness and crystallinity. In addition, the rare earth concentration was changed from a maximum of 1.6 mol% to zero by simultaneously sputtering an undoped ZnS target. Similarly, films containing two rare earths have been produced by simultaneously sputtering two rare earth containing targets. These films were used to determine the effects of concentration and energy transfer between rare earth dopants. The devices were then excited by electroluminescence to determine the optimal conditions for infrared emission. Finally, emission from materials with similar and dissimilar luminescent decay paths will be discussed.

TF-TuP22 Solutions for the Deposition of Complex Optical Filters with Dual Ion Beam Sputtering, ***R. Blacker****, D. Deakins, A. Dummer, J. George,* Veeco Instruments Inc., *Y. Godwal,* Colorado State University, *I. Kameyama, S.M. Lee, N. Van Lieu,* Veeco Instruments Inc., *C.S. Menoni,* Colorado State University, *D. Siegfried,* Veeco Instruments Inc., *G. Vaschenko,* Colorado State University, *C. Montcalm,* Veeco Instruments Inc.

Demand for complex optical filters with increasingly tighter tolerance specifications is expanding. The need for more complex strategies to meet filter performances is also becoming increasingly apparent. The requirements for ultra low loss filters, low reflectivity filters (<-40 dB), highly specified broadband filters (gain flattening, beam splitter) and tight narrow band filters (50 GHz and 25 GHz dense wavelength division multiplex) are becoming more stringent, hence the need for ever more complex strategies to meet these demands.This paper presents examples of such complex filters in the context of their usage and required specifications, illustrating the degree of accuracy required during deposition to allow such filters to be realized. We present techniques using ion beam deposition that allows the layer thickness accuracies to be increased over currently obtainable levels. Optical monitoring strategies, substrate temperature control, robust filter design and ion source improvements are illustrated as specific examples. The suitability of current technology for anticipated future needs is explored, and areas of potential improvement are identified.

TF-TuP23 Study of the Oxidation Rates of Vanadium and Scandium, ***N.D. Webb****, G.A. Acosta, D.D. Allred*, Brigham Young University

A study of the oxidation rates of thin films of vanadium and scandium was performed using an ellipsometer operating between 800 and 200 nm. Thin films of vanadium and scandium (between 40 and 150 A) were deposited on silicon substrates using a DC magnetron sputter system in a vacuum chamber. The samples were annealed at several temperatures between 90 to 200 C, with ellipsometric measurements taken periodically during the annealing process. This data was analyzed to determine the oxidation rates as a function of temperature and time, the activation energy of the oxides, and the swell factors. The oxidation states of the oxide films were determined using x-ray photoelectron spectroscopy. From our earlier work we found published, bulk constants were not appropriate for use with films this thin. We experimentally determined thin film, sputtered vanadium and scandium constants, as well as those for the subsequent oxides, in the visible and extreme ultraviolet (EUV). This work is part of a larger project; we are designing a vanadium and scandium multilayer mirror that will exhibit high reflectivity in the EUV.

TF-TuP24 The Distribution of Ge during Oxidation of epi-Si$_{1-X}$Ge$_X$, ***B.G. Min****, S.-K. Kang, Y.H. Hong, D.-H. Ko*, Yonsei University, Korea

Silicon Germanium alloys have been received considerable attention in recent years for their potential application in advanced electronic and optoelectronic devices. The oxidation behavior of this material continues to be a troublesome issue that impedes its timely development. The distribution of Ge and the oxidation mechanism of epi-$Si_{1-X}Ge_X$ have been investigated. The epi-$Si_{1-X}Ge_X$ was deposited by UHV-CVD at 650$_o$C. The atomic fraction of Ge were 0%, 15% and 30%. The thickness of epi-$Si_{1-X}Ge_X$ layer is 30nm. Oxidations were performed at 800, 850, 900°C under 1atm of dry and wet O_2 for various time. Oxidation rates were compared with various Ge contents from 0% to 30%. The formed oxide was pure SiO_2 and Ge atoms piled up at the SiO_2/ $Si_{1-X}Ge_X$ interface. Contents and regions of Ge-rich layer were varied with the Ge contents and oxidation rates. It was due to different diffusion mechanism of Si source in the epi-$Si_{1-X}Ge_X$ with that in pure Si substrates during oxidation. By AES and HRTEM analyses, we observed the contents of Ge and the width of Ge-rich layer. In addition, we will discuss the electrical properties of MOS capacitor with Pt gate electrode.

Vacuum Technology
Room: Exhibit Hall B2 - Session VT-TuP

Poster Session

VT-TuP1 The KATRIN Neutrino Mass Experiment - Vacuum Technological Aspects, ***C. Day***, *V. Hauer,* Forschungszentrum Karlsruhe, Germany, *J. Bonn*, University of Mainz, Germany

In modern particle physics, one of the most challenging task is to determine the rest mass of neutrinos. The energy spectrum of the electrons of the β decay can be used to derive upper limits of the electron neutrino mass. A new large tritium experiment is currently being planned, the KATRIN experiment, which is expected to increase the resolution of mass determination by one order of magnitude. It is an international effort and will be built up and operated in FZK, Germany. The KATRIN vacuum system can be subdivided into three main parts, the windowless gaseous tritium source (WGTS), the differential pumping section, and the pre- and main spectrometer. The WGTS introduces tritium gas into the central piping system, operated under fine vacuum conditions. Further in spectrometer direction follows a differentially pumped section to reduce the gas pressure by nine orders of magnitude. This is realised by a cascade of turbomolecular pumps combined with a cryogenic pump system (Ar frost). Between the tritium source and the main spectrometer a pre-spectrometer is inserted, acting as an energy pre-filter. The key component of the new experiment is the large MAC-E-filter with a diameter of 7 m and an overall length of about 20 m, designed for XHV conditions. The spectrometers are pumped by a two-stage system, comprising turbomolecular pumps with high compression ratio for hydrogen, and getter pump modules. This paper delineates the underlying concepts for the three different vacuum systems. Special requirements are full tritium compatibility, operation in strong magnetic fields and under high voltage conditions. The differential pumping section, especially the final cryogenic pump, must provide a capture probability of almost unity, to allow for XHV conditions in the pre-spectrometer tank. To limit the pumping speed requirements with respect to the getter pumps, the outgassing of the spectrometer vessel walls must be reduced to an absolute minimum.

VT-TuP2 Extended Measurements of Photon Stimulated Desorption from a Copper Beam Chamber after Removal of Surface Oxide[1], ***C.L. Foerster***, *C. Lanni*, Brookhaven National Laboratory

Photon Stimulated Desorption(PSD) was measured from a copper beam chamber after completely removing the vacuum surface oxide in order to reduce the PSD. Continuous measurements have been recorded for the chamber, over a year and a half exposure period, to determine long term exposure effects. The measurements of PSD and specular photon reflection were performed on NSLS beamline U9a at Brookhaven National Laboratory. It is well known that PSD causes a pressure rise in accelerator and storage ring vacuum, which limits their performance. For this experiment, a KEKB factory beam chamber from a previous experiment was chemically etched and chemically cleaned prior to installation on beamline U9a. Previous PSD measurements have shown that this chemical treatment removes any memory of prior exposure or conditioning. After installation, the copper chamber and end stop were vacuum baked to 250°C for more than a week to completely remove vacuum surface oxides. The chamber was exposed to more than $5x10^{24}$ photons direct from the source having a critical energy of 595 eV and striking at an incident angle of 100 mrad. The major PSD yields for hydrogen, carbon monoxide, carbon dioxide, and methane are reported as a function of accumulated photon flux and preparation. The PSD yields for the copper chamber, after oxide removal, were found to be greatly reduced when compared to previous measurements at this laboratory and by those reported from other laboratories. The PSD component gases remained the same during the long exposure and all were significantly reduced. Carbon dioxide and methane were reduced much more than hydrogen and carbon monoxide. Specular photon reflection did not change significantly during the extended exposure.

[1] Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VT-TuP3 Synchrotron Radiation-Induced Desorption of NEG-Coated Vacuum Chambers at the ESRF, ***R Kersevan***, European Synchrotron Radiation Facility, France

The outgassing yield of several vacuum chambers under exposure to synchrotron radiation at the European Synchrotron Radiation Facility (ESRF) is given. Recently, Non-Evaporable Getter (NEG) coatings have been applied in order to reduce the pressure profile inside narrow-gap vacuum chambers, with the aim of reducing the interaction between the 6 GeV electron beam and the residual gas. Chambers made out of stainless steel, with copper coating, and extruded aluminum have been studied. Wherever possible, comparison between un-coated and NEG-coated chambers of the same geometry is made. It is shown that the NEG-coated chambers give a reduced amount of bremsstrahlung radiation, a clear indication of a reduced outgassing yield and distributed pumping. A brief description of a NEG-coating facility, capable of coating chambers up to 6 meters in length, being built and commissioned at the ESRF is given.

VT-TuP4 New Absorber in a Ceramic Kicker-chamber for the TLS Electron Storage Ring, ***G.-Y. Hsiung***, *S.-N. Hsu, C.-S. Ho, J.-R. Chen*, Synchrotron Radiation Research Center, Taiwan

An insertion device of 6T super-conducting wiggler has been installed in the injection section of the Taiwan Light Source (TLS) electron storage ring. A ceramic kicker-chamber downstream the device subjects an intensive synchrotron radiation on both side-wall. A water-cooled copper absorber, installed inside the ceramic chamber to shield the inner wall from irradiation, might cause serious problems. The problems contain the induced arcing between the absorber and the ceramic chamber, the induced interference magnetic field, etc. during the ignition of the kicker magnet. The efficiency of beam injection and the beam life time could be seriously degraded. The solution to cure those problems, the design of the absorber, and the commissioning results will be described in this paper.

VT-TuP5 Numerical Simulation of the Ion Beams Transmission Efficiency For the Design of the DC-72 Cyclotron Vacuum System, ***A.V. Tikhomirov***, *G.G. Gulbekian, R.Ts. Oganessian*, Joint Institute for Nuclear Research, Russia

The results of transmission efficiency numerical simulation for the ion beams due to a charge exchange with the residual gas in the cyclotron vacuum system including: the axial injection system; the cyclotron vacuum chamber as well as transport lines for accelerated ion beams are presented. Simulation method have been developed and tested on the base of experiments at four heavy ion cyclotrons of FLNR. Simulation results have provided determination of the main parameters for the DC-72 cyclotron vacuum system.

VT-TuP6 Study of the Performance of a Precision Constant Volume Flowmeter for Vacuum Calibration and Measurement, ***Y.W. Chang***, *J.S. Lin*, Precision Instrument Development Center, Taiwan, R. O. C.

The Vacuum Laboratory at Precision Instrument Development Center in Taiwan has developed a high vacuum calibration and measurement system by the orifice flow method. A constant volume flowmeter is used to provide a measurable, steady and uniform gas flow to the vacuum chamber in the range 10^{-2} to 10^{-5} Torr.l/s. With this type of flowmeter gas is supplied from a reservoir of fixed and known volume. The pressure drop in the volume is measured and the product of reservoir volume and the pressure drop per unit time determines the gas throughput of flowmeter. A regulating valve at the exit of reservoir controls the gas flow rate. The performance of such a flowmeter is verified by introducing the known gas flow rate to an orifice calibration chamber to generate a pressure, which can be determined by the flow rate and the orifice conductance under molecular flow conditions. The predicted pressure is compared with the pressures simultaneously measured by a spinning rotor gauge calibrated at PTB in German and an ion gauge calibrated at NML in Taiwan. When the correction factors for two gauges show the same tendency in repeated measures, the variations of correction factors then indicate the performance of the flowmeter. The pressure drops in the reservoir are measured both absolutely and differentially. In absolute way the reservoir pressure is measured with a capacitance diaphragm gauge (CDG); while in differential way the pressure difference between the reservoir and a reference volume is measured with a differential CDG. The measurement results of gas throughput of the flowmeter by two ways are also presented in this study.

VT-TuP7 Influence of Temperature on the Sensitivity Coefficient of a Hot Cathode Ionization Gauge

H. Akimichi, *M. Hirata*, National Institute of Advanced Industrial Science and Technology, Japan

Hot cathode ionization gauges, such as a triode gauge and a Bayard-Alpert type gauge are used as reference, secondary and transfer standards in high and ultrahigh vacuum. For these applications, the stability of the sensitivity coefficient (S) of the gauge is very important. Under ideal conditions, the coefficient may be kept within 1%. It is well known, however, that the indication of the gauge is strongly affected by temperature. We studied the influence of temperature on the indication of the gauge. By cooling an ionization gauge with an electric fan, the indication at pressure lower than about 10^{-4} Pa decreased with temperature, which dues to the decrease in the outgassing from the gauge itself. Typically, the indicated pressure at $6x10^{-6}$ Pa decreases about 30 % by the decrease in the temperature (Tg) of the gauge head from 40 to 27 °C. In contrast, at pressure higher than about 10^{-4} Pa, the decrease in the temperature caused an increment of the indicated pressure at about 2 %. The shift in the indicated pressure was explained by the thermal transpiration effect $S'/S = \sqrt{(Tg/Tg')}$. Change in room temperature (Tr) from 22 to 32 °C, on the other hand, the sensitivity coefficient of the gauge changed from 0.128 to 0.125 Pa^{-1}. This result was also explained by the relations $S'/S = Tr/Tr'$, since the temperature change in vacuum chamber and in gauge head are much the same. These results mean that compensation of the temperature for the sensitivity coefficient is important for a precious pressure measurement using an ionization gauge.

VT-TuP8 Influence of Gas-Surface Interaction on Thermal Transpiration of a Capacitance Diaphragm Gauge

S. Nishizawa, H. Akimichi, ***M. Hirata***, National Institute of Advanced Industrial Science and Technology, Japan

For a capacitance diaphragm gauge (CDG), the temperature difference between the sensor head and the vacuum chamber gives a non-linear sensitivity, which is called thermal transpiration. This sensitivity depends on gas species and pressure. It is supposed that under the same condition of gas-surface interaction, the sensitivity should be normalized by mean free path regardless of gas species. However, the sensitivity dependence of mean free path is also different from gas species. For example, at molecular flow regime, the sensitivity of He is slightly small in comparison with Ar and N_2. It means that the gas-surface interaction should be different from each gas. In this study, by using a direct simulation Monte Carlo (DSMC) method, the influence of gas-surface interaction on thermal transpiration was analyzed. In case of random and cosign reflection models, the sensitivity has non-linearity and depends on mean free path. On the other hand, in case of a perfectly elastic reflection model, the sensitivity is constant regardless mean free path. In case of complex reflection that is composed of random and elastic reflections, as increasing the elastic reflection component, the sensitivity decreases from that of random and cosign reflection to elastic reflection. From these results, it is suggested that the elastic reflection component of He-surface interaction is larger than Ar and N_2 -surface interaction. It means that as decreasing the molecule diameter, the elastic reflection becomes important.

VT-TuP9 Vacuum Chamber with Distributed Titanium Sublimation Pumping for the G-Line Wiggler at Cornell High Energy Synchrotron Source

Y. Li, *Y. He, N.B. Mistry*, Cornell University

This paper describes a 3-meter long vacuum chamber for the newly installed wiggler magnet at the Cornell Electron Storage Ring (CESR) for the synchrotron light beam line of the Cornell High Energy Synchrotron Source (CHESS). Copper was chosen as the main chamber material for its good electric and thermal conductivities. Proper mechanical design and welding procedure were implemented to meet very tight tolerances to ensure adequate vertical aperture for the stored beams in CESR while allowing the required small wiggler gap. Distributed titanium sublimation pumping is incorporated along 3-meter length of the chamber to provide sufficient pumping speed and capacity for CESR and CHESS operations. The chamber pumping performance was evaluated prior to the installation. Linear distributed pumping speeds at the beam line of ~800 liter/sec/meter for N_2 and CO and ~4200 liter/sec/meter for H_2 were measured. The pumping speed is determined by the gas conductance of the slotted copper screen between the beam line and the TiSP compartments. The measured pumping capacities for N_2, CO and H_2 are ~1.0, ~2.0 and ~77 torr-liter, respectively, for each titanium sublimation cycle. Measurements also showed that CO molecules adsorb on the N_2 and H_2 saturated titanium films with virtually the same initial sticking coefficient as on a fresh titanium film. Detail analyses indicated very different CO adsorption mechanisms between the N_2 and H_2 saturated titanium films. While the replacement of surface H_2 by CO was observed, little desorption of N_2 was measured. Operational experience showed excellent vacuum pumping performance over seven months after the chamber installation.

VT-TuP10 XPS Studies of Al and Cu Samples Exposed to an Accelerator Environment

R.A. Rosenberg, *M.W. McDowell, Q. Ma*, Argonne National Laboratory

Designers of present and future particle accelerators are becoming increasing concerned about the influence of the components surface chemistry on the accelerator performance. Bombardment of these surfaces by photons can cause desorption of gases and production of primary and secondary electrons. In some cases interaction of these electrons with the particle beam and the chamber walls can lead to an amplification of the electron density which in turn can cause degradation of the beam. It is well known that exposure to an accelerator environment can cause "conditioning" of the chamber surfaces. In order to understand the manner in which the surface structure might influence the production of gases and electrons in the accelerator it is necessary to study such surfaces both before and after exposure to accelerator conditions. There have been numerous studies performed on representative materials prior to being inserted into an accelerator but very little done on materials that have "lived" in the accelerator for extended periods. In the present work we mounted Al and Cu coupons at different positions in a section of the Advanced Photon Source storage ring and removed them following exposures ranging from 6 to 18 months. XPS surface analysis was performed before and after exposure. Changes were observed that depended on the location and whether the coupon was facing the chamber interior or chamber wall. These results will be presented and compared to data obtained from laboratory measurements meant to simulate the accelerator conditions. Work supported by U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.

VT-TuP11 A Low Cost Method to Deposit Diamond Films on WC-Co and Si Substrates

S. Nasrazadani, University of North Texas

Diamond Coatings are known to be highly desirable for their wear resistance as well as high thermal conductivities. High hardness, low coefficient friction makes diamond attractive for mechanical properties while, high thermal conductivity make it suitable for substrate material as a heat sink. Low cost deposition of this material was investigated using hot filament chemical vapor deposition. Effects of chamber gas composition was evaluated in morphology of diamond films formed on WC-Co and Si substrates.

VT-TuP12 Method to Control the Amount of Helium Delivered during Leak Testing

F.E. Juravic Jr., Fermilab

Purpose The purpose of this paper is to demonstrate a method for limiting the amount of helium administered during leak testing and provide a method for keeping the atmospheric helium in a location to a minimum to eliminate backstreaming into the system. This method utilizes the permeability of a balloon. The transporting of helium to the leak check area is also safer by not requiring a cylinder in the leak check location. Utilizing the many shapes of balloons and partially filling of the balloon, any configuration can deliver helium to the leak location. The balloon I filled for the test fell to the floor with the amount of helium I put into the balloon.

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Situation where a high background of helium cannot be tolerated will be avoided by limiting the amount of helium brought into the room during leak checking. Transporting helium in the balloon into remote areas will allow the technician from accidentally introducing huge amounts of helium that can backstream into the msld and can be kept in the remote areas where the space in limited. This method can be applied to all forms of leak checking. This method is not recommended for certification for cryogenic systems.

Applied Surface Science
Room: C-106 - Session AS-WeM

Optical Methods and High-k Dielectrics Characterization
Moderator: H.G. Tompkins

8:20am **AS-WeM1 Verification of Silicon Native Oxide Growth Models using Spectroscopic Ellipsometry**, ***D.W. Crunkleton***, *V. Pawar, Z. Song, R.D. Geil, B.R. Rogers*, Vanderbilt University

The need for atomically clean silicon surfaces in microelectronics processing has lead to several proposed kinetic models of native oxide growth on silicon. In this work, we present new data sets from which these models are analyzed. We have measured the room temperature silicon dioxide growth on Si (100) samples pre-treated with various fluoride, chloride, and hydroxide base etchants. The oxide thickness is determined with multiangle spectroscopic ellipsometry. Many of the proposed kinetic models fit the trends in our data well; yet several tend to underestimate the final native oxide thickness.

8:40am **AS-WeM2 Measurement of Semi-Isolated Poly-Silicon Gate Structure with Optical Critical Dimension Technique**, ***D. Shivaprasad***, *J. Hu, M. Tabet, R. Hoobler,* Nanometrics, Inc., *W. Liu, H. Sasano, C. Bencher, D. Mui*, Applied Materials

The ITRS predicts the production of sub-100 nm transistor gates by 2004 pushing further the limit of the size and speed posed by 180 nm gates which are currently in use. With decreases in gate length, it has become extremely critical to measure these dimensions accurately using non-destructive techniques. Optical Critical Dimension (OCD) measurements are emerging as one of the most promising CD measurement techniques for sub-0.1 micron device fabrication. Compared to CD-SEM and X-SEM, OCD measurements are non-destructive, relatively high throughput, sensitive to sidewall profiles, and sensitive to sub-100nm linewidths. In the OCD technique, a broadband polarized light beam is focused onto the grating surface, and the spectrum of the 0th order reflection is measured. The spectrum contains a signature of the grating profile that is analyzed in real time using Rigorous Coupled Wave Analysis (RCWA). The real time curve fitting algorithms, which do not require library generation, make the analysis simple and easy to extend to a variety of grating structures. Since the OCD technique is based on specular diffraction, a primary requirement for the OCD measurement target is to have periodical grating structures with a line to space ratio typically 1:5. In this paper, we report using the OCD technique to measure poly-silicon gate grating with line to space ratio as large as 1:20. Poly-silicon gate grating structures with critical dimensions of 30â€”40 nm were measured with line to space ratios of 1:10 and 1:20. In both cases, the measurement showed excellent sensitivity to linewidth variations and detailed profile changes, without deterioration of repeatability. Data from an un-cleaned wafer with the hard mask still remaining will also be presented. This study has significantly extended the measurement range of the OCD technique and its application to isolated line measurements.

9:00am **AS-WeM3 Progress in Spectroscopic Ellipsometry: Applications from Vacuum Ultraviolet to Infrared**, ***J.N. Hilfiker***, *C.L. Bungay, R.A. Synowicki, T.E. Tiwald, C.M. Herzinger, B. Johs, G. Pribil, J.A. Woollam*, J. A. Woollam Co., Inc. **INVITED**

Spectroscopic ellipsometry (SE) is a non-contact and non-destructive optical technique for thin film characterization. In the past ten years, it has migrated from the research laboratory into the semiconductor, data storage, display, communication, and optical coating industries. The wide acceptance of SE is a result of its flexibility to measure most material types: dielectrics, semiconductors, metals, superconductors, polymers, biological coatings, and even multi-layers of these materials. Measurement of anisotropic materials has also made huge strides in recent years. Traditional SE measurements cover the ultraviolet, visible, and near infrared wavelengths. This spectral range is now acquired within seconds with high accuracy due to innovative optical configurations and new CCD detection. In addition, the wavelength range has recently been expanded both into the vacuum ultraviolet (VUV) and the mid infrared. This wide spectral coverage was achieved by utilizing new optical elements and detections systems, along with UV or FTIR light sources. Modern instrumentation is now available with unprecedented flexibility promoting a new range of possible applications. For example, the VUV spectral region is uniquely capable of characterizing lithographic materials for 157nm photolithography. The VUV also provides increased sensitivity for thin layers (e.g. gate oxides or self-assembled monolayers) and allows investigation of high-energy electronic transitions. The infrared spectral region contains new information about semiconductor doping concentration, phonon absorption, and molecular bond vibrations. In this work, we review the latest progress in spectroscopic ellipsometry hardware and software. Areas of significant application in both research and industrial fields will also be surveyed.

9:40am **AS-WeM5 Application of Bragg Light Scattering Method for Studying of Spatial Dispersion Effects in Ferroelectrics**, ***F.R. Akhmedzhanov***, Samarkand State University, Uzbekistan

Bragg light scattering method for studying of spatial dispersion effects was applied to pure $LiNbO_3$ and Mg doped $LiNbO_3$ ferroelectrics. The examined samples of pure $LiNbO_3$ and $LiNbO_3$ with Mg impurity (10^{-2} mol. %) were oriented along the axis of the third order with the accuracy of $10'$. Piezoelectric transducers of Lithium Niobate of appropriate cuts are used in order to excite the plane-polarized transverse acoustic waves with the frequencies of 0.4-1.5 GHz. Measurements of the dependence of the scattered light intensity from the distance to the piezotransducer along the direction of the acoustic wave propagation have been carried out in automatic regime. The scattered light intensity can be presented as function dependence of the light intensity I with respect to distance Z of acoustic wave shift: $I = I_o \exp(-A*Z) \mathrm{Cos}^2(D*Z + F)$, Here I_o is the scattered light intensity near piezotransducer, A is the attenuation coefficient of the acoustic wave, D - the specific rotation angle of the polarization vector and F - the initial phase angle. The obtained values of the scattered light intensities have been used to calculate the quantity and frequency dependence of the attenuation and of the specific rotation of polarization vector in given acoustic wave by modeling of above-mentioned equation. The effective constants of acoustical activity along the investigated direction were determined from the experimental data simultaneously. There has been shown the high efficiency and trustworthiness of the results of simultaneous calculation of attenuation coefficient and specific rotation of the polarization plane in gyrotropic crystals, as well as possibility of speculation of experimental curves by varying factors, which are changed in a real experiment.

10:00am **AS-WeM6 Titanium Dioxide Thin Film Growth on Si(111) by Chemical Vapor Deposition of Titanium(IV) Isopropoxide**, ***A. Sandell***, Uppsala University, Sweden, *M.P. Andersson,* Lund University, Sweden, *Y. Alfredsson,* Uppsala University, Sweden, *M.K.-J. Johansson,* Lund University, Sweden, *J. Schnadt, H. Rensmo, H. Siegbahn,* Uppsala University, Sweden, *P. Uvdal*, Lund University, Sweden

Due to its high dielectric constant, TiO_2 has been considered as a gate insulator material in Si-based MOSFETs, either in pure form or mixed with other compounds. In this contribution, I present a study of the initial stages of TiO_2 growth on Si(111)-(7x7) under ultra-high vacuum conditions using core level photoelectron spectroscopy (PES), x-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM). The TiO_2 film was formed by means of chemical vapor deposition of titanium(IV) isopropoxide at a sample temperature of 500 C. The thickness and composition of the amorphous interface layer and its subsequent transition to crystalline anatase TiO_2 are discussed. Three different stages are identified: In the initial stage (film thickness <1 nm), the oxygen atoms are coordinated mainly to Si atoms giving rise to Ti atoms with oxidation states lower than 4+. The next stage (<3 nm) is best described as an amorphous $TiSi_xO_y$ compound in which the oxidation state of Ti is 4+ and the x and y values vary monotonically with the film thickness. Finally (>3 nm) a stoichiometric TiO_2 layer starts to form. The TiO_2 phase is anatase and the layer consists of largely equidimensional particles, approximately 10 nm wide. In addition, I will also broach the differences that occur upon lowering the growth temperature to 300 C and how the properties of the film can be altered by pre-oxidation of the Si(111)-(7x7) surface.

10:20am **AS-WeM7 Nitrided Silicon-Silicon Dioxide Interface: Electrical and Physico-Chemical Characterization by Complementary Surface Techniques**, ***L. Vanzetti***, *E. Iacob, M. Barozzi, D. Giubertoni, M. Bersani, M. Anderle,* ITC-irst, Italy, *P. Bacciaglia, B. Crivelli, M.L. Polignano, M.E. Vitali*, ST Microelectronics, Italy

The scaling down of MOS devices into the submicron regime needs high-quality ultrathin gate dielectrics. Silicon oxide nitridation is widely used to improve oxide reliability and to reduce interface degradation induced by electrical stress. Analytical issues in this field include electrical characterisation, nitrogen quantitative depth distribution and chemical characterisation. In this work NO and N_2O nitrided oxide layers with thicknesses in the range 70-120Å were studied. Different analytical techniques were used, namely the Elymat (Electrolytic Metal Tracer), SIMS and XPS. Surface recombination velocity was obtained from photocurrent measurements by a modification of the Elymat technique allowing the control of surface potential. The so-obtained surface recombination velocity was shown to be directly related to the interface state density of the as-grown oxide. Surface recombination velocity was correlated with nitrogen content in the silicon oxide layer, obtained by SIMS measurements. XPS analyses allow to explain the different electrical behaviour. In fact XPS measurements provide a complete chemical characterisation of these interfaces. In addition a comparison between quantified SIMS depth profiles and XPS etch-back depth profiles shows very good agreement in nitrogen profile shape and quantification. This approach results very effective for the full characterisation of this type of materials.

10:40am **AS-WeM8 Accurate SIMS analysis of SiON Films**, ***S. Miwa***, *H. Kobayashi*, SONY Corp., Japan, *K. Nakajima*, *K. Kimura*, Kyoto University, Japan

Oxynitride (SiON) films are generally used in advanced CMOS LSIs as gate dielectrics instead of SiO_2 films. The nitrogen distribution in the SiON films strongly affects the performance of the transistors, so it is important to analyze exact nitrogen profiles. Secondary Ion Mass spectrometry is the most frequently used method for the analysis of SiON films. In the analysis, low-energy Cs primary ions and the very high incidence angle (about 80 degrees from the normal incidence) are recommended to avoid knock-on, atomic mixing, and matrix effect over the SiON/Si structure. On the other hands, secondary ion yield is sensitive for the surface concentration of primary ion species. In this case, the surface coverage of Cs is dramatically varied depending on the slight change of the incidence angle because the incidence angle of primary ions is very high. We have carefully investigated that the angle dependence of relative sensitive factors (RSF) and the sputtering rate around this very high incidence angle. We have found that RSF is varied about 10% when the angle changed by 0.3 degrees and that sputtering rate is varied about 10% when the angle changed by 0.5 degrees. In conclusion, the incidence angle of primary ions must be controlled within only 0.1 degree in order to keep the quantification errors within 5%. We can control the angles well reproducibly by means of monitoring the ratio of the intensities of two secondary ions ($SiCs^+$ and Cs_2^+). We have also compared the N concentration obtained by SIMS with that obtained by High-resolution Rutherford Backscattering Spectrometry.

Biomaterials
Room: C-201 - Session BI+AS-WeM

Ambient Surface Science Techniques
Moderator: M. Grunze, Heidelberg Universität, Germany

8:20am **BI+AS-WeM1 A Challenging Problem: Interfaces between Condensed Matter**, ***M. Buck***, StAndrews University, UK **INVITED**

Surface Science has developed a zoo of techniques which allow the characterization of chemistry and structures of surfaces and adsorbates at an impressive level of molecular detail. Unfortunately, the large variety of available techniques dramatically reduces when dealing with systems under non-vacuum environment and, therefore, an understanding on a molecular level is much harder to gain. In addition to problems on the technical side, the situation is further complicated by the fact that "real world" interfaces are, in general, more complex compared to systems studied in surface science, e.g. larger molecular entities with more conformational degrees of freedom, amorphous structures, and additional interactions due to the environment. The talk discusses various routes to unravel the relationship between structures and properties of biomaterials interfaces and highlights problems and possible pitfalls associated with the investigation of such type of interfaces.

9:00am **BI+AS-WeM3 Surface Chemistry of Environmentally Relevant Transition Metal Oxides Studied in Aqueous Solutions using Soft X-ray Spectromicroscopy**, ***B.P. Tonner***, *K. Pecher*, University of Central Florida

The surface chemistry of environmentally relevant inorganic oxides can now be reliably assessed in solution, with high spatial resolution, using a methodology based on x-ray absorption spectroscopy with microfocussing.[1,2] A crucial aspect of this research is that the studies are performed in the presence of a complete water layer, with control of parameters such as buffer concentrations, dissolved oxygen content, and pH. We have concentrated on the fate of Fe and Mn oxides in mineral model compounds, and in addition important nano-scale materials like the 'green rusts.' Spatial chemical inhomogeneities are prevalent in such nano-scale minerals, and are revealed by x-ray spectro-microscopy "chemical state mapping." The state of these studies has matured to the point where chemical intermediates, formed as a result of microbial metabolism, can be reliably detected and identified. This paper will emphasize the quantitative aspects of performing assays of surface transition metal oxide valence distributions using L-edge spectromicroscopy.

[1] Rothe, J., E.M. Kneedler, K.H. Pecher, B.P. Tonner, K.H. Nealson, T. Grundl, W. Meyer-Ilse, and T. Warwick, Journal of Synchrotron Radiation 6, 359-361 (1999).

[2] K. Pecher, E. Kneedler, J. Rothe, G. Meigs, T. Warwick, K. Nealson, and B. P. Tonner, X-ray Microscopy 1999, W. Meyer-Ilse, T. Warwick, and D. Attwood, ed., (American Institute of Physics, NY, 2000) p. 291-300.

9:20am **BI+AS-WeM4 Investigation of Protein Adsorption with Simultaneous Measurements of Atomic Force Microscope (AFM) and Quartz Crystal Microbalance (QCM)**, ***K.-H. Choi***, *J.-M. Friedt*, *F. Frederix*, *W. Laureyn*, *A. Campitelli*, *G. Borghs*, IMEC, Belgium

We have combined the tapping mode atomic force microscope (AFM) and quartz crystal microbalance (QCM) for the direct investigation and characterization of protein adsorption on various metallic surfaces. The adsorption of proteins, such as human plasma fibrinogen, γ-globulin and collagen, onto the metal/QCM surface were monitored using both methods at the same time when varying the concentration of them. We present the AFM images that shows the surface changes and the adsorption scheme of proteins with molecular resolution according to the shift of resonant vibration frequency of the QCM. The combination of AFM with QCM and the simultaneous measurements of the bio molecule adsorption with two techniques provide us with not only the sensing and detection technique but also the means for understanding the adsorption schemes of bio molecules on the metal surface.

9:40am **BI+AS-WeM5 Real-time AFM Investigations of the Enzymatic Degradation of DNA-polymer Dendrimer Complexes**, ***S.J.B. Tendler***, *H.G. Abdelhady*, *C.J. Roberts*, *S. Allen*, *M.C. Davies*, *P.M. Williams*, University of Nottingham, UK

Fundamental to surface recognition strategies is the need to develop both interfaces and imaging methods that allow the investigation of biomolecular recognition processes in solution, in-real time. One such set of processes is the enzymatic degradation of DNA, both when naked and when protected by polymeric (bio)materials. This system has clinical relevance in that polyelectrolyte complexes between polyamidoamine (PAMAM) dendrimers and DNA have emerged as potential non-viral vectors for therapeutic DNA delivery. Hence methods for analyzing the ability of PAMAM dendrimers to protect the DNA from degradative enzymes are of clinical significance. Here we have applied atomic force microscopy (AFM) in liquid to visualize at the molecular scale and in real time, the effect of the enzyme DNase I on generation 4 PAMAM dendrimers complexed with DNA (G4-DNA). The formation of G4-DNA is observed to provide a degree of protection to the DNA, the level of which rises with increasing PAMAM dendrimer to DNA ratio and to a certain degree with the time allowed for complexes to form.

10:00am **BI+AS-WeM6 Interaction of Water with Protein Resistant Self-Assembled Monolayers: Neutron Reflectivity Measurements of Water Density in the Interphase Region**, ***D. Schwendel***, *T. Hayashi*, *A.J. Pertsin*, *R. Dahint*, University of Heidelberg, Germany, *R. Steitz*, Hahn-Meitner-Institut, Germany, *F. Schreiber*, University of Oxford, UK, *M. Grunze*, University of Heidelberg, Germany

The interfacial behavior of surfaces, colloids, and molecules with water plays a substantial role in surface science and other areas. It is, in particular, responsible for colloid stability, micelle formation, biomembrane fusion, and the resistance of materials against proteins from biological media. These materials are of crucial importance in biotechnology and biomedical applications. One type of such bicompatible surfaces is represented by self-assembled monolayers (SAMs) on Au and Ag composed of undecanethiolates terminated oligo(ethylene glycols), (-O-CH2-CH2-)n (hereafter EGn). Neutron reflectivity measurements on protein resistant methoxy tri(ethylene glycol) (EG3-OMe) and hydroxy terminated hexa(ethylene glycol) (EG6-OH) undecanethiolate self-assembled monolayers (SAMs) in contact with deuterated water reveal the presence of an extended (~5 nm thick) water interphase with a noticeably reduced density (85-90 % of bulk water density). This result is in qualitative agreement with Grand canonical Monte Carlo simulations of water next to the SAM surface. For comparison, neutron reflectivity experiments have also been performed on non-functionalized hydrophobic octadecanethiolate and hydrophilic hydroxy terminated undecylthiolate SAMs. Additionally, neutron reflectivity measurements on protein resistant SAMs formed from hydroxy and methoxy terminated tri(ethylene glycol) (EG3-OH and EG3-OMe) against high concentrated protein solutions of BSA show that the free dissolved protein does not contact the surface but that it is repelled over a distance of few nm. The profiles strongly suggest a BSA depleted water layer at the SAM/bulk interface of 4 to 6 nm while BSA adsorption is observed for non-resistant propoxy terminated tri(ethylene glycol) (EG3-OPr).

10:40am **BI+AS-WeM8 Force Spectroscopy of Self-Assembled Monolayers Containing 'Sandwiched' Oligo(Ethylene Glycol) Interfaces on Gold under Electrolyte Solution**, ***G. Haehner***, *C. Dicke*, University of St Andrews, UK, *S. Herrwerth, W. Eck, M. Grunze*, University of Heidelberg, Germany

Non-specific interactions between biomolecules and (synthetic) organic surfaces, and in particular materials which are resistant to the adsorption of proteins from biological media, are of crucial importance to the fields of biomaterials, biosensors and medical devices. Chemically functionalized (charged and hydrophobic) scanning force microscope probes can mimic local structures of proteins and hence allow it to study the influence of these parameters on the overall observed interaction separately. Oligo(ethylene glycol) (OEG) terminated self-assembled monolayers on gold show high inertness towards the non-specific adsorption of proteins. The underlying mechanism, however, has not yet been resolved completely. It appears that water as well as hydronium and/or hydroxyl ions play a central role. In order to scrutinize the interaction, the accessibility of the OEG interface to molecules/ions from solution was varied. This was accomplished by the molecular structure: the functional (OEG) part was terminated with hydrophobic chains of different length resulting in 'sandwich'-film-structures. Force spectroscopy measurements on these layered structures with hydrophobic probes under electrolyte solution reveal the importance of the different contributing factors to the overall interaction.

Homeland Security
Room: C-209 - Session HS-WeM

Plenary Session on Homeland Security
Moderator: R.J. Colton, Naval Research Laboratory

8:20am **HS-WeM1 Chemical and Biological Agent Decontamination of Civilian Facilities**, ***T. Carlsen***, Lawrence Livermore National Laboratory **INVITED**

The purpose of this presentation is to discuss the existing and emerging decontamination technologies for use following a chemical and/or biological weapons incident at civilian and/or public sector facilities. Additionally, the necessary requirements of these technologies to successfully decontaminate civilian facilities and the approach needed to obtain regulatory compliance will also be discussed. The types of decontamination methods likely to be most successful are different than would be most effective in response to a military and/or wartime incident. Current military decontamination techniques aimed at CBW agents are corrosive and/or toxic and can cause collateral damage to facilities and equipment. As a result of recent terrorist events, there is increased interest in decontaminating agents and their effectiveness for the civilian sector. The optimum technology would be non-toxic, non-corrosive, and easily deployable, thereby insuring effective use by first-line responders. Methods should allow for detoxification and/or degradation to environmentally acceptable components rather than necessitate complete destruction. Effective decontamination requires the use of reagents that can be dispersed as solids, liquids, and/or gases, depending on the particular scenario involved. Several technologies currently under development are aimed at meeting these requirements. however, there are some distinct scenarios for which current technology is still inadequate to respond in a rapid and effective manner. Effective decontamination also requires effective sampling and verification methods to demonstrate that cleanup goals have been attained. The final decontamination must be defensible to regulatory agencies and to an uninformed public. In order to accomplish this we must understand and even influence the answer to the question: "How clean is clean enough?" The level of decontamination required will influence the choice of these systems under consideration.

9:00am **HS-WeM3 Science and Technology for Combating Terrorism**, ***A.T. Hopkins***, Defense Threat Reduction Agency **INVITED**

This briefing describes the Defense Threat Reduction Agency's (DTRA) efforts to accelerate research and development programs for combating terrorism. DTRA is a combat support agency providing a unique blend of operational and technical expertise and experience to reduce weapons of mass destruction threats. DTRA's Technology Development portfolio includes programs in nuclear weapon effects technology, integrated systems applications that include advanced concept technology demonstrations, counterproliferation technology, and nonproliferation and arms control technology. Technology challenges include the detection of dispersed and non-dispersed nuclear, chemical and biological threats, remote detection of weapons of mass destruction, force protection technologies, microscale hazard prediction, information management, hard and deeply buried target defeat, and agent defeat.

9:40am **HS-WeM5 Basic Research Needs for Countering Terrorism**, ***T. Michalske***, Sandia National Laboratories **INVITED**

Improving our ability to counter threats of terrorism has become a high priority in the U.S. and many other countries around the world. While it is widely recognized that science and technology will play an important role in this effort, it must also be recognized that terrorism is a highly complex socio-political problem for which there are simply no "silver bullets" to easily solve the problem. This presentation summarizes key points and recommendations from a recent U.S. Department of Energy Workshop that involved experts familiar with counter-terrorism technologies, strategies, and policies. Direct connections between technology needs for countering terrorism and the underlying science issues are defined along with some specific examples that show how previous science investments have led to new approaches to counter terrorism threats associated with weapons of mass destruction.

10:20am **HS-WeM7 Panel Discussion: Science & Technology Issues for Homeland Security, T. HOPKINS, Defense Threat Reduction Agency; T. MICHALSKI, Sandia Nat. Labs; E. RABER, Lawrence Livermore Nat. Lab; M.J. SAILOR, UC, San Diego; D. WALT, Tufts Univ.; L.J. WHITMAN, NRL INVITED**

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI-WeM

Magnetic Recording: GMR, Tunneling, and Media
Moderator: W.H. Rippard, NIST

8:20am **MI-WeM1 Perpendicular Recording Media Near 100 Gbit per square inch**, ***D. Weller***, *B. Lu, Y. Kubota, J. Ahner, G. Ju, X. Wu, D. Karns, A. Sunder*, Seagate Research, *C.H. Chang, C. Brucker, R. Ranjan*, Seagate Recording Media Operations, *M. Kryder*, Seagate Research **INVITED**

Media noise suppression via reduced grain and magnetic cluster size and at the same time thermal stability are general requirements to advancing magnetic recording technology to higher areal densities, beyond 100 Gbit per square inch. In perpendicular recording, using a hard/soft dual layer media scheme, one seeks to use magnetically harder media. Such media sustain smaller stable grains and can be written owing to the improved write field geometry that perpendicular pole heads in conjunction with soft magnetic underlayers offer over the conventional ring head geometry used in longitudinal recording. Modeling suggests, that this technology is extendible to areal densities of the order of Terabit per square inch. In this paper, we review current-state-of the art perpendicular media and review testing results near 100 Gigabit per square inch recording densities. The key challenges relate to controlling average grain sizes and their distributions as well as intergranular exchange coupling in the hard layer and at the same time generating a low noise, high permeability soft magnetic underlayer. We have fabricated both CoPtCr-type alloy and CoCr/Pd-type multilayer media and obtained grain sizes of D=10.5+/-2.2nm and D=13.1+/-2.5 nm, respectively. These media have full remanence squareness (S=1), negative onset fields for reversal > 2000 Oe, thicknesses in the range 10-18 nm and are thermally stable. The soft underlayer material is an amorphous FeCoB alloy with 1.9 T flux density and a static permeability of >400; it is stabilized into a single domain, noise free state, via an induced radial magnetic anisotropy field > 50Oe. The spacer between the soft underlayer and hard layer is an alloy seed layer structure of total thickness less than 5 nm. This interlayer controls the microstructure of the subsequent recording layer and is key to enhancing the performance of perpendicular media.

9:20am **MI-WeM4 High Frequency Noise Measurements in Spin-Valves**, ***N.A. Stutzke***, Boise State University, *S.E. Russek*, NIST, Boulder, *S.L. Burkett*, Boise State University

High-frequency magnetic noise in magnetoresistive devices, being developed for read-sensor and magnetic random access memory applications, may present fundamental limitations on the performance of sub-micrometer magnetic devices.[1] High-frequency magnetic noise arises from intrinsic thermal fluctuations of the device magnetization. High-frequency noise spectroscopy provides a powerful tool to characterize the dynamics and response of multilayer magnetic devices. In this study, the noise characteristics of micrometer-dimension spinvalves have been investigated at frequencies in the range of 0.1-6 GHz. 1/f noise dominates at frequencies below this range. High-frequency noise measurements as a function of temperature, bias current, and magnetic field are obtained for IrMn-exchange biased spinvalves using a 50 GHz spectrum analyzer, low-noise amplifier, and a cryogenic microwave probing system. Temperature is varied from 100-400K. The magnetic noise is obtained by taking the difference between the noise spectrum of the device in a saturated and unsaturated state. The data can be fit to simple models that predict the noise power to be proportional to the imaginary part of the free-layer magnetic susceptibility.[2] Noise is observed to shift to higher frequencies and decrease in amplitude with decreasing temperatures. This is consistent with an increase in magnetostatic anisotropy due to the increase in the saturation magnetization as the temperature is lowered. There are some important differences between the high-frequency noise measurements and direct measurements of the device susceptibility (both at the device and wafer level). The noise measurements show a smaller damping constant (a smaller ferromagnetic resonance linewidth) and show additional features due to the presence of additional magnetostatic modes.

[1] N. Smith and P. Arnett, Appl. Phys. Lett. 78, 1448 (2001).

[2] N. Smith, J. Appl. Phys. 90, 5768 (2001).

9:40am **MI-WeM5 Theory of Spin-dependent Tunneling**, ***J. Mathon***, City University, UK **INVITED**

Rigorous theory of the tunneling magnetoresistance (TMR) based on the real-space Kubo formula and fully realistic tight-binding bands fitted to an ab initio band structure is decribed. It is first applied to calculate the TMR of two Co electrodes separated by a vacuum gap. The calculated TMR ratio reaches some 65% in the tunneling regime but can be as high as 280% in the metallic regime when the vacuum gap is of the order of the Co interatomic distance (abrupt domain wall). It is also shown that the spin polarization P of the tunneling current is negative in the metallic regime but becomes positive P~35% in the tunneling regime. Calculation of the tunneling magnetoresistance of an epitaxial Fe/MgO/Fe(001) junction is also described. The calculated optimistic TMR ratio is in excess of 1000% for an MgO barrier with 20 atomic planes of MgO and the spin polarization of the tunneling current is positive for all MgO thicknesses. Finally, it is demonstrated that the TMR ratio calculated from the Kubo formula remains nonzero when one of the Co electrodes is covered with a copper layer. It is shown that nonzero TMR is due to quantum well states in the Cu layer which do not participate in transport. Since these only occur in the down-spin channel, their loss from transport creates a spin asymmetry of electrons tunneling from a Cu interlayer, i.e. nonzero TMR. Numerical modelling is used to show that diffuse scattering from a random distribution of impurities in the barrier may cause quantum well states to evolve into propagating states, in which case the average TMR tends to zero but large quantum oscillations of TMR about zero average remain.

10:20am **MI-WeM7 In-Situ Conductance Measurements of Giant Magnetoresistive Multilayers**, ***A.T. McCallum***, *S.E. Russek*, National Institute of Standards and Technology

In-situ conductance measurements can detect the changes in electronic structure during deposition of a multilayer with submonolayer resolution. Here, we present conductance verses thickness data, taken every half monolayer, for both top and bottom pinned spin valves at different temperatures. These measurements can clearly identify bulk scattering processes and interfacial scattering. For example, our data shows adding Co onto Cu adds strong interfacial scattering mechanisms. The conductance verses thickness data were compared to a Boltzmann transport equation (BTE) model. Bulk conductivities were measured by extending the measurements out to large layer thicknesses. Bulk electron mean free paths were calculated from the measured conductivites and the results of other experiments. Transmission probabilities and specular reflection probabilities were deduced from this model. The spatial distribution of current density in the multilayer, was then calculated using the BTE model. In-situ conductance measurements were used to characterize thin oxide layers, which are used as insulating barriers in magnetic tunnel junctions and specularly reflecting surfaces in giant magnetoresistance devices. For these applications it may be necessary to completely oxidize one layer of metal and not oxidize the metal underneath. The dynamics of oxidizing an Al surface were observed using in-situ conductance measurements and a vibrating crystal thickness monitor. The thickness monitor measures the oxygen uptake over time while in-situ conductance measures the amount of Al oxidized and the change in specularity due to the oxide. Using these techniques we characterized several oxidization procedures to determine the details of the oxidization process and to find an optimum oxidization procedure.

Microelectromechanical Systems (MEMS)
Room: C-210 - Session MM+NS-WeM

Nanotechnology and Nanofabrication in NEMS
Moderator: H.G. Craighead, Cornell University

8:20am **MM+NS-WeM1 Probing Nanomechanical Systems with Electron Tunneling Devices**, ***A.N. Cleland***, University of California, Santa Barbara **INVITED**

We have been integrating active electronic devices with nanomechanical systems, in order to probe both the mechanical and thermodynamical behavior of the integrated system. I will discuss experiments in which we have developed fabrication approaches allowing the integration of superconductor-normal metal tunnel junctions with suspended mechanical structures to develop an ultrasensitive bolometer and calorimeter, with which we have been able to confirm the observation of the quantum of thermal conductance, the integration of single-electron transistors with mechanical resonators, displacement sensing using an integrated quantum point contact, and the development of a double quantum dot integrated with an L-band mechanical resonator. I will briefly discuss the potential application of these types of integrated probes for quantum-limited measurements.

9:00am **MM+NS-WeM3 Fabrication and Characterization of a Carbon Nanotube Torsional Oscillator**, ***P.W. Williams***, *A.M. Patel, S.J. Papadakis, M.R. Falvo, S. Washburn, R. Superfine*, University of North Carolina

Carbon nanotubes have extraordinary mechanical properties and have been demonstrated to show atomic scale effects in the frictional[1] and electronic properties[2] of their contacts. We are exploring the applications of these properties in nanoelectromechanical Systems (NEMS). Torsional oscillators represent a device geometry for the measurement of fundamental properties of nanotubes as well as high frequency oscillators and sensors.[3] Using individual multi-wall carbon nanotubes as torsional springs, we have fabricated NEMS paddle oscillators. We will report on the fabrication of these structures as well as measurements of their torsional compliance using atomic-force-microscope force-distance curves. The measured shear modulus will be compared with existing theoretical expectations, and unexpected hysteresis effects will be discussed. Along with compliance measurements, progress toward characterization of resonant behavior including measurements of quality factor and resonant frequencies will be presented. This work is supported by the National Science Foundation and the Office of Naval Research.

[1] M. R. Falvo, J. Steele, R. M. Taylor, et al., Physical Review B 62, R10665 (2000).

[2] S. Paulson, A. Helser, M. B. Nardelli, et al., Science 290, 1742 (2000).

[3] S. Evoy, D. W. Carr, L. Sekaric, et al., Journal of Applied Physics 86, 6072 (1999).

9:20am **MM+NS-WeM4 Femtogram Detection using Nanoelectromechanical Oscillators**, ***B. Ilic***, *D. Czaplewski, H.G. Craighead*, Cornell University, *P. Neuzil*, Institute of Microelectronics, Singapore

Micro and nanoelectromechanical systems (MEMS and NEMS) represent an emerging sensor technology that provides a closely coupled link between the physical, chemical and biological worlds. Nanomechanical systems can be used as mass based sensors with sensitivity several orders of magnitude better than conventional quartz crystal oscillators. Here we present a resonant frequency-based NEMS mass sensor, comprised of surface micromachined low-stress polycrystalline silicon cantilever beams for the detection of self assembled monolayers. In our experiment, we demonstrate a method for detecting the mass of Aminopropyltriethoxysilane (APTS), Hexamethyldisilazane (HMDS) and Octadecyltrichlorosilane (OTS) self assembled monolayers (SAM) using a resonant frequency-based detection sensor. The highly sensitive balance considered here is a resonating cantilever beam fabricated using electron beam lithography. For this experiment, devices with dimensions of varying length (l) from 3µm to 15µm, width (w) of 500nm to 2µm and thickness (t) of 150nm and 320nm, were used. Devices were coated with various monolayers and resonant frequency was measured before and after the addition of SAM. Signal transduction was accomplished in vacuum by employing an optical interferrometric system to measure the frequency shift due to the additional mass loading. The measured frequency shift was correlated to the mass of the SAM and was found to be in good agreement with the analytical results. For the smallest device geometry, we observed a resonant frequency shift due to the presence of 4 femtograms of HMDS. By further tailoring cantilever dimensions, the sensitivity of our devices can be greatly improved, thus extending their application to DNA, viruses and other analytes with mass on the order of attograms.

9:40am **MM+NS-WeM5 IR Imaging Using Uncooled Nanostructured Microcantilever Thermal Detectors**[1], ***P.G. Datskos***, Oak Ridge National Laboratory and University of Tennessee, *S. Rajic, L.R. Senesac, J. Corbeil, N.V. Lavrik*, Oak Ridge National Laboratory

Bimaterial microcantilevers have been shown to detect infrared (IR) radiation and can operate as uncooled thermal detectors. The transduction mechanism is the bending of the bimaterial microcantilever due to thermally-induced stress. Therefore, it is important to minimize cantilever deflections caused by factors other than IR radiation (e.g. intrinsic mechanical stresses and ambient temperature fluctuations) while increasing photon absorption in the desired spectral region. In this paper we report on IR imaging using optimized microcantilever designs that are immune to ambient temperature changes and other sources of interfering mechanical stresses. In addition, we achieved increased absorption of IR photons using resonant nanostructured detector surfaces. We modeled and experimentally measured responses of such devices to IR radiation as well as to ambient temperature changes. We will present and discuss our latest results.

[1] We like to acknowledge support from the Defense Advanced Research Projects Agency, the National Science Foundation and DOE. This work was partially supported by the Laboratory Director's Research and Development Program of Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by UT-Battelle under contract DE-AC05-96OR22464.

10:00am **MM+NS-WeM6 Frequency and Phase Entrainment in MEMS Oscillators**, *M. Zalalutdinov, **K.L. Aubin**, A.T. Zehnder, B. Ilic, D. Czaplewski, L. Sekaric, J.M. Parpria, H.G. Craighead*, Cornell University

Synchronization of light-induced self-sustained vibration of MEMS resonators by external parametric perturbation was demonstrated. Self-oscillation of disc-type MEMS resonators induced by CW laser light has been described earlier.[1] In the work presented here, partial modulation of the laser power was used to provide additional parametric excitation through the laser beam induced stress as a physical mechanism to control the parameter - the effective spring constant of the resonator. Modulation depth as low as 5% of CW laser power at frequencies near n times (n=1,2,3...) the natural resonant frequency of the oscillator was shown to cause the frequency and phase of the mechanical motion to become entrained to the modulation frequency (over n). The range of frequencies over which entrainment was possible was shown to vary with modulation amplitude. Once entrainment of the mechanical vibrations is achieved, one can tune the mechanical frequency of vibration by about 10% by changing the modulation frequency. During that tuning, the phase difference between the modulation signal and the mechanical motion was shown to vary as much as 130°. In a synchronized state, stability of the vibrations appears to be limited only by that of the modulation source, allowing us to demonstrate better than 10^{-9} stability for the frequency of the mechanical motion. Integration of entrained MEMS and NEMS oscillators into a phase-locked loop (PLL) circuit in order to build a high stability reference oscillator is currently under study.

[1] M. Zalalutdinov, A. Zehnder, A. Olkhovets, S. Turner, L. Sekaric, B. Ilic, D. Czaplewski, J. M. Parpia and H. G. Craighead, "Auto-Parametric Optical Drive For Micromechanical Oscillators" Appl. Phys. Lett., Vol. 79, pp 695 (2001).

10:20am **MM+NS-WeM7 Fabrication of Submicron-Scale Metallic Comb-Drive Actuators**, ***S.W. Park***, *N.A. Kumar, J.B. Lee*, The University of Texas at Dallas

Comb-drive actuators have been widely used for more than a decade in many applications including resonators, accelerometers, and tunable capacitors with the advance of micromachining technologies. While single crystal or poly Si have been preferred materials for comb-drive actuators, metallic high aspect ratio comb-drive actuators were also of interest due to its electrical property such as lower resistivity in some applications. In this paper, we report the development of fabrication of a sub-micron scale (sub-micron gap and width) all metallic comb-drive actuator with small overall foot-print. All metallic comb-drive actuators with sub-micron gap/width and small foot-print have many advantages over traditional silicon-based micron scale comb-drive actuators. Such advantages include large increase of capacitance per unit area (good for sensing applications) and higher quality factor due to low equivalent series resistance of the metallic comb-finger structures (good for tunable capacitor application). The comb-drive actuator was designed as a tunable capacitor and intensive modeling of such tunable capacitor was carried out. Fabrication of such comb-drive actuators was started with a multiple spin-coatings of polymethyl methacrylate (PMMA) or SU-8 on an oxidized silicon substrate. PMMA was investigated for low aspect ratio and SU-8 was investigated as a potential electron beam photoresist for high aspect ratio comb-drive actuator fabrication. Numerous experimental runs were performed to find optimum exposure doses, developing conditions, etc. Different metals such as Cu, Cr, Ti/Cu, and Cr/Cu were investigated as candidate materials for comb-drive actuators. Optimum fabrication process based on PMMA was developed for 1:1 aspect ratio all metallic 500-nm width/gap comb-drive actuator. Preliminary results on negative tone SU-8 resist based comb-drive actuator with a goal of achieving high aspect ratio (up to 5:1 aspect ratio) structure will also be reported.

10:40am **MM+NS-WeM8 Controlling Energy Losses in Nanoscale Structures with Surface Chemistry**, ***J.A. Henry***, *Y. Wang, M.A. Hines*, Cornell University

Why are we unable to predict the dynamic properties of nanoscale devices from the well-known behavior of bulk materials? For example, the quality (or Q) of nanoscale resonators is often orders of magnitude lower than similar macroscopic devices. Here, we show that simple changes in the surface chemistry of MHz silicon resonators can lead to large changes in Q, indicating that surface loss mechanisms become very important at this length scale. For example, the oxidation of H-terminated silicon resonators causes the Q to plummet by as much as 50% while inducing only a minuscule change in frequency of approximately 0.05%. The scaling of both the energy losses and the frequency shifts with oscillator size and thickness are consistent with a surface-driven process. Infrared absorption measurements confirm that chemical changes are limited to a few monolayers of the surface. Possible mechanisms for these losses will be discussed.

Nanometer Structures
Room: C-207 - Session NS-WeM

Nanostructured Materials
Moderator: W.N. Unertl, University of Maine

8:20am **NS-WeM1 Electronic Structure of Nitrogen Doped Ultrananocrystalline Diamond**, ***J. Birrell***, University of Illinois at Urbana-Champaign, *O. Auciello, J.A. Carlisle, J.E. Gerbi, J.M. Gibson, D.M. Gruen*, Argonne National Laboratory

The local bonding structure of ultrananocrystalline diamond (UNCD) thin films synthesized using $Ar/CH_4/N_2$ microwave plasmas has been investigated using near-edge x-ray absorption fine structure (NEXAFS). These films exhibit a dramatic increase is electrical conductivity (up to 150 Ω^{-1} cm^{-1}) as nitrogen gas is added to the plasma. Theoretical models predict that this is due to an increase in band gap states due to the presence of nitrogen at the grain boundaries. C 1s NEXAFS experiments have been performed to ascertain the ratio of sp^2/sp^3 bonded carbon in these films. It was found that, as nitrogen is added, the amount of sp^2-bonded carbon increases by roughly %50 compared to the undoped films, but overall the films remain largely sp^3-bonded. The sp^3 σ^* exciton, located at ~289 eV, diminishes in intensity, however, in spite of an observed increase in grain size with nitrogen content in the plasma. These results, as well as previous experiments using high resolution transmission electron microscopy, are used to explain the observed changes in the materials properties of nitrogen doped UNCD.

8:40am **NS-WeM2 Growth, Microstructure and Properties of Fullerene-Like Carbon Nitride Thin Solid Films Deposited by DC Magnetron Sputtering**, ***Zs. Czigány***, *J. Neidhardt, I.F. Brunell, L. Hultman*, Linköping University, Sweden

Fullerene-like CN_x ($x \leq 0.2$), as an inherently nanostructured material, were deposited as thin solid films by reactive magnetron sputtering of graphite in a nitrogen and argon discharge. The films were characterized by HRTEM, EELS, XPS and nanoindentation. Most fullerene allotrope synthesis is completed in the gas phase at high temperatures and the resulting material does not form a dense solid film. In comparison, the route to fullerene-like material presented here is by continuous surface nucleation and growth of curved basal planes at relatively low temperature. Plasma characterization revealed low flux of low energy species in the deposition flux with high portion of reactive complexes (e.g., CN, C_2N, C_2N_2). In the fullerene-like structures N substitutes for C and reduces the energy barrier to form pentagons in graphite sheets, thus inducing curvature of the basal planes. N also increases the reactivity of the neighboring C atoms, thus promoting sp^3 cross-linking between C atoms in neighboring fullerene domains and provides solid CN_x films with high elasticity. TEM imaging of fullerene-like structures in a thin solid film form gives rise to difficulties compared to isolated fullerene features. Sample preparation methods for artefact-free specimens with thickness compatible with the characteristic feature size of fullerene-like domains will be discussed.

9:00am **NS-WeM3 Selective Oxidation of Faulted Halves of Si(111): (7x7) with Ozone**, ***K. Miki***, NRI-AIST and NIMS, Japan, *T. Narushima*, NRI-AIST, Japan, *M. Kitajima*, NIMS, Japan

For nano-scale devices, an electronic isolation technique is desired since the working current is very small and therefore leakage through the substrate should be suppressed. In this paper we demonstrate a nano-scale selective reaction to realize this isolation technique. For this model case, we used an ozone radical to selectively oxidize one subunit of Si(111)-7x7. This surface has two different subunits; the faulted and unfaulted halves. Due to whether or not a stacking fault exists, the electronic states of the two halves differ, especially around 0.5 eV below Ef. This state is the backbond state of the adatoms. Therefore we could expect selective oxidation with some radicals on either the faulted or the unfaulted half. In conventional thermal oxidation, this possibility has already been denied, while ozone remains a possibility. We introduced highly concentrated ozone gas onto 7x7 reconstructed Si(111) surface in a UHV chamber in a split second. At room temperature, by means of scanning tunneling microscopy, it is found that the faulted sites are imaged as depressions at the sample bias of 0.8 V, but the other sites are mostly unchanged. This depression could be due to back bond oxidation. The reactive site of the oxygen changed with temperature, up to 873 K. As the substrate temperature increased, the chemical reaction selectivity disappeared. This may be due to diffusion of backbond oxygen atoms, which has a barrier height around 1eV. We intend to make 2.7 nm-size nano structure (unit size of 7x7) with atomic scale isolation of backbond oxidation state. It is very useful because it does not involve processing at high temperature, which could induce damage, or disappearance, of nano structures.

9:20am **NS-WeM4 Dynamics of Br-Si(100)-(2x1): Surface Modification in the Absence of Desorption**, ***E. Graugnard***, *G. Xu, V. Petrova, K.S. Nakayama, J.H. Weaver*, University of Illinois at Urbana-Champaign

The dynamics of surface modification of Si(100)-(2x1) with Br has been studied using variable temperature scanning tunneling microscopy (STM). A clean surface was saturated with Br at room temperature and then heated on the STM stage to 700 K, where no surface modification was expected. To our surprise, we found that the surface was, in fact, modified after heating for several hours. From sequential images of the same area, we were able to observe the formation and growth of novel defect structures, which consist of parallel atom vacancy lines separated by a single dimer row and could grow to be 120 nm in length. The formation of these vacancy lines was accompanied by Si adatom transfer onto the terrace, where regrowth dimers could form. The vacancy lines were often terminated at regrowth chains or dimer vacancy pits. We observed diffusion of regrowth features, but diffusion was limited to regions of the terrace where there were no vacancy structures. Thus, regrowth islands formed on defect-free areas of the terrace, and these islands limited the growth of the defect lines. As the surface roughened, the dynamics of the features became increasingly complicated with the atom vacancy lines converting into dimer vacancy lines and vice versa. The formation mechanisms and dynamics of these surface structures will be discussed.

9:40am **NS-WeM5 Surface, Bulk and Interfacial Analysis of Self-assembled NAno-phase Particle (SNAP) Films**, *L.S. Kasten*, AFRL/MLBT (UDRI), Wright-Patterson AFB, *V.N. Balbyshev*, AFRL/MLBT (UTC), Wright-Patterson AFB, *D.J. Gaspar*, Pacific Northwest National Laboratory, ***M.S. Donley***, AFRL/MLBT, Wright-Patterson AFB

The chemistry, structure, and morphology of Self-assembled NAnophase Particle (SNAP) coatings were investigated using a variety of surface analysis methods. A new method of forming functionalized silica nanoparticles in-situ in an aqueous sol-gel process, and then crosslinking the nanoparticles to form a thin film, is an excellent example of a nanoscience approach to coatings. Results will be presented on the surface morphology, structure, surface chemistry, and chemical structure of SNAP films. The surface chemistry of the films was investigated using X-ray photoelectron spectroscopy (XPS), grazing angle XPS, and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The surface morphology of films was examined using Atomic Force Microscopy (AFM), while X-ray Diffraction (XRD) was used to investigate film structure. The chemical structure and adhesion mechanism of SNAP coatings were also investigated via TOF-SIMS. Very little chemical difference between the outermost surface and bulk regions is seen, while the adhesion mechanism is related to the nature of the cross-linking agent. The results of these analyses will be discussed in detail and a model of the proposed chemical structure will be presented.

10:20am **NS-WeM7 Electronic Structure of Ag/Cu Striped Nanostructures**, *J. Lobo*, ***E.G. Michel***, Universidad Autonoma de Madrid, Spain, *A. Bachmann*, Universitaet Osnabrueck, Germany, *S. Speller*, Katholieke Universiteit Nijmegen, The Netherlands, *L. Roca*, LURE-CNRS, France, *J. Kuntze, J.E. Ortega*, Donostia International Physics Center and Centro Mixto CSIC/UPV, Spain

The deposition of Ag on a stepped Cu surface gives rise to a periodic faceting of the surface.[1] The superstructure obtained is a very regular distribution of Cu and Ag stripes, with a lateral width in the range of 50-100 Å. The electronic band structure of this nanostructure has been studied using angle-resolved photoemission, for a range of Ag coverages between 0 and 1.2 ML. The photoemission experiments have been performed at the SU8 undulator beam line at LURE (Orsay, France). Surface states at Ag/Cu one-dimensional striped nanostructures are decoupled into Ag- and Cu-like stripe states. A model potential scaled from the infinite system explains the results. As a consequence, both Cu-like and Ag-like states display the characteristic periodicities of the corresponding facet plane. Furthermore, Cu-like stripe states exhibit the same terrace quantum-size effects observed in the infinite Cu(111) vicinal crystals.

[1] A. R. Bachmann, A. Mugarza, J. E. Ortega, and S. Speller, Phys. Rev. B 64, 153409 (2001).

10:40am **NS-WeM8 Patterned Anodization on Aluminum Surfaces**, ***J. Yan***, *V. Goparaju, P. Atanasov, G. López*, The University of New Mexico

Nanoporous aluminum oxide (AAO), highly ordered arrays of uniform and straight pores with tunable features, can be formed through anodization of aluminum in an acid solution. Through-hole AAO membranes have recently been explored as an alternative to conventional lithographic techniques to achieve high resolution, to fabricate fine patterns over a large area, and to minimize costs. The inherent fragility of AAO membranes, however, limits their integration into established microfabrication process. To address this issue, we pre-patterned bulk aluminum sheets and vacuum-evaporated thin aluminum films on glass with silica through a sol-gel process or chemical vapor deposition. After a two-step anodization, we observed highly ordered, uniform and straight nanopores on uncovered areas, and no pores were observed for the covered areas after silica had been removed, thus providing intermittent aluminum supports to the fragile nanoporous AAO. This work allows facile incorporation of AAO in a robust form into microdevices for microelectronics, microfluidics and integrated optics.

Organic Films and Devices
Room: C-102 - Session OF+EL+SS+SC-WeM

Metal-Organic Interfaces
Moderator: L.J. Guo, University of Michigan

8:20am **OF+EL+SS+SC-WeM1 Interfaces between Metals and Conjugated Organic Materials: From Physisorption to Covalent Bonding**, ***N. Koch***, Princeton University, *J. Ghijsen*, Facultes Universitaires Notre-Dame de la Paix, Belgium, *A. Rajagopal*, Rutgers University, *C. Chan*, Princeton University, *J.J. Pireaux*, Facultes Universitaires Notre-Dame de la Paix, Belgium, *J. Schwartz, A. Kahn*, Princeton University **INVITED**

The electronic properties of interfaces formed between conjugated organic materials (polymers and small molecules) and other organic and inorganic materials are of paramount importance in terms of the performance of organic-based devices (e.g., light emitting diodes, thin film transistors). The alignment of energy levels at such interfaces is a direct consequence of the physical and chemical interactions between the materials. Using mainly photoemission spectroscopy (PES), we show that the nature of interaction between low work function metals and phenylene-based electroluminescent oligomers and polymers covers the whole range from physisorption (aluminum and samarium) to chemical reduction (calcium), and to charge transfer reactions (alkali metals). Although PES is a very powerful experimental tool to determine electronic properties of interfaces, great care must be taken in the interpretation of the data when wide band-gap materials, such as conjugated organic materials, are being investigated. We demonstrate that the observation by PES of a finite density of occupied states at the Fermi-level on an organic film in which alkali metal atoms have been intercalated does not necessarily imply metallicity nor the presence of negative polarons (radical anions), as previously proposed. From a combination of ultraviolet PES and Kelvin probe measurements, evidence is obtained that the substrate and the surface of the organic film are not necessarily in thermodynamic equilibrium, leading to potential misinterpretations of the Fermi level position at the surface of organic films.

9:00am **OF+EL+SS+SC-WeM3 Structural and Electronic Properties of the Interfaces between Au(111) and the Organic Semiconductors Pentacene and p-sexiphenyl**, ***C.B. France****, P.G. Schroeder, B.A. Parkinson*, Colorado State University

Thorough understanding of the interface between organic semiconductors and metal contacts is important because of charge transfer events that take place in new devices based on organic semiconductors. Transistors[1] and photovoltaic devices[2] have been fabricated using pentacene as the organic semiconductor. In the interest of understanding the structural and electronic environments of these interfaces we have investigated thin films of pentacene and p-sexiphenyl on the Au(111) surface in ultrahigh vacuum using multiple characterization techniques. The entergetics of these heterojunctions have been measured using photoemission spectroscopy. Large interfacial dipole barriers exist at the interface of both systems. Temperature programmed desorption has been used to investigate the binding environment of the organic semiconductors on the metal substrate. Two different binding environments have been uncovered for both molecular semiconductors on the Au(111) substrate. Scanning tunneling microscopy has been used to investigate the coverage dependant structures that are formed by thin films of semiconductor molecules on the Au(111) surface. Pentacene was found to generate many overlayer structures at differing film thickness. Structures found on low coverage, monolayer and multilayer films will be discussed.

[1] Schön, J. H.;Berg, S.;Kloc, C.;Batlogg, B. Science 2000, 287, 1022.

[2] Schön, J. H.;Kloc, C.;Bucher, E.;Batlogg, B. Nature 2000, 403, 408. .

9:20am **OF+EL+SS+SC-WeM4 Growth of Organic Molecules on Ferromagnetic Substrates for Hybrid Organo-metallic Spintronic Devices**, ***M.V. Tiba****, O. Kurnosikov, B. Koopmans, J.T. Kohlhepp, C.F.J. Flipse, W.I.M. de Jonge, U.S. Schubert*, Eindhoven U. of Technology, CNM, The Netherlands

Motivated by the success of polymer based- and molecular electronics, a challenging new field is emerging. Recent work has demonstrated the feasibility of hybrid organo-metallic spintronics, in which the spin degree of freedom is explicitly being used. Application in future magnetic sensor and memory technology has been proposed. Improved characteristics of such devices require very clean interfaces, therefore deposition of organic molecules in UHV environment is desirable. A severe complication of growing ordered structures of organic molecules on transition metal ferromagnetic substrates is their high reactivity. In this work we investigate the influence of substrate passivation on the bonding to the substrate (and hence the molecular ordering) for different organic molecules. Selection of the molecules is based on their electronic properties as well as their tendency to form well ordered layers. In the particular case of PTCDA molecules deposited on a Ni(111) substrate we show that quarter monolayer of oxygen reduces enough the reactivity of Ni to enable the molecules to form an ordered structure.[1] Current activities aiming at the fabrication of organo-metallic hybrid magnetic tunnel junctions having polycrystalline Co electrodes and organic barriers will be addressed as well.

[1] M.V.Tiba et al. Surf. Sci. 498 (2002) 161.

9:40am **OF+EL+SS+SC-WeM5 Controlling Metallic Contacts to Molecular Electronic Devices**, ***A.V. Walker****, T.B. Tighe, O. Cabarcos, B.C. Haynie, D.L. Allara, N. Winograd*, Pennsylvania State University

In the development and design of molecular electronic devices, it is vital to understand the nature of the metal-organic monolayer interaction. To fully characterize these interactions, we employ a multi-technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. Using an unfunctionalized molecular wire (4-[4?-(phenylethynyl)-phenylethynyl]-benzenethiol) monolayer on Au, we demonstrate that the metal-monolayer contact can be varied from complete destruction of the monolayer to contact formation at the monolayer terminus to complete penetration through the layer. For example, we show that upon deposition of Cu or Ag, the Cu and Ag atoms simultaneously interact with the terminal phenyl ring and penetrate to the Au/S interface. In contrast, Au penetrates through the monolayer at all coverages studied. By using metals specifically tailored for the chemistry of the device molecule as well as for electronic states, the characteristics of the metal-molecule contact can also be controlled. These types of data provide a foundation for rational design of contacts in molecular electronic devices.

10:00am **OF+EL+SS+SC-WeM6 DLC Thin Film as Electron Injection Layer in Organic LEDs**, ***M. Cremona***, Pontificia Universidade Catolica do Rio de Janeiro, Brazil, *R. Reyes*, Universidad Nacional de Ingeniería, Perú, *C.A. Achete, P.I. Guimarães, S.S. Camargo, Jr.*, Universidade Federal do Rio de Janeiro, Brazil

Recently, there has been an increased interest in organic light emitting diodes (OLEDs) due of their potential applications to color flat panel displays and in new optoelectronic components. These devices are assembled using three organic molecular materials: an electron injection layer, the emitting one and finally the hole injection layer. However, in most cases the electron injection is more difficult to achieve than hole injection. In this work two different diamond like carbon (DLC) thin films cathode were used to decrease the electron injection barrier. The first kind were nitrogen-doped amorphous hydrogenated hard carbon films deposited by rf glow discharge from methane-nitrogen mixtures onto the TPD/Alq_3 layer structure thermally deposited. DLC films were obtained for different N_2 partial pressures (bias voltage V_b=â€“370 V and total pressure P=8 Pa). Next, amorphous carbon nitride thin films (a-CN_x) have been deposited using a rf diode sputtering system onto the same organic structure. In this case the DLC films were deposited in reactive nitrogen-argon atmospheres. The partial pressure of nitrogen ranged from 0% to 100% at two different deposition pressures (P = 2 Pa and P = 8 Pa). In both cases a thick (150 nm) aluminum electrode were deposited onto the whole structure. The deposition process for the organic compounds is performed in high vacuum environment ($6x10^{-6}$ Torr) on glass substrates coated with an hole injecting ITO transparent layer. A preliminary investigation was conducted on the properties of the OLED device with the two DLC intermediate layers. The relationship between the properties of the DLC deposited films on the electroluminescent characteristics of the different devices are investigated. The refractive index of the DLC film deposited, their conductivity and optical absorption, the OLED I-V curves, a preliminary photoluminescent and electroluminescent OLED results are presented and discussed.

10:20am **OF+EL+SS+SC-WeM7 Self-assembly of Molecular 1D wires on Cu(110)**, ***Y. Naitoh****, F. Rosei, P. Thostrup, M. Schunack, F. Besenbacher*, University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110) surface.[1] By exposing the surface to low doses of oxygen at elevated temperatures, we form a nanopattern of alternating bare Cu(110) regions and (2x1)-O reconstructed regions aligned parallel to the [001] direction. The oxygen-induced reconstruction reveals a long-range ordering of Cu-O rows 20-50 Å wide. When deposited on this template, Lander molecules adsorb preferentially on bare Cu regions. By tuning the oxygen dosing, thereby adjusting the lateral periodicity of the template, and by varying molecular coverage in a controlled manner we can form long 1D rows of molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

10:40am **OF+EL+SS+SC-WeM8 Dip Pen Nanolithography on Insulating Substrates**, ***S.E. Kooi****, P.E. Sheehan, L.J. Whitman*, Naval Research Laboratory

Methods of assembling nanoscale components at chosen locations on a surface are needed to produce nanoscale electronic and sensor devices. Dip pen nanolithography (DPN) has been successful in producing such features as small as ~10 nm wide and one monolayer thick in several different molecule - surface combinations. The most studied systems have been alkyl and aryl thiol depostion on gold surfaces; however, DPN has also been demonstrated for inorganic salts on silicon, biomolecules on gold, and silazanes on semiconductor surfaces. We explore the application of DPN to write functional molecules on a technologically important insulating surface, namely silicon oxide. We have written several different trichlorosilane molecules directly onto thermally-grown silicon oxide substrates. By choosing an appropriate trichlorosilane and post-deposition chemical modification of the written molecules, we can direct the deposition of other nanostructures (such as carbon nanotubes, semiconducting nanowires, or nanoparticles). For example, by writing 10-undecenyltrichlorosilane onto silicon oxide, we can create a terminal carboxylic acid group with a post-deposition chemical oxidation. Subsequent deprotonation of the patterned carboxylic acid groups produces a negative charge that directs the deposition of positively-charged nanostructures. The ability to place nanoscale components at chosen locations on a surface, in combination with traditional (e-beam) lithographic techniques, opens up the possibility of interfacing nanoscale components with traditional devices.

Plasma Science
Room: C-103 - Session PS+NT-WeM

Plasma Science and Technology for Nanostructures
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

8:20am **PS+NT-WeM1 Plasma Enhanced Chemical Vapor Deposition of a Dense SiO_2 Cap Layer on Low-k Nanostructured Porous Silica**, ***Y.B. Jiang***, *N. Liu*, *C.J. Brinker*, *J.L. Cecchi*, University of New Mexico

Surfactant-templated self-assembled nanostructured porous silica is a promising material for low-k interlevel dielectrics (ILDs) in integrated circuits. With mono-dispersed pore sizes as small as 2 nm and an ordered pore structure, nanoporous silica has excellent mechanical and thermal properties, even at porosities high enough for k values of 2 and below. For ILD applications, the pores must be capped to prevent adsorption on pore surfaces during subsequent processing, such as the deposition of a copper diffusion barrier. In this work, we report on a process for capping nanoporous silica with a dense-but-thin SiO_2 layer that acts as a diffusion barrier without significantly increasing the overall dielectric constant of the ILD. Nanoporous silica was deposited on a silicon wafer by spin coating with a sol-gel solution. After spin coating, the films were solidified by heating. The pore surfaces were rendered hydrophobic by soaking the films in a 6% HMDS solution, which terminated the pore surfaces with methyl groups. An SiO_2 cap layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) in an inductively-coupled plasma reactor, using a $SiH_4/O_2/Ar$ gas feed mixture. RF power, total pressure, gas composition, and flow rate were varied systematically to produce a high-density film with low surface roughness. The corresponding deposition rate resulted in 50 nm-thick films in approximately 15 minutes. N_2 absorption measurements performed with a surface acoustic wave (SAW) technique indicate a reduction of more 10 between the capped and the uncapped nanoporous film. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements both confirm that the pore structure in the nanoporous silica is unchanged by the capping process. Fourier transform infrared (FTIR) detection of methyl groups shows that the hydrophobicity of the nanoporous silica remains after the dense SiO_2 cap layer is deposited.

8:40am **PS+NT-WeM2 RIE processes of Formation of Nanometer-Scale Dot Arrays**, ***Y. Zhang***, *K.W. Guarini*, *E. Sikorski*, *C.T. Black*, *T.J. Dalton*, IBM T.J. Watson Research Center

Nanometer scale structures are increasingly merging into microelectronics and other applications. One of the challenges of fabricating nanometer scale structures is the simultaneous scaling of vertical and horizontal features. As the horizontal feature scale shrinks down to nanometer sizes, the vertical scale often shrinks at a faster rate. When using these materials for masking layers, this leads to new challenges in fabricating multi-layer nanometer scale structures for a variety of microelectronics applications. In this paper, we explore the challenges of plasma RIE processing to fabricate densely-spaced, uniformly-sized nanometer-scale dot arrays over large wafer areas based on self-organizing diblock copolymers. High selectivties among variety materials, precise CD control, real time process monitoring, and flexible and uniform plasma processing conditions are necessary for fabricating nano-scale structures with high aspect ratios (AR), e.g., ~ 20nm polysilicon hole or column arrays with AR > 15:1. The results show the versatility of RIE process techniques through examples of dot arrays formed of conducting, insulating, and polymeric materials. These fabrication processes vary in complexity, utility, and degree of optimization, and we discuss the relative merits of each. The ability to create uniform nanoscale features below lithographic resolution limits may enable key applications in fields such as magnetic recording and microelectronics.

9:00am **PS+NT-WeM3 Efficient Production of Single-Wall Carbon Nanotubes by Means of the Gravity-free Gas Arc Dischargee**, ***T. Mieno***, Shizuoka University, Japan, *M. Kanai*, University of London, UK, *H. Shinohara*, Nagoya University, Japan **INVITED**

Single-wall carbon-nanotube (SWNT) are attracting much attention by their unique structures and properties, and applications of nanotubes are demonstrated as a cold electron emitter, strong wire, electronic devices and hydrogen absorber. The SWNT are produced by the gas-arc method as same as the fullerene production method. A carbon anode mixed with metal catalyst is arc sublimated in He gas (p> 40 kPa), and high density carbon particles deposit on metal particles in hot gas atmosphere making nano-pipe structures, diameter of which is about 1 nm. As these nanotubes, metal particles and another carbon clusters are flown up by the heat convection, the reaction time is limited by this heat convection. If the heat convection is suppressed by the gravity-free condition, diffusion speed of these particles is suppressed and longer reaction time can be expected.[1] In order to examine this gravity effect, the 12m-high vertical swing tower[1] is used and the carbon nanotubes are produced in the gravity-free condition.[2] Integrated gravity-free sublimation time is about 14 min. After the discharge, the carbon soot is collected and its weight is measured. As a result, production rate of the carbon soot including SWNT about 7 times increase in the gravity-free condition compared with that of the normal gravity condition. By the TEM (microscope method) their morphology is observed and more (about 2 times) dense bundle of SWNT is confirmed in the gravity-free condition. Thickness of the produced nanotube is measured by the Raman scattering method, and fatter nanotube (mainly d= 1.4 nm) is produced in the gravity-free condition compared with the normal-gravity case.

[1] T. Mieno, Jpn. J. Appl. Phys. 37 (1998) L761.

[2] M. Kanai, T. Mieno, H. Shinohara et al, Appl. Phys. Lett. 79 (2001) 2967.

9:40am **PS+NT-WeM5 Patterned Growth of Vertically Aligned Carbon Nanofibers using a High Density Plasma Enhanced Chemical Vapor Deposition Process**, ***J.B.O. Caughman***, *L.R. Baylor*, *M.A. Guillorn*, *V.I. Merkulov*, *D.H. Lowndes*, Oak Ridge National Laboratory

Patterned arrays of vertically aligned carbon nanofibers (VACNFs) have been grown using a high density plasma enhanced chemical vapor deposition process. The nanofibers are grown from a nickel catalyst that can be patterned to form arrays of individual isolated electron emitters. Forests of nanofibers, as well as single isolated nanofibers have been grown. An inductively coupled plasma source is used to grow the fibers. The plasma source operates at 13.56 MHz and couples power via a flat spiral coil. The plasma is composed of hydrogen and either acetylene or methane. The VACNFs are grown on a heated substrate located downstream from the ionization zone. Typical growth temperature is 700 degrees C. The energy of the ions impacting the growth surface is controlled by radio frequency bias, with typical self-bias voltages of between -50 and -300 volts. Plasma conditions are related to growth results by comparing optical emission from the plasma to the physical structure and electron emission from the nanofibers. For example, as the acetylene flow increases, the optical emission from the plasma indicates a decrease in atomic hydrogen production and an increase in molecular carbon production. The decrease in atomic hydrogen production results in a decrease in the chemical etching component during nanofiber growth. Plasmas that contain a high hydrogen to carbon ratio result in fairly narrow nanofibers, while plasmas with a high carbon to hydrogen ratio result in nanofibers with a broader base with more of a cone-like structure. The threshold electric field from isolated emitters has been measured and is typically 30-50 volts/micron and can vary with growth conditions. The relationship between plasma conditions and growth results/performance will be presented.[1]

[1] Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

10:00am **PS+NT-WeM6 Carbon Nanotubes by ICP-CVD: Growth, Characterization, Plasma Diagnostics, and Modeling**, ***D.B. Hash***, *L. Delzeit*, *K. Matthews*, NASA Ames Research Center, *B.A. Cruden*, Eloret Corporation, *M. Meyyappan*, NASA Ames Research Center

Applications in field emitter devices, electrode and sensor development require a very high degree of vertical orientation of carbon nanotubes (CNTs) on the substrate. This is not possible using thermal CVD. The inherent electric field in a direction normal to the substrate in a plasma process enables achievement of vertical orientation of the nanotubes. We have built an ICP reactor and grown multiwalled carbon nanotubes (MWNTs) from hydrocarbon feedstock (CH_4, C_2H_2, and C_2H_4) diluted with hydrogen. The MWNTs have been characterized using SEM, HRTEM, and Raman scattering. The MWNTs are highly aligned and suitable for the applications mentioned above. Results as a function of pressure, substrate power, and temperature will be discussed. To understand the effects of process parameters on growth as well as mechanisms - including identification of species responsible for nanotube growth, we have undertaken a 2-D plasma modeling of the process. Modeling results are compared with plasma diagnostics using optical emission spectroscopy, UV Absorption, and Residual Gas Analysis (RGA).

10:20am **PS+NT-WeM7 Zinc Oxide Nanowires Grown by Plasma Assisted Chemical Vapor Deposition**, ***J.B. Baxter***, *E.S. Aydil*, University of California, Santa Barbara

Zinc Oxide is a wide band gap semiconductor (Eg=3.37eV) that can exhibit visible and UV luminescence, piezoelectricity, and high conductivity. ZnO nanowires and hexagonal columns have been grown using plasma assisted chemical vapor deposition, using either metallic zinc or metalorganic precursors. Nanowire growth is catalyzed by monodisperse gold nanoparticles (20 nm diameter) dispersed on a substrate from a colloidal solution. Transmission electron microscopy and electron diffraction show that single crystal ZnO nanowires grow from the gold particles in the <0001> direction. The nanowires have monodisperse diameters determined by the diameter of the gold particles (~ 20nm), and can grow to several microns in length. Energy dispersive x-ray spectroscopy confirms that the wires have a Zn:O ratio of 1:1. ZnO columns were formed by subliming metallic zinc in oxygen plasma, with the columns growing in the <0001> direction from the zinc surface. The columns are several 100 nm in diameter and are hexagonally faceted. Cathodoluminescence results show that both wires and columns emit photons upon excitation by electrons, with the columns emitting most light through the top face. This suggests that ZnO nanowires act as light pipes by internally reflecting the emitted light, making them good candidates for UV lasing. Because the gold particles from which the wires grow can be closely packed, the wires can be grown on a substrate in very dense, high surface area arrays. This property suggests that ZnO nanowires are also ideally suited toward application as the mesoporous semiconductor in dye sensitized (Gratzel) solar cells.

Plasma Science
Room: C-105 - Session PS-WeM

Conductor Etch II
Moderator: S.J. Ullal, Lam Research Corporation

8:20am **PS-WeM1 Plasma Etch Chemistries for III-V Lasers and Light-Emitting Diodes**, ***S.J. Pearton***, University of Florida **INVITED**
A review will be given of plasma chemistries for etching AlGaN/InGaN, InP/InGaAsP and AlGaAs/GaAs diode lasers and light-emitting diodes. With Cl$_2$-based chemistires, it is generally necessary to heat the sample when etching In-containing compounds, because of the low volatility of InCl$_x$. By contrast, the use of Br$_2$ or I$_2$ based chemistries produces practical etch rates at room temperature. Plasma-induced damage can play a significant role in determining device performance through effects on ohmic contact resistances or optical output power. Special attention must be paid to the quality of the initial lithography for patterning resist, since sidewall roughness is transferred into the semiconductor during subsequent etching. Gratings for DBR or DFB layers are also readily created using holographic lithography and plasma etching.

9:00am **PS-WeM3 Surface Chemical Changes of Aluminum During NF3-Based In-Situ Chamber Cleaning: Critical Discharge Parameters**, ***X. Li***, *G.S. Oehrlein, X. Hua, L. Ling*, University of Maryland, *E. Karwacki, B. Ji*, Air Products
During plasma-based in-situ chamber cleaning of deposited dielectric films using NF3, a significant transformation of aluminum into AlF3 can occur. We studied the roles of fluorine atoms and ion bombardment in this process by employing NF3 discharges mixed with He, Ne or Ar. Polished Al 6061 alloy coupons and sputter-deposited Al films were used. Typical process conditions were a pressure of 1 Torr, a total flow rate of 300 sccm, and power levels up to 300 W RF bias power for a 125 mm diam wafer. Aluminum erosion rates and surface chemistry changes, and information on the species that evolve from the surfaces during the process were obtained by real-time ellipsometry and mass spectrometry, respectively. X-ray photoemission spectroscopy characterization of processed Al surfaces was also performed. We find that a complex Al-fluoride layer is produced by the plasma processes. For RF-based discharges employing NF3 a threshold RF power exists below which a thicker reacted Al-fluoride layer is not produced (about 2 W/cm2 for our reactor). When Al is exposed to an NF3 RF discharge above this power level, a thick reacted Al fluoride layer is produced. If instead a He/NF3 discharge is used, the Al surface modifications are minimized at high RF power as long as the NF3 concentration is less than 40%, and an increasingly thicker Al fluoride layer is produced with a greater proportion of NF3 in He/NF3. In addition, we will report RF electrical characterization of NF3/He discharges under these processing conditions, and results of comparative studies using Ne/NF3 and Ar/NF3 discharges, and microwave remote plasma production.

9:20am **PS-WeM4 Metal Etching in High-Density Plasmas**, ***R. Blumenthal***, *A.S. Orland*, 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 ranging from the more traditional etching of the metals with Cl$_2$ to the more novel example of CO-NH$_3$ etching and finally to a new etch chemistry based on H$_2$-CO 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.

9:40am **PS-WeM5 Effects of Dry Etch Process for Platinum Upper Electrodes on Electrical Properties of High-k (Ba,Sr)TiO$_3$ Thin-Film Capacitors**, ***D.-S. Wuu***, *R.-H. Horng, C.-Y. Kung*, National Chung Hsing University, Taiwan ROC
Inductively-coupled-plasma (ICP) etching behavior of the platinum (Pt) thin films has been characterized with Ar gas by varying the etching parameters such as chamber pressure, ICP power, and bottom rf power. After the dry etch process, the restoring method of plasma-induced damage was investigated in terms of rapid-thermal and furnace annealing. Quantitative analysis of the etch damage was attempted to discuss the mechanism of leakage current density and dielectric constant with various bottom rf power and ICP power in Pt/(Bs,Sr)TiO$_3$(BST)/Pt capacitor. It was found that the parameters of etching process for the top electrodes of BST capacitors would influence the methods of recovering technique. In this study, a better condition with lower leakage current density was observed under a coil power of 1000 W, bottom rf power of 100 W, and chamber pressure of 0.67 Pa. The plasma-induced damage samples can be effectively recovered with furnace annealed at around 600°C in oxygen ambience. It can not only improve the leakage current density less than $5x10^{-8}$ A/cm^2 under an applied voltage of 1 V, but also enhances the dielectric constants to 350 for the damaged samples.

10:00am **PS-WeM6 Residual-Free Reactive Ion Etching of the Bell Contact Ti/Pt/Au**, ***G.F. Franz***, *R. Kachel, S. Sotier*, University of Applied Sciences, Germany
The etching of the complete Bell contact consisting of a layer of Ti/Pt/Au was performed in highly reactive plasmas containing Cl$_2$ for Ti, PF3$_3$/NF$_3$ for Pt, and Cl$_2$ and/or BCl$_3$ for Au. All the constituents of the Bell contact form volatile compounds in either capacitively-coupled low-density plasmas or high-density plasmas generated by electron cyclotron resonance. This is a conditio sine qua non for surfaces and sidewalls which have to remain free of any residues. Its functionality was demonstrated as self-adjusting mask for a surface-emitting laser.

10:20am **PS-WeM7 Advanced Metal Gate Etch with 193nm Lithography in a Silicon Decoupled Plasma Source Etcher (DPSII)**, ***D. Yan***, *M. Shen, D. Shashank*, Applied Materials, *T. Chowdhury, C. Yang*, Cypress Semiconductor
193nm lithography is becoming increasingly important as the critical dimensions of semiconductor devices continue to scale down towards sub-0.10um. From dry etching perspective, however, 193nm resist brings new challenges due to its poorer plasma etch resistance, line edge roughness and lower thickness compared to 248nm DUV resist. Consequently, issues such as line edge roughness and poor profile control were observed after dry etch processing using etch processes developed for 248nm resist. This paper presents a successful development of advanced 0.1mm metal gate application using 193nm lithography on Applied Materialsâ€™ decoupled plasma etcher (DPSII). The integrated process involves a hard mask open with ex-situ resist strip followed by metal/poly dual gate etching. Process chemistry and process parameters for nitride mask step were thoroughly investigated. With CF4/CHF3 based chemistry, the process achieved high nitride to resist selectivity with straight nitride profile and smooth sidewall. Less than 7nm 3-sigma of CD bias uniformity was obtained across the wafer with edge exclusion up to 4mm on a 200mm substrate. Process parameters such as pressure, gas ratio and the total fluorine-containing flow were shown to be the most influential on resist selectivity, profile and CD control. A careful balance of these parameters needs to be maintained in order to deliver an overall process. The subsequent W/WN/poly gate etch features a three-step approach that has produced straight profiles, excellent CD control and excellent gate oxide integrity. Post-etch measurement of line edge roughness shows comparable performance to that obtained on 248nm resist. Bright field ultra sensitive defect monitoring on product wafers showed comparable performance to previous 248nm resist poly gate process. Process trends and proposed mechanisms are addressed in detail in the paper.

10:40am **PS-WeM8 Effect of Carbon Based Polymer Formation on Process Stability in Polysilicon Etching**, *S. Xu, S. Deshmukh*, ***Th. Lill***, Applied Materials, *O. Joubert*, CNRS/LTM, France
High density plasma at low pressure has been used extensively in etching ultra-small feature devices to achieve precise critical-dimension control. In such a processing environment, plasma properties become significantly dependent on the wall condition of the reactor through plasma wall interactions. Commonly, halogen containing silicon oxides are deposited on the chamber walls during polysilicon etching. Recently, in-situ dielectric mask open or dielectric anti-reflective coating open steps are being used

more frequently. These steps generate carbon based deposits on the chamber walls. Another source of carbon polymers are CF4 and other CxHyFz additives used in silicon etching to achieves good n/p etch behavior and dense/iso microloading. This paper extends previously published studies on the influence of polymer formation on the chamber walls to carbon based polymers. The effect of surface polymerization has been characterized by studying the variation of the plasma properties and process performance. Clean, oxide covered and carbon covered chamber wall are being compared in terms radical densities, plasma emission properties, etch rates, and critical gate dimensions. Effective approaches to reduce the impact of chamber wall on the plasma and process stability will be discussed.

Surface Science
Room: C-110 - Session SS+EL-WeM

Nucleation & Growth of Semiconductors

Moderator: B.S. Swartzentruber, Sandia National Laboratories

8:20am **SS+EL-WeM1 Nucleation and Epitaxial Growth of Gallium Nitride on Sapphire (0001) using Ion-beam-assisted Molecular Beam Epitaxy**, ***B. Cui**, I.P. Steinke, P.I. Cohen*, University of Minnesota

Molecular beam epitaxy (MBE) is a far from equilibrium growth technique that relies purely on thermal energy to provide high quality thin films. At the relatively low temperatures used a key limitation is often the widely disparate adsorptive and diffusive properties of the film constituents. To provide additional control over the growth kinetics, we have used a low energy ion beam from a Kaufman source to impinge on the surface at low glancing angle of about 4 degrees. First experiments examined the nucleation and growth of GaN on the basal plane of sapphire. The sapphire substrates were pretreated in an ion flux and then annealed for cleaning. The sapphire was then nitrided at 1100K for about 10 min. Then GaN was nucleated by a sequence of adsorption and annealing steps. Finally, a very thin film of GaN was grown under conditions of excess Ga. Ammonia was the nitrogen source throughout. For comparison a GaN film was grown under identical procedures but using an ion beam. An Ar ion beam at 300 eV with a current of 20 micro A/cm2 was incident on the sample after a few of the initial nucleation steps were carried out. Atomic force micrographs of the resulting films showed films with a granular structure. The grains were nearly doubled in size. Small islands apparent in the normal growth were not present when the films were grown using the ion beam. The evolution of the island sizes is compared to a rate equation model of the ion-assisted growth. Partially supported by the National Science Foundation and the Office of Naval Research.

8:40am **SS+EL-WeM2 STM Characterization of Ge Nucleation on Ge(001)**, ***M. Li**, E.I. Altman*, Yale University

The initial stage of Ge homoepitaxial growth has been studied using scanning tunneling microscopy (STM). When 0.12 ML of Ge was deposited on the Ge(001) surface at 310 K, <130>-oriented metastable clusters dominated the surface with very few epitaxial dimer rows oriented across the substrate dimer row. Increasing the Ge coverage to 0.18 ML led to an increase in the density of epitaxial dimer rows. Metastable dimers disappeared at the same Ge coverage but at a higher growth temperature of 420 K, which can be explained by the competing process of the transition from metastable dimers to stable epitaxial dimers against that of the coalescence of metastable dimers to form <130>-oriented metastable clusters. At the same temperature, a myriad of epitaxial structures including single buckled B dimers, single nonbuckled dimer rows with ends terminated by either B and D dimers or D dimers only; single buckled dimer rows; pairs of buckled dimer rows with local c(4x2) structures; pairs composed of one buckled and one nonbuckled dimer rows; as well as larger epitaxial islands were first observed. The observed islands as well as second-layer nucleation elongate preferably along 2x direction of the islands and substrate respectively, which can be explained by 1) the fast diffusion of ad-dimers along 1x direction (dimer row direction) of the islands and substrate; and 2) the strong capture probability of diffusing ad-dimers along 2x direction of the islands and substrate. Nonbuckled SA steps and nonbonded SB steps, which were claimed not to exist on stepped and singular Ge(001) surfaces, were populated on single dimer rows. The interactions between various steps of epitaxial structures and neighboring dimers are also discussed.

9:00am **SS+EL-WeM3 High Resolution Large Area STM Analysis of Nucleationless Island Formation in SiGe/Si(100)**, ***P. Zahl**, P.W. Sutter, J.S. Palmer, E.A. Sutter*, Colorado School of Mines

We present an STM analysis of quantum dot (QD) island self-assembly in lattice-mismatched heteroepitaxy. A primary objective of recent research on QD growth is the creation of long-range ordered arrays of QDs of uniform size, a major technological milestone that would pave the way for application of these nanostructures in electronic and optoelectronic devices. The formation of epitaxial QD islands is generally assumed to involve nucleation, a statistical process that would severely impede QD organization. Our recent observations by atomically resolved large area STM document the complete transition from initial surface roughening to the formation of faceted QDs in the heteroepitaxial SiGe/Si(100) system. QD self-assembly occurs in a coninuous process that avoids nucleation.[1,2] Combining growth with in-situ STM, we analyze the surface morphology evolution with increasing coverage. The key aspect of this analysis is the capability of our system to acquire very large STM scans (up to 400nm x 1000nm with 0.1nm resolution), with an unprecedented combination of image detail and statistics. The 2xn reconstruction and step meandering are analyzed at lower coverages, with the goal of identifying mechanisms that induce long-range order in the nucleationless islanding process. Statistical information is extracted using a SPA-LEED[3,4] like analysis of STM images in reciprocal space. At higher coverages the surface gets micro-rough and a transition to 3D growth of faceted, pyramid shaped QDs occurs. The arrangement and influence of the surrounding micro-rough area is analyzed in detail, depending on germanium concentration and growth conditions.

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9:20am **SS+EL-WeM4 Scanning Probes and Transition States: Uncovering the Low-barrier Si ad-dimer Diffusion Mechanism on Si(001) by its Electric Field Dependence**, ***T.R. Mattsson**, B.S. Swartzentruber*, Sandia National Laboratories, *R. Stumpf*, Motorola Labs, *P.J. Feibelman*, Sandia National Laboratories

Surface diffusion and reactions occur on a picosecond time scale, making direct observation of their atomic mechanisms difficult. Yet, understanding these processes is necessary to control the evolution of surfaces at the nanoscale. We show that the electric field dependence of barriers for surface diffusion and other surface processes can be used to discriminate between different proposed atomic mechanisms. Using density functional theory calculations, we show that "piecewise diffusion", the previously accepted atomic mechanism for ad-dimer diffusion on Si(001), where the ad-dimer partly splits during the transition, has the opposite field-dependence to what is observed. It therefore cannot be the dominant mass-transport mechanism. We describe an alternate process wherein the ad-dimer "walks" along the dimer row, combining rotational and translational motions. This process has a low barrier at zero electric field and a field dependence in agreement with measurements. This approach, comparing the measured and calculated effects of an electric field, is not limited to diffusion on semiconductors, but can also be used to study, e.g., dissociative adsorption barriers. Thus, the electric field in a scanning probe should not be considered a nuisance which is to be corrected for by extrapolating results to zero field, but instead a tool that helps us study states otherwise inaccessible. T.R.M. acknowledges support from the Motorola/SNL computational materials CRADA. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04- 94AL85000.

9:40am **SS+EL-WeM5 Simulations of Surface Diffusion on Amorphous Silicon**, ***A.S. Dalton**, E.G. Seebauer*, University of Illinois

Surface diffusion over amorphous materials plays a governing role in an increasing variety of applications, including reflow of amorphous metals and oxides, and nanostructure formation for electronic memory devices. However, there exists little literature describing diffusion on amorphous surfaces. The structural and energetic heterogeneity of amorphous surfaces should lead to diffusivities that differ significantly from crystalline ones. Our recent experimental work has confirmed that that activation energy for surface-self diffusion on amorphous Si (a-Si) differs significantly from that for crystalline Si (c-Si), and that the activation energy is temperature dependent. Here we describe the results of molecular dynamics simulations to gain atomistic insights into these phenomena. Calculations using a modified Stillinger-Weber potential confirm marked differences between diffusion parameters on a-Si vs. c-Si, with lower activation energies for a-Si. Collective motions involving two or three atoms play a significant role, as do long hops over several atomic diameters. Both hopping motion and formation of mobile atoms can be described with distribution functions, which ultimately give rise to temperature-dependent Arrhenius parameters for diffusion.

10:00am **SS+EL-WeM6 Relaxation of a Single Silicon Mound during Silicon Deposition on the Si(111)(7x7)**, ***A. Ichimiya***, *Y. Tsutsui*, Nagoya University, Japan

Isolated single three dimensional (3D) silicon mounds on the Si(111)(7x7) surface between 700K and 800K have been produced using a tip of a scanning tunneling microscope (STM). Produced 3D mounds are like pyramids with certain facets for the both surfaces. Indices of main facets of the mounds on the Si(111) surface are {311} and small facets are {221}. Without silicon deposition, the pyramid begins to decompose just after the deposition. During the decomposition of the mound, the facets of the pyramid transform into multi-bilayer steps. Finally the mound becomes a bilayer (2D) island with a truncated triangle shape. When silicon atoms are deposited on the surface with retracting the STM tip, the decay rate is reduced due to increasing chemical potential on the surface. For deposition of $5x10^{12}$ atoms at 700K, the mound is grown slowly just after the production. The height of the mound decreases and the top of the pyramid is truncated. The facets of {311} increase the area and the {221} facets are reduced. Then the pyramid becomes truncated pyramid with stable height of about 10 bilayers. Shapes of the bottom and the top layers are just triangles while these shapes become truncated triangles during decay of the mound without deposition. The difference between the shapes with and without deposition is due to the difference of the chemical potentials on the silicon surface. Therefore the {311} facets of the pyramid become dominant and the {221} facets disappear at growth mode of silicon on the Si(111). The behavior of the pyramid during deposition has been expected that the shape changes into two dimensional island, and the {221} facets remain, because silicon mounds tend to two dimensional island during growth on silicon surfaces. It is noted that the present result is different from expectation from the results of the decay process of the pyramid on the Si(111).

10:20am **SS+EL-WeM7 Morphology of Crystal Growth on Vicinal Surfaces: MBE and H-assisted MBE Growth on Laser-textured Ge(001)**, *A. Raviswaran*, ***D.G. Cahill***, University of Illinois

We delineate the growth conditions of temperature, substrate vicinality, and concentration of surface adsorbates that produce rough and smooth crystal growth of Ge by molecular beam epitaxy. Ge(001) substrates are modified by laser texturing to produce a large range of vicinalities $0<\theta<10°$ within a 5 µm diameter laser-dimple. We then deposit Ge on these modified substrates over a wide range of growth temperatures $150<T<450$°C, with and without an atomic hydrogen flux of 10^{13} cm^{-2} s^{-1}, and characterize the morphologies by atomic-force microscopy. Hydrogen flux suppresses the growth-mound instability at low vicinality and reduces the epitaxial critical thickness at large vicinality. Highly-elongated mounds continue to dominate the morphology to surprisingly high growth temperatures; at even higher temperatures, the morphology of vicinal surfaces is dominated by step-bunching instabilities and the formation of low angle facets. Hydrogen adsorbates continue to play a role in the growth morphology at $T=450$°C when the steady-state hydrogen coverage is only a few percent.

10:40am **SS+EL-WeM8 Characterization of Si(100) Homoepitaxy Grown in the STM at Low Temperatures**, ***H. Grube***, *G.W. Brown*, *M.E. Hawley*, Los Alamos National Laboratory

We explore the growth of low-temperature bulk-like Si(100) homoepitaxy with regard to microscopic surface roughness and defects. We characterize films grown at different temperatures up to 500K in-situ by means of an effusion cell added to our UHV-STM. The development of novel architectures for future generation computers calls for high-quality homoepitaxial Si(100) grown at low temperature.[1] Even though Si(100) can be grown crystalline up to a limited thickness,[2] the microstructure reveals significant small-scale surface roughness[3] and defects specific to low-temperature growth.[4] Both can be detrimental to fabrication and operation of small-scale electronic devices.

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Surface Science
Room: C-112 - Session SS-WeM

New Opportunities and Technique Innovations
Moderator: A.R. Laracuente, Naval Research Laboratory

8:20am **SS-WeM1 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation: Experiments and ab initio Calculations of Ethoxy Adsorbed on Cu(100)**, ***M.P. Andersson***, *P. Uvdal*, Lund University, Sweden

We compare high sensitivity experimental reflection-absorption IR spectra of ethoxy adsorbed on Cu(100) with ab initio calculations. The high sensitivity allows for detection of binary combinations of CH bend modes, i.e. overtones and combination bands. As their presence cannot be explained using a strictly harmonic approximation, we include anharmonic effects in the ab initio treatment as well. Calculations at the harmonic level are performed for an ethoxy-Cu17 cluster with a hybrid DFT method. Anharmonic effects are computationally more demanding and are therefore calculated for the free ethanol molecule using the same method and basis set as for the cluster. The anharmonic effects are then added through a standard expression involving third and fourth derivatives of the energy. The method allows for inclusion of both intramode anharmonicity and anharmonic resonance effects such as Fermi resonances due to accidental degeneracy. The experimental spectrum is reproduced in detail, including CH bend overtones and combination bands in resonance with CH stretch fundamentals. The mean absolute deviation is only 10 cm-1 and all intensities are also very well reproduced.

8:40am **SS-WeM2 Development of a Time-of-Flight HREELS Using Pseudorandom Modulation**, ***R.H. Jackson***, *Z. Yang*, *L.J. LeGore*, *P. Kleban*, *B.G. Frederick*, University of Maine

We have constructed a prototype high resolution Time-of-Flight HREELS utilizing pseudorandom modulation. The instrument is comprised of an LK-3000 HREELS, a custom designed TOF analyzer with a double mu-metal shielded 1.5m flight tube, a Bradbury-Neilsen Gate modulator, a microchannel plate detector, and a Fast Com Tek time to digital converter with 250 ps time bins. The electron optics have been shown to pass a beam of electrons to the detector with energies as low as 0.5eV over a 1m flight length. The TOF spectra are recovered using the Lucy maximum likelihood deconvolution algorithm. Initial measurements show that the method can recover well resolved <4meV peaks at 6eV flight energies to within the capability of the current data acquisition electronics. We will present the methodology for using and calibrating the instrument and show loss spectra of PTFE films comparing the TOF and conventional spectra.

9:00am **SS-WeM3 The STM as Operative Tool: Physics and Chemistry with Single Atoms and Molecules**, ***K.H. Rieder***, Free University Berlin, Germany **INVITED**

Recent progress in using the scanning tunneling microscope (STM) for manipulation of individual atoms and molecules is reviewed. Topics include - build-up of artificial nanostructures by lateral manipulation (pulling, pushing, sliding) - determination of physical properties like electron phase relaxation lengths in artificial structures - manipulation and contacting of complex molecules as well as manipulation into parts of molecules with consequences to molecular electronics - induction of all steps of chemical reactions with tips funcionalized by vertical manipulation - investigation of electronic and vibrational influences upon electron induced formation of ice clusters - experiences with attempts to transfer manipulation techniques from metal surfaces to thin insulating films. * In collaboration with: Gerhard Meyer (IBM ZRL), Francesca Moresco, Karina Morgenstern, Ludwig Bartels (UC Riverside), Kai-Felix Braun, Stefan Falsch (PDI-Berlin), Saw-Wai Hla (Ohio State Univ.), Reinhold Koch (PDI-Berlin), Jascha Repp (IBM ZRL), Jens Schulz (PDI-Berlin), Sven Zaphel (Createc)

9:40am **SS-WeM5 Microscopic Nature of the Interaction of Water with Noble Metal Surface**, ***H. Fukidome***, *Y. Kim*, RIKEN, Japan, *Y. Sainoo*, University of Tsukuba, Japan, *T. Komeda*, RIKEN, Japan, *H. Shigekawa*, University of Tsukuba, Japan, *M. Kawai*, RIKEN, Japn

Interaction of water on solid surfaces has been one of the central issues in science.It has been, however, hard to microscopically investigate the interaction of water with solid surfaces by traditional macroscopic spectrscopies, such as infrared spectroscopy and electron energy-loss spectroscopy. One of the reasons for this is that water can form various types of cluster owing to its hydrogen-bonding. A STM-IETS, which can do a spectroscopy at a sinlge-molecular level,[1] was used in our work in order to microscopically study the interaction of water with Pd(110) surface. In our STM-IETS spectra of water monomer, a huge and asymmetrical feature appeared at 57 meV. This can be assigned to the frustrated translational mode of water perpendicular to the surface (Tz).[2] On the contrary, no feature was absent at 57 meV in a spectra of water tetramer. The above-mentioned asymmetrical lineshape of the Tz mode of water monomer arises from the interference between elastic and inelastic tunneling processes. More interestingly, the lineshape of the Tz mode drastically changed within the molecule. This drastic change is caused by the mixing of two molecular orbitals that are responsible for the tunneling processes associated with Tz mode. A comparison between our STM-IETS results and a detailed theory now under construction would tell the microscopic picture of the interaction of water molecules with metal surfaces that has ever remained to be seen.

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[2] R. Brosseau, T.H. Ellis, and M. Morin, J.Vac.Sci.Technol. A8 (1990) 2454.

10:00am **SS-WeM6 First Principles Simulation for NC-AFM Images of Si(111) Ö3xÖ3-Ag Surface**, *N. Sasaki,* University of Tokyo and Japan Science and Technology Corp. (JST), Japan, *S. Watanabe, **M. Tsukada***, University of Tokyo, Japan

Quantitative, or sometimes even qualitative interpretation of non-contact atomic force microscopy NC-AFM images is extremely difficult, which contracts with the case of STM (scanning tunneling microscopy). Therefore theoretical simulations of NC-AFM images based on the first-principles density functional theory play very important role for the analyses of the experimental date. Effects of the tip structure and atom kind dependence can be also clarified, by the theoretical simulation. There have been some extrordinary features have been experimentally reported for the Si(111) √3x√3 surface(refferd to √3-Ag hereafter), which await theoretical explanation. Recently Scanning Tunneling Microscopy (STM) experiment of √3-Ag surface have been reproduced well based on the assumption of fluctuated Ag atoms among different energetically stable phases of Inequivalent-Triangle (IET) structures[1] without the tip effects using Monte Carlo simulation.[2] However NC-AFM experiments of the √3-Ag surface at room temperature[3] have not been fully understood yet. Important point here is that, in the case of NC-AFM, the tip effects are much stronger than in the case of STM, which give remarkable influences on the surface dynamics.Therefore in this work, NC-AFM images of √3-Ag surface at both room and lower temperatures have been reproduced by DFT calculations.[4,5] First we report that calculated images successfully reproduce experimental ones for both room temperature[5] and lower one. For the room temperature image, thermal fluctuation is described by the weighted average of the two IET phases with the Boltzmann factor counting the difference of the interaction energies. Energetically stable IET structure appears in the lower temperature image. Thus it is clarified that, as far as only the room temperature NC-AFM experiment is observed, we cannot obtain information of truly stable IET structure of √3-Ag surface.Next we show a remarkable tip-height dependence of the lower temperature NC-AFM images. In this case the Hydrogen-terminated Si tip is used. As the tip approaches the surface the NC-AFM image pattern changes from that of IET phase to HCT phase, and another IET phase. We explain this transition from the standpoint of the atom relaxation of tip-surface system. Thus our calculated results mean that Scanning Probe Microscopy (SPM) has an ability of not only directly observing dynamic feature of the surface but also mechanically controling the surface structures.

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10:20am **SS-WeM7 Single Molecular Motion and Reaction Induced by STM Inelastic Tunneling**, *Y. Sainoo,* RIKEN and Tsukuba University, Japan, *Y. Kim, T. Komeda, **M. Kawai***, RIKEN, Japan

Inelastically tunneled electrons using STM device enable vibration excitation of individual molecules applicable to vibration spectroscopy, mode selective reaction and so on. Here we present that the selective excitation is ruled reflecting the symmetry of adsorbed molecules and that the vibrationally excited molecules may react along the reaction coordinate through their multiple excitation state. Examples for selective excitation are given for trans-2-butene on Pd(110) surface where methyl groups are lifted towards vacuum and butadiene with flat-laying geometry. The C-H stretching vibration is clearly observed for trans-2-butene and not for butadiene. Symmetry of the adsorbed states for both adsorbates is determined by XAS and HREELS. Motions of isolated cis-2-butene molecule on the Pd(110) surface at 4.7 K between four equivalent positions were induced and monitored with tunneling electrons of scanning tunneling microscope (STM). These motions were consisted with two different flip-flop motions, and clear threshold energy indicated the existence of different potential barriers for the corresponding motions. The strong dependences of these motions rate on the tunneling current support multiple vibrational excitation mechanism via inelastic tunneling process.

10:40am **SS-WeM8 Dry De-intercalation in Layered Compounds upon Controlled Surface Charging in XPS**, *Y. Feldman, A. Zak, R. Tenne, **H. Cohen***, Weizmann Institute of Science, Israel

2H platelets and inorganic fullerene-like (IF) MS_2 (M=W,Mo) powders, intercalated with alkaline (A=K,Na) atoms,[1] are studied using controlled surface charging (CSC) in XPS.[2] The degree of intercalation, expressed in terms of A/M concentration ratios, is found to tightly correlate with the presence of 'open' (hk0) edges, typically absent from the closed IF nanoparticles. Under strong electric fields, applied by an electron flood gun, diffusion of the intercalants towards the surface is observed. This out-diffusion process is negligible with low flood gun voltages, indicating that a critical field is needed for this type of dry de-intercalation. Diffusion rates out of 2H matrixes are generally higher than in corresponding IF samples, while those of K are far better than Na. These observations, closely related with the initial intercalation efficiency, provide helpful information about the actual intercalation states and their diffusion mechanisms.

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Thin Films
Room: C-101 - Session TF+VT-WeM

Atomic Layer Deposition - Barriers & Nitrides
Moderator: S.M. Rossnagel, IBM T.J. Watson Research Center

8:20am **TF+VT-WeM1 The PE-ALD of Ta Based Metals/Nitrides: The Growth, Materials Properties, and Applications to Future Device Fabrications**, ***H. Kim**, S.M. Rossnagel*, IBM T.J. Watson Research Center **INVITED**

Thin film deposition techniques producing high quality and highly conformal films with atomic level control are increasingly required as semiconductor device size shrinks into nanoscale regime. Atomic layer deposition (ALD) is expected to play an important role in depositing thin layers in nanoscale Si device manufacturing. Plasma enhancement of the process allows deposition at significantly lower temperatures than both conventional thermal ALD and chemical vapor deposition. Among the key materials used for today's semiconductor processing, thin films of inert, refractory 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. In this presentation, the Ta-based ALD systems have been explored at low temperature for a variety of semiconductor devices applications. Ta-based metals/nitrides films were grown by plasma-enhanced atomic layer deposition (PE-ALD) at temperatures from room temperature up to 400 °C using an inorganic halide source and RF plasma-produced atomic H as metal precursor and the reducing agent, respectively. The growth mechanism, microstructure, and chemical composition were studied using various ex situ analyses techniques. Good quality films with low contamination levels were obtained at low growth temperatures. Additionally, thermal stability, diffusion barrier property, resistivity, and other electrical properties, which are the essential materials properties for semiconductor device fabrication, were investigated. These results indicate that the PE-ALD process scales to manufacturing dimensions and applications and will facilitate the extension of interconnect technology beyond 100 nm dimensions.

9:00am **TF+VT-WeM3 Characteristics of TiN Films Deposited by rf Remote Plasma Enhanced Atomic Layer Deposition (ALD) Method using Metal Organic Precursor**, ***S. Seo**, J. Kim, Y. Kim, Y.D. Kim, H. Jeon*, Hanyang University, Korea

Titanium nitride (TiN) has been most widely used as a diffusion barrier in ULSI devices because of its very low resistivity, good chemical and thermal stability, and impermeability to Si diffusion as well as the excellent adhesion to Si and SiO_2 films.[1-3] TiN barrier layer has been deposited predominantly by sputtering and chemical vapor deposition method.[4] However, as the device dimension has been shrinking down continuously, TiN films deposited by sputtering and CVD have faced the serious problems such as poor step coverage and conformality. Also, especially for the TiN films deposited by CVD using metal organic precursors, a relatively considerable amount of carbon impurity is still incorporated into the TiN films. For these reasons, we investigated TiN films deposited by rf remote plasma enhanced atomic layer deposition (ALD) technique which is expected to reduce or eliminate the problems related with sputtering and CVD.[5] TiN films were deposited using tetrakis-dimethyl-amido-titanium (TDMAT) as Ti precursor and ammonia (NH_3) and reactant gas at the optimized ALD processing windows. Rf remote plasma was used to reduce the carbon incorporation and to enhance chemical stability. The physical, chemical and electrical characteristics of TiN films were analyzed using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), rutherford backscattering spectrometer (RBS), cross-sectional transmission electron microscope (XTEM) and four-point probe method.

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9:20am **TF+VT-WeM4 Importance of Hydrogen Recombination on Flow Tube Walls During Hydrogen Radical-Assisted Metal Atomic Layer Deposition**, ***R.K. Grubbs***, *S.M. George*, University of Colorado, Boulder

Many metals can be deposited with atomic layer control using hydrogen radical-assisted metal atomic layer deposition (ALD). Designing the hydrogen plasma source and hydrogen radical delivery for efficient hydrogen radical-assisted metal ALD in a viscous flow reactor offers many challenges. In particular, hydrogen recombination on the flow tube walls to form H$_2$ is a serious loss to the hydrogen radical flux. To quantify the hydrogen radical flux and its loss caused by hydrogen recombination on the flow tube walls, a dual thermocouple probe was constructed based on exposed and covered Pt/Rh thermocouple junctions. This probe measured hydrogen radical concentration by determining the heat evolved from hydrogen radical recombination on the exposed thermocouple surface. The thermocouple probe was then employed to measure hydrogen radical concentration versus distance from the hydrogen radical source for four flow tube materials. The hydrogen radical concentration decreased dramatically versus distance and was different for stainless steel, aluminum, pyrex and quartz flow tube materials. By modeling the decrease in hydrogen radical concentration versus distance, a hydrogen radical recombination coefficient could be determined from the data. The recombination coefficient ranged from γ= 1.5x10^{-4} for stainless steel to γ= 5.7x10^{-5} for pyrex. Given the magnitude of the hydrogen radical recombination coefficients, the reaction chamber for hydrogen radical-assisted metal ALD must be positioned very close to the hydrogen radical source.

9:40am **TF+VT-WeM5 Improved Nucleation of TiN ALD Films on Low k Polymer Dielectrics Using Al$_2$O$_3$ ALD Adhesion Layers**, ***C.A. Wilson***, *J.W. Elam, M. Schuisky, Z.A. Sechrist, S.M. George*, University of Colorado

Diffusion layers are required to prevent copper from diffusing into low k polymer dielectrics in backend interconnects. The ability to deposit conformal diffusion layers, such as TiN, onto high aspect ratio low k polymer features requires atomic layer deposition (ALD) techniques. This study examined TiN ALD on low k polymer dielectrics using tetrakis-dimethylamino titanium (TDMAT) and NH$_3$. X-ray fluorescence spectroscopy (XRFS), optical microscopy and surface profiling of the TiN ALD films deposited on the low k polymer dielectrics revealed discontinuous films displaying distinct patchy regions of thinner TiN coating. To study TiN ALD nucleation, in situ quartz crystal microbalance (QCM) measurements were performed by spin-coating a low k polymer dielectric onto the QCM sensor. Subsequent QCM measurements during TiN ALD revealed very low initial TiN ALD growth rates indicating poor nucleation. Al$_2$O$_3$ ALD was then performed on the low k polymer dielectric using trimethyl aluminum and H$_2$O. Surface profiling, XRFS, QCM and transmission electron microscopy measurements revealed that the Al$_2$O$_3$ ALD films nucleate immediately on the low k polymer dielectric producing continuous Al$_2$O$_3$ films. In addition, QCM measurements showed that TiN ALD nucleates readily on the Al$_2$O$_3$ surface. Intermediate Al$_2$O$_3$ ALD adhesion layers may facilitate the growth of continuous TiN ALD films on low k polymer dielectrics. Examination of TiN ALD films prepared on low k polymer dielectrics with progressively thinner Al$_2$O$_3$ ALD adhesion layers revealed that 10 Al$_2$O$_3$ ALD cycles are sufficient to promote the nucleation of the TiN ALD films.

10:00am **TF+VT-WeM6 Alternating Layer Deposition of Dielectric Films**, ***A.P. Paranjpe***, *B. McDougall, K.Z. Zhang, W. Vereb*, TORREX **INVITED**

Interest in alternating layer deposition (ALD) for the deposition of thin films used in semiconductor devices has grown rapidly due to the numerous advantages offered by ALD. Often, relatively high exposure doses are required to achieve self-limited surface saturation that is necessary for good uniformity, conformal deposition in high aspect ratio features, low impurity incorporation, and superior electrical properties. The low deposition rates make ALD using conventional reactors impractical in a semiconductor manufacturing environment for film thickness values > 10 nm. We describe a Parallel Wafer Processing reactor architecture capable of processing 1 - 25 wafers simultaneously that provides a 3X - 4X throughput advantage over single wafer ALD processes for both standalone and clustered operation. This reactor architecture is well-suited for the deposition of SiN and SiO$_2$, since initial surface chemisorption rates are relatively high, but high exposures (> 10 Torr-s) are required to achieve self-limited surface saturation. Exceptionally smooth (Ra < 0.15 nm), stoichiometric SiN films with conformality of ~ 100% in high aspect ratio features can be deposited at 0.1 - 0.2 nm/cycle in the temperature range of 450 - 550°C. The hydrogen content and wet etch rates are significantly lower than CVD SiN films deposited at equivalent temperatures confirming that ALD provides superior film quality. Electrical leakage is lower compared to SiN deposited in a conventional furnace at 750°C. SiN films have also been deposited via cyclic CVD which is analogous to ALD except that the chemisorption of the Si source deviates from the ideal self-limited behavior. Cyclic CVD offers deposition rates that are up to 50% higher than deposition rates achievable in ALD, but film properties including conformality are intermediate between ALD and CVD films. We will also discuss the deposition of other dielectric films using the Parallel Wafer Processing reactor.

10:40am **TF+VT-WeM8 Photochemically-Assisted ALD of BN Thin Films**, ***J. Olander***, *M. Ottosson, K.M.E. Larsson*, Uppsala University, Sweden

Boron nitride-based materials have properties like high thermal stability, oxidation resistance and interesting electronic properties and are thus suitable materials for electronic devices, heat resistant semiconductors and lubricants. Thin films of BN materials have only to limited extent been prepared and the film properties are not well known. A combined experimental and theoretical investigation of BN growth from NH3 and BBr3 has been performed. Thin films of Boron Nitride have been deposited on SiO2 by means of Laser-Assisted Atomic Layer Deposition (ALD) using an ArF excimer laser. The deposition temperatures were between 300 and 750 °C. In order to investigate the growth at an atomic level, theoretical calculations have been performed using the DFT method. Theoretically, the adsorption of the NH3 and BBr3 and their fragmented components were found to be favorable for continued growth of cubic BN. However, the films obtained in the present study are of turbostratic structure. Both NH3 and BBr3 were observed to strongly absorb light from the ArF excimer laser. As a result of the photofragmentation of the precursors, the growth rate of the BN films was increased. At lower temperatures, the densities of the grown BN films were also enhanced.

Vacuum Technology
Room: C-104 - Session VT-WeM

Outgassing
Moderator: L.A. Westerberg, The Svedberg Laboratory

8:20am **VT-WeM1 Influence of Thermal and Surface Treatments on the Outgassing Of Austenitic Stainless Steels Studied by Thermal and Electron Stimulated Desorption**, *C. Benvenuti*, ***P. Chiggiato***, *G. Chuste, I. Wevers*, CERN, Switzerland **INVITED**

Austenitic stainless steel is at present the most widely used material for UHV applications. In order to improve its vacuum behavior, several post-production treatments are usually applied. Surface chemical and electrochemical processing are used to reduce surface contamination and/or roughness, while heating, either under vacuum or in air, is applied to decrease hydrogen thermal outgassing. The effect of these treatments on the content and on the binding state of surface and bulk gases has been studied by thermal desorption spectroscopy and electron stimulated desorption. The enrichment of hydrogen induced by surface electro-polishing and the effect of the residual hydrogen pressure during vacuum firing have been studied in detail.

9:00am **VT-WeM3 Comparison of Outgassing Rates of Bare and TiN-coated Stainless Steel Vacuum Chambers***, *P. He, H.C. Hseuh, M. Mapes*, ***R. Todd***, *D. Weiss, D. Wilson*, Brookhaven National Laboratory

The stainless steel vacuum chambers of the 248m accumulator ring of Spallation Neutron Source (SNS) are to be coated with ~ 100 nm of TiN to reduce the secondary electron yield. Each SNS chamber is approximately 4m long and over 20cm in diameter. The coating is produced by DC magnetron sputtering using a long cathode imbedded with permanent magnets. Reports in literature suggest that the potential benefit of a TiN coating as a hydrogen permeation barrier that reduces the ultimate outgassing rate. The outgassing rates of several SNS chambers were measured with and without TiN coating of various thicknesses, and before and after in-situ bake. No improvements in outgassing were observed with the coated chambers. The results of the coated chambers were compared with the surface structure and thickness of the TiN coatings as analyzed using AES and SEM. A correlation between film density and outgassing rate was found. *Work performed under the auspices of the U.S. Department of Energy.

9:20am **VT-WeM4 Degassing of Static Expansion Vacuum Gauge Calibration Chamber**, ***J. Setina***, Institute of Metals and Technology, Slovenia

Laboratory of Pressure Metrology at the Institute of Metals and Technology is developing a static expansion system for calibrations of vacuum gauges. The gasses evolved from the chamber walls significantly affect the accuracy of generated calibration pressure at low pressures below 1mPa. The chambers of the expansion system were designed in accordance with established ultrahigh vacuum practice and are made from stainless steel. We studied the outgassing characteristics of the large calibration chamber by the gas accumulation method. The chamber was sealed-off from the pump and the rate of pressure rise was measured using the spinning rotor gauge (SRG). From this the total outgassing rate can be determined. At the end of the accumulation period the chamber was evacuated again. During evacuation the composition of the accumulated gas was dynamically analyzed with the quadrupole mass spectrometer. The method of dynamic gas analysis will be described and outgassing of unbaked and baked chamber will be compared. Bake-out temperature was gradually increased from 60 °C to 250 °C. By bake-out at 100 °C for 50 hours we effectively removed water vapour and other adsorbed gases and the main outgassing component became H2 at a rate of 1x10-11 mbarls-1cm-2. Final outgassing rate after 160 hours of bake at 250 °C was 2.4x10-13 mbarls-1cm-2. Measured H2 outgassing rate after bake-out at 100 °C increased by a factor of 3 compared to the initial value of unbaked surface. This indicates the importance of the adsorbed layer on stainless steel surface on the kinetics of H2 evolution. The diffused hydrogen atoms from the bulk must recombine into H2 molecule in order to be de-sorbed. Other adsorbed gasses can hinder the recombination of hydrogen atoms.

9:40am **VT-WeM5 Organic Contaminants Adsorption Behavior on Silicon Wafer Surface Under Reduced Pressure**, ***T. Hayashi***, *T. Kawaguchi, N. Tanahashi,* Tohoku University, Japan, *M. Saito, K. Suzuki,* Tokyo Electron Ltd., Japan, *Y. Wakayama,* Taisei Corporation, Japan, *Y. Shirai, T. Ohmi*, Tohoku University, Japan

It is known that organic contaminants on silicon wafer surface cause many detrimental effects, such as degradation of gate oxide integrity, yield losses, and so on. To prevent that, closed manufacturing system has been proposed. However, these are considered only for outside of process chamber under atmosphere pressure. And now, the low-pressure processes such as CVD, sputter, dry etching, etc. are routinely used under several hundred mTorr or less. The organic contamination behavior on silicon wafer surface in low-pressure chamber has not been reported yet. In this study, we clarified the organic contamination behavior on silicon wafer surface under reduced pressure. We have researched the following three results; 1) The amount of organic compounds adsorbed onto a silicon wafer stored in a chamber under reduced pressure was much more than that stored under atmosphere pressure. 2) The volatile level released from pure n-Eicosane, typical hydrocarbon contaminant, does not depend on the pressure. 3) The adsorption behavior for the amount of volatile from n-Eicosane adsorbed onto silicon wafer surface coexisted with n-Eicosane in the low-pressure chamber is in accordance with Langmuir model of monolayer adsorption and the amount of adsorption saturated is in inverse proportion to pressure. In conclusion, we clarified that the inner pressure of a chamber become lower, the partial pressure of released organic compounds from chamber components becomes higher, that is, the contact frequency between organic compounds and silicon wafer surface become higher. As a result of that, the much amount of organic compounds is adsorbed onto silicon wafer surface.

10:00am **VT-WeM6 Study on Desorption of Carbonaceous Gas Molecules from Copper Surfaces under Electron Bombardment and the Surface Characterization**, ***M. Nishiwaki***, KEK, Japan, *S. Kato*, KEK & The Graduate University for Advanced Studies, Japan

In particle accelerators, the carbonaceous gas desorption is generally observed as a result of the energetic particle stimulation at ducts and r.f. component surfaces during the operation and would deteriorate the beam performance. Therefore we aim to understand origin of the desorbed carbonaceous gas from the copper surface using carbon isotope. The passive layer cannot be formed at the surface of the oxygen free copper adopted to the beam duct. Since the surface should be easily altered due to irradiation of energetic particles and/or exposure to residual gas, the carbonaceous gas desorption mechanism from the surface is of high interest. In this study, we focused on the electron stimulated desorption (ESD) from the copper surface and its in-site surface characterization by x-ray photoelectron spectroscopy and Auger electron spectroscopy. For the surface cleaning and initializing, the copper samples were sputtered with Ar^+ ion beam and annealed. Exposure of ^{13}C isotope gas and ^{13}C ion implantation were done to the samples with the known quantities respectively. Afterwards, ESD rates from the samples were measured using throughput method with a calibrated residual gas analyzer quantitatively. By using the isotope, influences of ^{12}C in the residual gas and the bulk of copper can be eliminated during observation of desorbed gas from the sample under electron bombardment. The ESD of ^{13}C related gas species from the surface exposed to $^{13}CO_2$ were not observed. In the experiments of ^{13}C implanted samples, the ESD of ^{13}C related gas species with a low current density were not observed either at the room temperature. However the ESD rates of ^{13}C related gas species from the heated ^{13}C implanted sample around 65 degrees C were as high as the thermal desorption rates at around 250 degrees C. These results showed that the diffusion of implanted ^{13}C from the bulk was enhanced by heating and/or electron bombardment depending on the beam current density and might suggest that origin of the desorbed carbonaceous gas is not the top surface but the bulk possibly in a range of the electron penetration depth.

10:20am **VT-WeM7 Solubility and Diffusion of Hydrogen in Ordered Metals**, ***P. Repa***, *L. Peksa, T. Gronych, R. Ulman*, Charles University, Czech Republic

In the materials with ordered structure, such as the nanocrystalline and gradient materials, a relatively great part of the material is influenced by the interfaces between the crystals or between the components. As the interfaces differ from the bulk by the density and the topology of atoms, physical properties of the materials are influenced. As a result, the metals of that structure exhibit changes not only in ductility and other mechanical properties but also in the electric and magnetic properties as well when exposed to hydrogen. That's way knowledge of hydrogenation kinetics of the materials have become in the great interest recently. Since the measurement of the solubility and diffusion coefficient of hydrogen in the ordered metals is complicated due to mechanical properties of the measured samples, requirements on the experimental set up and measuring procedure is discussed. Results of the measurements are presented in which a sample was exposed to the hydrogen at elevated temperature in a filling chamber for a satisfactorily long time period to be saturated. Then the saturated sample was gradually heated up in a UHV system and the variations of the total pressure and partial pressures of several selected gases were registered. The total amount of gas dissolved in the sample, the values of solubility and diffusion constants could be estimated by an analysis of the obtained experimental data. A strong dependence of the solubility of hydrogen on the structure and composition of structured metals was discovered.

Biomaterials
Room: Exhibit Hall B2 - Session BI-WeP

Biointerfaces and Surfaces II

BI-WeP1 Bioactive Surfaces for Control of Stem Cell Differentiation, ***J. Kelly***, *D. Dahlborg, S. Svedhem, D. Sutherland,* Chalmers University of Technology, Sweden, *P. Eriksson,* Sahlgrenska University Hospital, Sweden, *J. Gold*, Chalmers University of Technology, Sweden

Tissue engineering of the peripheral and central nervous systems stands to make great progress if the regenerative potential of the recently isolated neural stem cells can be harnessed and directed by the use of synthetic materials and constructs. We have produced surfaces with bound stimulatory molecules (proteins and growth factors) to control neural progenitor cells from the hippocampus of adult rats (AHPs) which have the ability to regenerate the progenitor phenotype or differentiate down one of two possible lineages to become neuron- or glial-like cells. The stimulatory molecule of interest may be patterned on surfaces with high spatial resolution by microcontact printing with a stamp fabricated by casting polydimethyl siloxane on a master with a negative of the desired pattern. We have combined this initial biopatterning step with either adsorption of a second, co-active protein or with a supported lipid bilayer (SLB). SLBs are membrane-like thin films which form by fusion of lipid vesicles on SiO2 or glass surfaces. Unmodified SLBs are resistant to protein adsorption and cell adhesion thus offering the ability to pattern areas of adhesive and unadhesive character. Moreover by inclusion of modified lipids we functionalised a SLB with a neuroactive 19-mer IKVAV sequence derived from laminin, via a maleimide coupling. This surface promoted high levels of cell attachment and presented an otherwise non-perturbing background to cells and proteins. We have assessed the biological activity of several proteins for control of cell function and lineage, including laminin, ciliary neurotrophic factor (CNTF) and fibroblast growth factor (FGF-2) by adsorption or printing on glass surfaces. Laminin supported a mixed population of proliferative and differentiated cells. AHPs on CNTF differentiated to glial phenotype as shown by expression of glial fibrillary acidic protein while on FGF-2, cell proliferation was maintained without differentiation.

BI-WeP2 Oriented Immobilization of Anti-Human Chronic Gonadotropin for Biosensor Applications, ***L. Liu***, *S. Chen, S. Jiang*, University of Washington

The orientation of immobilized antibodies on solid surfaces, is important to performance of a biosensor. Our previous studies show that it is possible to control antibody orientation during physical adsorption via adjusting surface and solution properties. For biosensor applications, it is desirable to chemically immobilize antibody molecules on surfaces. Our previous studies further show that chemical linkers (e.g., NHS/EDC and GLU) used for chemical immobilization alter surface charges, thus antibody orientation. In this work, we present a new method, which combines the site-directed immobilization (via the conservative carbohydrate or histidine rich region located in the Fc portion of the IgG) and the charge-control methods, for the oriented immobilization of antibodies on self-assembled monolayers (SAMs)/Au(111). Monoclonal anti-hCG (human chronic gonadotropin) will be a model antibody studied in this work. Surface charge is adjusted by changing SAM terminal groups and solution pH values. Atomic force microscopy (AFM) is used to characterize adsorbed antibody molecules on surfaces. Low detection limit and saturated adsorbed amount in surface plasmon resonance (SPR) biosensors are determined in this work for various antibody immobilization methods. Results from this work show significant improvement over those based on conventional immobilization methods.

BI-WeP3 Protein Absorption in Engineered MEMS Test-beds, ***D. Henry***, *K. Lenghaus, U. Jalgaonkar, J. Dale, J.C. Henderson, J. Hickman*, Clemson University

We are studying the influence of surface modification, channel geometry, flow conditions, etc., on protein absorption. The information found from these experiments will help create new knowledge for developing biocompatible MEMS systems. To this end we have developed a test system that involves clamping two silicon wafers together that have half of a channel or device etched in them, which allows for separation and examination of the wafer surface after the enzyme flow experiments have been conducted. The enzyme absorption to the channels can thus be investigated by standard enzyme assays as well as surface analysis directly in the channel halves. The primary enzymes used in this study include alkaline phosphotase, glucose oxidase, and TAQ polymerase. We have engineered a working version of this system, however, during development of the clamping system a problem arose with fluid leaking over and out of the channels. We hypothesized this was because the surface of the silicon wafer is hydrophilic and the fluid was drawn between the wafers rather than just flowing through the channels. Our results will present the solution to this problem via hydrophobic surface modification on the interior face of the silicon wafers. We will also present results on the development of the system, our experiment to optimize it, its application to determine how the proteins bind in the channels, where they bind in the channels, and if there is a difference in binding between angled and straight channels.

BI-WeP4 Experimental and Modeling Results for Protein Interactions with MEMS Devices, ***F. Wang***, *J. Hickman, R.A. Latour,* Clemson University

Microelecromechanical systems (MEMS) for biomedical devices and applications generally are used to interact with simple and complex biological fluids. Undesirable biomolecular surface adsorption, which causes channel plugging, is a leading factor in the failure of such systems. We are attempting to characterize these interactions using a combination of experimental analysis and a computational fluid dynamics (CFD) model. The adsorption process includes transport of biomolecules onto the surface and the adsorptive reaction at the surface. We model the transport by Navier-Stokes equations, which accounts for the mass, momentum and energy conservation for the flow; and the adsorptive reaction is modeled by a modified Langmuir adsorption isotherm. These two parts are integrated by incorporating the surface adsorption kinetics into the transport equation as a boundary condition. A commercially available CFD code, CFD-ACE+, based on a finite volume method is employed as a starting point. BioOpter, a peripheral to this code, has been developed to extract kinetic parameters by minimizing the least-square difference between the simulation and experiment data. We will present preliminary optimization results for experiments in which a 60ng/mL Alkaline Phosphatase solution was passed through a polyethyletherketones(PEEK) modified capillary (65 microns diameter by 100 mm long) at flowrate of 0.1mL/hr which gave the adsorption/desorption parameters as: Ka=7.2 x 10^{5}/m-s and Kd=2.1^{-5}/s. An optimization error surface model was used to visualize the location of the optimal parameters.

BI-WeP5 Fabrication and Characterization of Regular Porous Polymer Films for Biomedical Devices, ***M. Tanaka***, *M. Takebayashi, K. Sato, M. Miyama, K. Nishikawa, J. Nishida, M. Shimomura*, Hokkaido University, Japan

Porous polymer matrices are widely used in biomedical applications such as tissue engineering and artificial organs. The present studies describe the fabrication and characterization of highly regular porous polymer films formed by simple casting technique. The micro porous films were fabricated from biodegradable polymer such as poly(ε-caprolactone), poly(lactic acid-co-glicolic acid), poly(3-hydroxybutylate) and poly(L-lactic acid). Various experimental factors affecting pore size and thickness of the film, solvent, cast volume and so on, were studied. The porous film shows a highly regular hexagonal arrangement of holes in a large area and can be easily peeled off from a glass substrate as a self-supported porous film. The pore size can be controlled in the range from 1 to 50µm by changing the evaporation time of the polymer solutions. The thickness of the film becomes thinner with decreasing the concentration. The pores were connected to each other in the porous film. The films with 1-5 g/L of concentration of the polymer had the penetrated structure. On the other hand, the un-penetrated structure was formed when the concentration of the polymer exceeded 5 g/L. The porous film with controlled pore size is used for cell separation and biomedical devices.

BI-WeP6 Patterned Construction of Three-dimensional Neuronal Networks Using Ink Jet Directed Layer-by-Layer Deposition, ***T. Xu***, *M. Das, J. Hickman, T. Boland*, Clemson University

The ability of building three-dimensional constructs for tissue engineering applications has many obvious advantages. In particular, the outgrowth and regeneration of neurons depend on a three dimensional matrix of growth factors. We present here the use of an inkjet-based system to generate three-dimensional patterns for directing neuron growth. Using a home built inkjet printing system, a mixture of collagen and poly-D-lysine was printed with a pre-designed pattern onto a glass surface that was pretreated with agarose. Primary rat E18 hippocampal neurons were cultured on the surface and allowed to attach to the pattern. After 24h incubation, a second layer of the mixture of collagen and poly-D-lysine was printed on the surface. The hippocampal neurons were again seeded on the surface and allowed to form a second layer. This was achieved by a fixing and locking mechanism built into the printer. Communication between the different layers of the hippocampal neurons was tested and results of electrophysiological tests will be presented. The layer-by-layer approach proved successful in 3D network design and may have many other applications in tissue engineering applications.

BI-WeP7 A Novel Surface Chemistry Platform for Biochips and Bioanalytical Devices, ***M.J. Lochhead***, *S. Metzger*, Accelr8 Technology Corporation

Biochips, biosensors, and other advanced bioanalytical devices require exquisite control of biomolecular interactions with surfaces. Specificity, signal to noise ratios and detection limits of these systems are often limited by surface non-specific binding, particularly in protein-based applications. Inhibition of non-specific binding is thus a critical performance feature in the design of improved synthetic materials that contact and operate in biological fluids. While non-specific binding to surfaces is most often undesired, specific biomolecule, particle or cell binding at surfaces often is desired. The goal is to bind only one type of molecule, particle, or cell, and to do so in a manner that preserves its recognition activity and native structure. We have developed a suite of functionalized surface coatings - OptiChem - that demonstrate both low non-specific binding and robust specific biomolecule attachment. OptiChem coatings can be applied to virtually all materials commonly used in bio-analytical devices including glass, silicon, and several plastics. The coatings are organic films that combine a low binding matrix with functional groups that provide for covalent attachment or affinity binding. Reduction of non-specific binding and control of reactive group density translates into increased signal to noise ratios, thus improving upon conventional surface chemistries resulting in faster assay turnaround and lower consumption of valuable or rare samples. The capacity for coating various substrates, ready scale-up of convenient fabrication and low preparation costs make the surface chemistry ideal for many microarray applications.

BI-WeP8 New Diazonium-Functionalized Support for Fabrication of Protein Microarrays, ***Y. Wu***, *G.P. Lopez*, University of New Mexico

Microarray technologies have rapidly become a major trend in high-throughput functional genomic study since its birth at the early 1990s. Recent advances of this technology have been focused on high-throughput proteomic analysis. The difficulty in immobilizing proteins onto solid surfaces without denaturation has led to the search for new general methods for coupling proteins to solid substrates. To this end, a chemical process for covalently linking proteins onto an ordinary microscope slide in a manner that preserves the ability of the immobilized proteins to interact with other proteins has been studied. The method uses p-aminophenyl trimethoxysilane (ATMS) /diazotization chemistry that was previously developed for formation of DNA microarrays. Preliminary results showed that protein microarrays fabricated on ATMS/diazotized surfaces produced enhanced levels of protein-protein interaction, low background fluorescence and high selectivity. Orientation of the immobilized proteins on the surfaces was also studied. In addition, the antigen-antibody reaction data has been analyzed quantitatively and successfully correlated with solution concentrations. In general, this method allows binding of protein onto a solid substrate that can lead to considerable improvements in antibody-antigen interaction, stability of affixed biomolecules, and preferable protein orientation.

BI-WeP9 Multi-Electrode Arrays Surface Modification by Aligned Microcontact Printing, ***W. Wang***, *M. Poeta, J. Hickman, T. Boland*, Clemson University

Multi-electrode arrays are widely used for neuron stimulating and recording. However, such stimulating and recording efforts are most efficient when neurons are placed precisely on the electrode sites. Microcontact printing is a versatile method allowing spatially resolved surface modification and has hence been used frequently to provoke cell attachment and spreading onto engineered patterns. Microcontact printing may have applications in forming artificially designed neuronal networks in vitro. In the present study, we use microcontact printing to modify the surface of a multi-electrode array with the aim of attracting neurons to only grow on the electrode areas of the arrays. We will present several methods to fabricate stamp replicas of the electrode arrays, and to align the stamps and the multi-electrode arrays surface. We achieve this by using micromanipulators to adjust the stamp and multi-electrode arrays and patterning under a microscope. As a result, the deviation between the patterned position and the electrodes are less than a few micrometers. The usefulness of this method of creating cell arrays will be presented.

BI-WeP10 Temperature-Responsive Polymer Coatings by Plasma Polymerization and Applications for Protein and Cell Patterning, ***X. Cheng***, *Y. Wang, Y. Hanein, K. Bohringer, B.D. Ratner*, University of Washington

The thermo-responsive polymer, poly (N-isopropylacrylamide) (pNIPAM), is of great interest for research and industrial applications in separation, controlled release, tissue engineering, sensor technology, etc. In this study, RF-plasma deposition is used to create temperature responsive ppNIPAM (plasma polymerized NIPAM) coatings. Films with a good retention of the monomer side-chain functionality are produced using low power continuous plasma deposition. Protein adsorption on the coating is studied at below and above the lower critical solution temperature (31°C) using both 125I-proteins and SPR. Dramatic increases of fibrinogen, IgG and BSA adsorption (8 fold, 8 fold and 10 fold respectively) are demonstrated at 37°C on ppNIPAM films compared to the adsorption at room temperature. Proteins adsorbed at 37°C do not detach two hours after switching the incubation temperature to 23°C, in contrast to the reported reversible cell detachment from pNIPAM upon temperature drop. Antibodies adsorbed on ppNIPAM at 37°C remain functionally active, as demonstrated by SPR studies. The coating has been deposited on micro-heater arrays. The individual micro-heaters control the phase transition of the ppNIPAM directly on top of it. Spatially controlled protein adsorption on the array has been visualized through a fluorescent marker. Based on preferential adhesion of cells to certain proteins, cells can be patterned on the protein arrays and used for tissue engineering applications.

BI-WeP11 Silicone Transfer during Microcontact Printing, ***K. Glasmästar***, *J. Gold, A.-S. Andersson, D. Sutherland, B. Kasemo*, Chalmers University of Technology, Sweden

Microcontact printing, muCP, is a widely used technique for fast and low-cost micropatterning of large surface areas. Within the field of biointerfaces it is routinely used to directly pattern SAM's and proteins or indirectly control cell adhesion and growth. During microcontact printing a stamp of an elastomer, typically PDMS, inked with molecules of interest, is brought into contact with the substrate and then removed, leaving a pattern of the "ink" on the surface of the substrate. Several reports have indicated that PDMS can be transferred to the substrate under particular conditions. However, this issue has earned surprisingly little attention so far. We have systematically studied the transfer of PDMS to the substrate during muCP. XPS, ToF-SIMS and water condensation patterns were used to identify and measure the transfer. Stamps were cast from Sylgard 184 silicone elastomer (Dow Corning). Stamps were used without further treatment or after UV/ozone treatment and no external force was applied during stamping. Significant amounts of PDMS were transferred from non-treated stamps during muCP under the model conditions used. The XPS results showed that the transfer of PDMS onto both Ti and Au was significantly lowered by UV/ozone treatment of the stamp. ToF-SIMS of Au samples stamped with flat stamps confirmed the XPS results. However, the use of a patterned stamp (5 µm lines, 15 µm space) transferred more silicone to Au than a flat stamp, and UV/ozone treatment appeared to be less effective in reducing PDMS transfer. In this work we show that the UV/ozone treatment of PDMS stamps before printing lowers the amount of silicone transferred to the substrate. Oxygen plasma treatment of the stamp is likely to have the same effect. It is important to consider the potential for transfer of PDMS onto substrates when using muCP to pattern SAM's or biological molecules for biointerface applications.

BI-WeP12 X-Ray PhotoEmission Electron Microscopy of Micro-contact Printed Protein and Polymer Coated Surfaces, ***C. Morin***, *A.P. Hitchcock*, McMaster University, Canada, *D.G. Castner, B. Wickes*, University of Washington, *A. Scholl, A. Doran*, Lawrence Berkeley National Laboratory

Synthetic biomaterials are widely used in medical applications. However, their interaction with the body is mediated through passive adsorption of a disorganized adsorbed protein monolayer. Mis-recognition of this adsorbed disorganized protein layer by surrounding cells may lead to the classic foreign body reaction and device encapsulation.[1] Next generation biomaterials, or 'engineered biomaterials', are being designed in which the surface contains specific bio-recognition moieties which control the biological response of the host. Microcontact printing (µCP) is one such method which can deposit biological signalling agents with spatial resolution and fidelity.[2] It uses an elastomeric template to transfer protein molecules to a surface of interest. µCP is combined with thiol-Au self assembly to form patterns on surfaces. We are exploring the use of X-Ray photoemission electron microscopy[3] to monitor methods for preparing patterned functionalized biomaterial surfaces, and to investigate the specificity of the interaction of model surfaces with key proteins. To test the reliability of the surface patterning method, we use highly specific bio-recognition pairs, such as the biotinylated ferritin-streptavidin couple, to probe the quality of the patterned surface. Such structures are then investigated with elemental (Fe 2p) and molecular (C1s and N1s) speciation using NEXAFS microscopy recorded at the ALS BL 7.3.1 X-PEEM. This work is supported by research and partnership grants from NSERC (Canada) and a Canada Research Chair (APH). NESAC/BIO (DGC) is supported by NIH grant RR-01296 from the National Center for Research Resources. ALS is supported by U.S. DoE under contract DE-FG02-89ER60858.

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BI-WeP13 X-ray PhotoEmission Electron Microscopy of Polymeric Thin Films, ***A.P. Hitchcock***, *C. Morin*, McMaster University, Canada, *S.G. Urquhart*, University of Saskatchewan, Canada

Patterned thin polymer films are of increasing importance in biomaterials, displays, electronic materials, etc. High spatial resolution, high chemical sensitivity analytical microscopy techniques are needed to optimize these systems. We are using X-ray Photoemission Electron Microscopy (X-PEEM) for chemical imaging of phase segregated polymer blends, patterned biomaterials for non-fouling and bio-passivatable applications, and interactions of test proteins with these surfaces. Optimization of X-PEEM has been optimized for insulating, radiation sensitive organic thin films. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are completely immiscible and thus PS/PMMA blends may be a suitable model for patterned biomaterial-protein interactions. Spun cast thin film blends of mono-disperse high (1 Mdalton) and low (100 Kdalton) PS and PMMA with bulk compositions from 66/33 w/w up to 10/90 w/w PS/PMMA have been studied by X-PEEM and atomic force microscopy (AFM).[1] C 1s X-PEEM shows that there is significant enrichment of PS at the surface relative to the bulk and that the PMMA-rich domains contain PS. AFM shows the latter is a consequence of incomplete phase segregation, which results in a bimodal distribution of PS domain sizes, with the PS signal in PMMA domains arising from very small PS domains at the surface. This contribution will report on alternative techniques to prepare fully surface segregated PS-PMMA blends, and the outcome of protein attachment studies to these surfaces. 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.

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BI-WeP14 NEXAFS Characterization of Poly (Amino Acids) at the Carbon, Nitrogen and Oxygen Edges, ***N.T. Samuel***, University of Washington, *D.A. Fischer*, National Institute of Standards and Technology, *D.G. Castner*, University of Washington

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy has established itself as a powerful tool to characterize small molecules at interfaces. Recent developments in instrumentation have made it possible to image polymers and other biological molecules at very high spatial resolution and chemical specificity. In addition, NEXAFS offers the possibility to probe orientation and order in biological molecules at interfaces. Poly(amino acids) represent an important system of model compounds, since amino acids are the building blocks of proteins and peptides. Previous NEXAFS studies were done at the carbon and oxygen edges of individual and di amino acids. However, nitrogen is present in the backbone and some side chains of amino acids. In the present study, sixteen poly-amino acids were spin-cast or deposited as thick films onto silicon substrates. The samples were characterized by x-ray photoelectron spectroscopy (XPS) to ensure that a uniform film was obtained and no contaminants were present. The carbon edge spectra of these samples agrees well with the earlier work on amino acids. The nitrogen edge spectra of the poly(amino acids) exhibits three characteristic peaks, one due to the amide π^* resonance and the other two due to C-N σ^* resonances. Also, a pre-edge feature was observed that was associated with x-ray beam induced sample degradation. Overall, these poly-amino acids captured the major resonances in peptide and protein NEXAFS spectra. The different information content of NEXAFS and XPS will also be highlighted. These results coupled with previous results from our group indicate that NEXAFS can be used extract information about the orientation and order of biological molecules at interfaces.

BI-WeP15 Nanoporous Aluminum Oxide as Support Material for Enzyme Biosensors, ***A. Heilmann***, *N. Teuscher*, Fraunhofer-Institute for Mechanics of Materials, Germany, *D. Janasek, U. Spohn*, Martin-Luther-University, Germany

Enzyme sensors are of growing interest as detection tool in various clinical and food analysis. Up to now, limited operational stability of enzyme is even yet the main hindrance to their wider application to solve analytical problems. In the paper, we describe a novel method to create biosensors with good long-time stability by using nanoporous alumina oxide with well-defined pore sturcture as host material for enzyme immobilisation. The nanoporous aluminum oxide was made by anodic oxidation od alumnium in polyprotic acids. Free-standig membranes were realized by lifting the membrane film from the metal substrate. In this free-standig membranes, different enzymes were immobilized. e.g. pyruvate oxidase (PyrOD) from lactobacillus plantarum was enclosed in poly(carbamoylsulphonate) hydrogel and sucked into the porous structure before polymerization. In the paper, calibration curves and long-time stability of varous enzyme sensors were disccused, also by consideration the nanostructure of the filled alumina pores studied by scanning electron microscopy.

BI-WeP16 Formation of Biotin-reactive Silane Surfaces on SiO_2 for Specific Immobilization of Biomolecules, ***H.H.J. Persson***, *L.A. Ruiz-Taylor, D.A. Quincy, S. Follonier, J.K.C. Huang, T.L. Martin, A. Acharya, G. Kilcher, K. Belghiti, H.B. Lu, R.L. Cicero, P. Kernen, P. Wagner*, Zyomyx, Inc.

To provide robust and versatile surfaces for protein biochip applications, we have synthesized triethoxy silanes with thiol-reactive groups and report here on the formation of thin films on silicon oxide surfaces. Several surface analytical techniques such as contact angle, XPS, and ellipsometer have been applied to characterize such silane layers. Emphasis was given to layer thickness, wettability, molecular organization, homogeneity and reactivity. Effects of substrate pre-treatment, silanization conditions as well as post-silanization procedures have been evaluated. We used thiol reactive silane layers as reactive intermediates to produce reactive surfaces presenting biotin by in-situ coupling of PEGylated thiol-biotin crosslinkers. Streptavidin has been shown to bind to the surface specifically. Surface coverages, homogeneity, and reactivity of the streptavidin layer were evaluated mainly by radiometry.

BI-WeP17 Alkylsiloxane Self-assembled Monolayers on Titanium, *R.A. Brizzolara*, ***R.M. Lennen***, Naval Surface Warfare Center

Preparations of self-assembled monolayers (SAMs) of alkyltrichlorosilanes on silicon wafers or glass are well documented in the literature. On the other hand, little work has been done regarding SAM formation on other hydroxylated metal surfaces and little is known about the nature of the SAM. We have investigated the adsorption of different chain lengths of alkyltrichlorosilanes with different terminal functional groups on hydroxylated titanium as a function of reaction conditions using x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurements. Angle-resolved XPS data was used for qualitative comparison of the vertical composition of the coatings, and the C1s/CKVV peak intensity ratio[1] enabled the calculation of comparative average layer thicknesses of the coatings. Reaction conditions included relative humidities of less than 1% and greater than 30%, with and without oven cure, and varying immersion times of the substrate in the adsorbate solution. 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.

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BI-WeP18 A Novel Approach for the Detection of Antibiotics using Mixed SAMs of Thiols on Gold, ***K. Bonroy***, *F. Frederix*, IMEC, Belgium, *P. Cliquet*, University of Ghent, Belgium, *W. Laureyn, A. Campitelli, G. Borghs*, IMEC, Belgium, *E. Cox*, University of Ghent, Belgium, *P. Declerck*, KULeuven, Belgium

In numerous applications in the clinical, environmental and toxicological field, there is an increasing need for the detection of low concentrations of different biochemical parameters with low molecular weight. For example, the detection of antibiotic residues in milk is important because of the potential toxic and allergic effect for humans. Immunosensors have a huge potential as a fast and reliable system for the detection of such low molecular weight analytes. Our research is not only focussing on the transducer part of a biosensor, but also on the biological recognition layer. This biological recognition layer mainly determines the specificity, stability, reproducibility and durability of the biosensor. For the detection of small molecules, different assay principles are possible. In the current study an indirect competitive assay was used. Therefore antibiotics were immobilised on the sensor surface and the optimal concentration of a monoclonal antibody (directed against b-lactam antibiotics), allowing quantification of antibiotics, was established.[1] For this competitive method, a reproducible and tuneable immobilisation of the antibiotics on the sensor-surface is indispensable. In order to realise such an immunosensor we coupled the antibiotics covalently to mixed Self-Assembled Monolayers (SAMs) of thiols deposited on gold. These mixed SAMs consist of two different thiols: one to bind the antibiotics and another thiol component to avoid non-specific adsorption 2. The binding of the antibiotics on mixed SAMs was characterised with cyclic voltammetry and GA-FTIR and the competitive immunoassay was evaluated using Surface Plasmon Resonance. In conclusion, we have developed a competitive immunoassay for the detection of antibiotics using a biosensor interface based on mixed SAMs of thiols.

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BI-WeP19 Poly(ethylene oxide)-Terminated Monolayer Formed at Solid/Vapor Interface, ***A. Hozumi***, *Y. Yokogawa, T. Kameyama*, National Institute of Advanced Industrial Science and Technology, Japan

Poly(ethylene oxide) (PEO) has been widely applied to the fabrication of protein or cell repellent surfaces in biotechnical and biomedical applications. Although extensive research on PEO-coating techniques has been reported in the literature, there have been few reports on preparing PEO-terminated monolayers from the vapor phase. Here, we report on the formation of a PEO-terminated monolayer on SiO_2/Si sample substrates through a chemical vapor deposition (CVD) method. Si substrates covered with native oxide (SiO_2/Si) were first cleaned by UV/ozone treatment. The cleaned samples were then exposed to vapor of organosilane, that is, 2-[methoxy (polyethyleneoxy) propyl] trimethoxysilane (MPEOPS) for 1~7 hours at 150 °C. We have investigated in detail chemical and electokinetic properties of this PEO-terminated monolayer. The SiO_2/Si surface after CVD became relatively hydrophobic showing a water-contact angle of ca. 67±2. Thickness of the MPEOPS-monolayer was ca. 0.8±0.1 nm as estimated by ellipsomrtry. As confirmed by AFM, the surface was very smooth and homogeneous with almost identical to that of the SiO_2/Si substrate. Zeta-potentials of the MPEOPS-monolayer covered SiO_2/Si substrates were measured as a function of pH by means of an electrophoretic light scattering spectrophotometer. Isoelectric point of the MPEOPS-monolayer covered surface was observed at around pH 5 which was higher than that of SiO_2/Si (~pH 2.0). These results are attributable to a reduction in the density of surface silanol (Si-OH) groups on the SiO_2/Si substrate. Si-OH groups were consumed due to the formation of siloxane bondings with the MPEOPS. Furthermore, we demonstrated micropatterning of this MPEOPS-monolayer based on the photolithography using an excimer lamp radiating vacuum ultra violet light of 172 nm in wavelength.

BI-WeP21 Study of Bone Repairing Employing a Ricinus Camunis-based Biopolymer Additioned with Ascorbic Acid and Epidermal Growth Factor in a Rat Tibia Model[1], *C. Mendoza-Barrera*, UPIITA-IPN and Cinvestav-IPN, Mexico, ***M. Melendez-Lira***, *V. Altuzar, S.A. Tomas*, Cinvestav-IPN, Mexico

There is a huge demand of graft material to accelerate the bone healing process of lesions experienced after surgical interventions related with bony tumors or traumatic experiences. Autografts, allografts and biomaterials are sources of graft materials but it would be highly desirable to have materials without the limitations of the first two aforementioned. We discuss the effect of a Ricinus Camunis-based biopolymer mixed with Ascorbic Acid (AA)and/or Epidermal Growth Factor (EGF) on the bone repairing employing a rat tibia model. The bone healing process was monitored through the interface bone-graft material. No implant rejection or inflammatory reaction was observed during a 8 weeks period in our in vivo studies. The evolution of the osteogenesis in the lesion area was followed employing scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), Photoacoustic Spectroscopy (PAS) and X-ray diffraction (XRD). Our study clearly indicates that the combined use of the Ricinus Camunis-based biopolymer, AA and EGF improves the remodeling characteristics of the biomaterial. XRD allow us to identify the structural characteristics of the biopolymer and its evolution during the bone healing process. Bone resorption was monitored by EDX studying the Ca/P ratio as function of time. PAS presents features that could be correlated with cellular activity during the bone mineralization process. All the results showed a good correlation and allowed us to obtain information to improve the composition of the biomaterial.

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[1] This work was partially supported by CONACYT-Mexico.

Dielectrics
Room: Exhibit Hall B2 - Session DI+EL-WeP

Poster Session

DI+EL-WeP2 Remote Plasma-assisted Cleaning, Oxidation and Oxidation/Nitridation of GaN for Low Defect Density GaN-SiO_2 Interfaces, ***C. Bae***, *G.B. Rayner, G. Lucovsky*, North Carolina State University

In previous studies, device quality Si-SiO_2 interfaces and dielectric bulk films (SiO_2) were prepared using a two-step process; i) remote plasma-assisted oxidation (RPAO) to form a superficially interfacial oxide (~0.6 nm) and ii) remote plasma enhanced chemical vapor deposition (RPECVD) to deposit the oxide film. The same approach has been applied to GaN-SiO_2 system. After a 300 °C remote N_2/He plasma treatment of the GaN surface, residual C and Cl were reduced below Auger electron spectroscopy (AES) detection, and the AES peak ratio of O KLL and N KLL was ~0.06 or ~0.1 monolayer of oxygen. RPAO of GaN surfaces using O_2, N_2O, and N_2O in N_2 source gases was investigated by AES and x-ray photoelectron spectroscopy (XPS) to determine the oxidation kinetics, chemical composition of the interfacial oxide and oxidation state of interfacial Ga. Without an RPAO step, subcutaneous oxidation of GaN takes place RPECVD deposition of SiO_2, and on-line AES indicate a ~0.6-0.8 nm subcutaneous oxide. Compared to single step SiO_2 deposition, significantly reduced defect state densities are obtained at the GaN-SiO_2 interface by independent control of GaN-GaO_x interface formation by RPAO and SiO_2 deposition by RPECVD.

DI+EL-WeP3 Screen Printing of PMN-PT Thick Films on the Pt-coated Silicon Wafers, ***B.M. Park***, *Y.-S. Seo, G.S. Lee*, University of Texas at Dallas

$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) is one of the widely studied relax ferroelectrics with excellent piezoelectric and electrostrictive properties. Single crystals, ceramics, and thin films of PMN-PT have been investigated for various applications such as actuators, transducers, and etc. However, there have not been enough studies for thick film fabrication of PMN-PT and its applications. For a promising application of the mechanical actuating of PMN-PT in the silicon-based integrated processing, an easy and low-cost technique for the thick film fabrication should be developed. The screen printing is one of the well known techniques to make thick films easily. Thus, in this study, we investigated a screen printing of PMN-PT thick films for electronic applications. The two kinds of pastes with different ratios between 0.9PMN-0.1PT ceramic powders and vehicle such as 6:4 and 7:3 were used. Thick films were printed through 200 mesh or 325 mesh screens on the platinum coated silicon wafers. The printed films were burn out at 600°C then heat treated at various conditions for the sintering of ceramic powders. The films were characterized by using optical and scanning electron microscopes and X-ray diffraction. As the results, the uniform thick films of PMN-PT could be made and the thickness of a singly printed film was about 10µm after heat treatment. When the printed films were heat treated at higher temperatures and for longer times, it caused to form the pyrochlore phase. The pure perovskite PMN-PT film could be obtained when it was heat treated at 800°C for 1hour or less. To prevent the pyrochlore phase from being formed, the additions of small excess amount of PbO and MgO were studied also. The addition of excess PbO or MgO can be expected to retard the pyrochlore formation. Some electrical properties of these screen printed films will be discussed also here.

DI+EL-WeP4 Influence of Impurities on Attenuation of Acoustic Waves in $LiNbO_3$ Crystals, *F.R. Akhmedzhanov*, ***M.M. Akhmedjanova***, Samarkand State University, Uzbekistan

In present work the attenuation of longitudinal and transverse acoustic waves in pure LiNbO3 and Mg, Zn, Cu and Cr doped LiNbO3 crystals have been investigated in detail. The weight concentration of above-mentioned impurities in investigated samples was consisted 0.01-0.02 percents. The measurements of attenuation coefficient carried out by Bragg light scattering method at the temperatures 295 K and 480 K. Piezoelectric transducers of Lithium Niobate of appropriate cuts are used in order to excite the longitudinal and the transverse acoustic waves with the frequencies of 0.3-1.8 GHz. The values of attenuation coefficients were determined from the measurements of the dependence of the scattered light intensity from the distance to the piezotransducer along the direction of the acoustic wave propagation. The obtained values of the scattered light intensities have been used to calculate the quantity and frequency dependence of the attenuation coefficient of the acoustic wave. The velocities of all the investigated waves were with sufficient accuracy determined from the experimental data simultaneously. The results of measurements have shown that in crystals with impurities are observed the changes in the attenuation of acoustic waves. Also have shown that the impurity of Cr causes increase of the attenuation of longitudinal waves on 20-50% but at the same time decreases the attenuation of transverse waves almost in two times. At the same time impurities of Cu, Zn, Mg reduce the decrease of attenuation the longitudinal waves in 1,5-2 times and insignificantly increase of the attenuation of the transverse waves. The obtained results are interpreted in framework of various mechanisms of attenuation including the electron-phonon, Akhiezer and Landau-Khalatnikov mechanisms. The influence of dielectric losses on the attenuation of piezoactive acoustic waves in LiNbO3 crystals is also discussed.

DI+EL-WeP5 Study of Molecularly Templated Nanoporous Silica Dielectrics with an a-SiC:H Etch Stop Layer Deposited by High Density Plasma Chemical Vapor Deposition, *F.M. Pan*, ***B.W. Wu***, *A.T. Cho, T.G. Tsai, K.C. Tsai,* National Nano Device Laboratories, Taiwan, R.O.C., *C.M. Yang, K.J. Chao*, National Tsinghau University, Taiwan, R.O.C.

α-SiC:H thin films were deposited on nanoporous silica thin films as the etch stop layer by high-density plasma chemical vapor deposition (HDP-CVD) using trimethylsilane (3MS) as the precursor. The α-SiC:H thin film can effectively improve hydrophobicity of the nanoporous film during HDP-CVD deposition, and, therefore, improve the dielectric property of the nanoporous dielectric layer. Electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) depth profiles reveal that the methyl groups uniformly distribute in the nanoporous film after the α-SiC:H film deposition. After the α-SiC:H film deposition and hydrogen plasma treatment, the effective dielectric constant of the α-SiC:H/silica film can be as low as 1.65, and slowly rises to 1.98 after a 25 day storage in the cleanroom ambient. This study shows that hydrophobicity modification of the nanoporous silica film and the etch stop layer deposition can be completed at the same time during the α-SiC:H depostion. Moreover, calcination of the surfactant templated nanoporous film can be accomplished in the same HDP-CVD before the etch stop layer deposition. This obviously simplifies the integration steps of nanoporous silica materials in the dual-damascene interconnect technology.

DI+EL-WeP6 Degradation and Modification of Gate Dielectric in MOS Structures by High-field Multilevel Current Stress, ***G.G. Bondarenko***, Moscow Institute of Electronics and Mathematics, Russia, *V.V. Andreev, A.A. Stolyarov, V.E. Drach*, Bauman Moscow State Technical University, Russia

A new technique for the modification and the degradation analysis of gate dielectric in the MOS structures by means of high-field tunnel electron injection is proposed. It was found out that the injection treatment of the MOS structures by multilevel current stress allows to increase the charge-to-breakdown. The technique is proposed to be used for investigation of the gate dielectric degradation in the MOS structures during and after high-field stress. The proposed technique differs from an ordinary constant current stress technique in the additional measuring level of current, thus providing the possible to estimate the dielectric charge change. The additional measuring level of injection current allows to decrease significantly the error of positive charge density measurement in the dielectric. Disregarding of positive charge trapping during the initial part of injection of electrons into dielectric while stress mode is being established causes the error above. The technique allows right after high-field injection without sample re-switching to investigate both the generation and the relaxation of positive charge, created by injected electrons into MOS structure gate dielectric in wide range of electric fields. Using the technique proposed, the injection degradation of the MOS structures with thermal SiO_2 film was studied. Furthermore, the possibility of modifying the film above to increase the injection reliability was shown.

DI+EL-WeP7 Improvement of (Ba,Sr)TiO_3 Dielectric Properties by in-situ Formation of IrO_2 on Ir Electrodes, ***C.H. Lai***, *Y.C. Wu, W.C. Chen,* National Tsing Hua University, Taiwan, *S. Ma*, Applied Materials

The (Ba,Sr)TiO_3 (BST) thin films grown on Ir bottom electrodes have showed high dielectric constants and low leakage current density, which are generally attributed to the formation of IrO_2 at the BST/Ir interface. The IrO_2 can decrease the accumulation of the oxygen vacancies, and typically was formed during the post-annealing process. In this work, we use high working pressure (47 mtorr) during rf sputtering deposition to enhance the in-situ formation of IrO_2 without post-annealing. We verified that oxygen plasma bombardment on the Ir surface during the deposition of BST films was the dominant mechanism for IrO_2 formation under the condition of high working pressure. The as-deposited BST films of 100 nm grown at 500 C show a dielectric constant as large as 550 (at 10 kHz); however, the leakage current is relatively large (10^{-4} A/cm^2 at 200 kV/cm). The large leakage current resulted from rough interface due to formation of thick IrO_2. To reduce leakage current, the double-layer technology was used, in which a thin BST film (5 nm) was deposited with pure Ar, and followed by deposition of a thick film (95 nm) with mixture gas (Ar/O_2). The thin BST layer can significantly reduce the roughness of IrO_2, resulting in lower leakage current (10^{-6} A/cm^2); however, since this thin BST layer is oxygen-deficient, the dielectric constant is slightly reduced. When the total BST thickness decreased, the reduction of dielectric constant becomes significant in the double-layer structure. For 30 nm BST films, we applied a dc substrate bias (-100V) during BST deposition to manipulate the film structure. The substrate bias significantly increases the film density and grain size, and at the same time reduces the roughness. Consequently, a large dielectric constant (220 at 10KHz) and a quite low leakage current (10^{-9} A/cm^2) were obtained in 30 nm BST films.

DI+EL-WeP9 Medium to High Vacuum Metal Organic Chemical Vapor Deposition of Al_2O_3, ***Z. Song***, *R.D. Geil, V. Parwar, D.W. Crunkleton, C.A. Hales, B.R. Rogers*, Vanderbilt University

Al_2O_3 is one of the most promising medium-k gate dielectric materials to replace SiO_2 in future high performance integrated circuits. Because of good interfacial properties of the Al_2O_3/Si system, the 2001 update of the ITRS indicates the possibility of using Al_2O_3 as an interfacial layer between silicon and high-k dielectrics that tend to form interfacial SiO_2 or silicate layers. This presentation reports results of our work on the deposition of Al_2O_3 onto cleaned silicon substrates. We have performed two types of deposition experiments. First, Al_2O_3 films were deposited on p-type Si(100) substrates by metal organic chemical vapor deposition from aluminum tri-s-butoxide. We used a temperature range of 300 - 450 °C and a pressure range in the medium to high vacuum regimes. Second, silicon surfaces were briefly exposed to the precursor gas at low temperatures in our one-of-a kind UHV-CVD system. The gas was then pumped out and the silicon substrate was heated to a preset temperature. The gases released during temperature ramping were analyzed by in-situ quadruple mass spectroscopy (QMS). The properties of the films were characterized by Spectroscopic Ellipsometry (SE), Time of Flight Medium Energy Back Scattering (ToF-MEBS), RBS, XPS, XRD and ATR FT-IR.

DI+EL-WeP10 N Composition and Chemical State Profiling in Thermally and Plasma Nitridated Silicon Oxide Films, ***Y.S. Chung***, Samsung Advanced Institute of Technology, Korea, *H.S. Chang, D.W. Moon*, Korea Institute of Standards and Science

The composition and chemical state of N in thermally and plasma nitridated silicon oxide films were depth profiled by X-ray Photoelectron Spectroscop (XPS) using a chemical etching method with HF. The nitrogen profile of thermally nitridated film differs from plasma nitridated one. Nitrogen is rich at surface in plasma nitridated oxide films, while N is rich at interface in thermally nitridated film. The N depth profiles from XPS were compared with those from medium energy ion scattering spectroscopy in a good agreement. The N 1s core level of plasma nitridated oxide shows a main species with N?Si3 bonding and small amounts of defect nitrogens due to plasma treatment. The change of chemical composition with annealing to cure these defect also will be discussed.

DI+EL-WeP11 Study on Damage Recovery of Etched ($Ba_{0.6}$,$Sr_{0.4}$)TiO_3 Thin Films in Ar/CF_4 Plasma, ***P.S. Kang***, *D.P. Kim, K.T. Kim, C.I. Kim,* Chung-Ang University, Korea, *T.H. Kim,* YIT, Korea, *S.J. Lee*, ETRI, Korea

In this study, ($Ba_{0.6}$,$Sr_{0.4}$)TiO_3 (BST) thin films on Pt/Ti/SiO_2/Si substrates were deposited by a sol-gel method and the inductively coupled plasma (ICP) etching behavior of BST thin films had been investigated by a function of Ar/CF_4 gas mixing ratio. We also investigated the influence of etching damage in BST films during the ICP process. For analysis of the Ar/CF_4 plasma-induced damage in the Pt/BST/Pt capacitor, measurements of leakage current density and dielectric constant was carried out at different substrate bias voltage, ICP power and gas mixing ratio. The physical damage and structure of etched BST thin films were investigated by atomic force microscopy (AFM) and x-ray diffraction (XRD). The existence of contamination on the surface of the etched BST was measured using an x-ray photoelectron spectroscopy (XPS) analysis. Fluorine atoms definitely disappeared after O_2 annealing at 700°C. From the electrical property and structure analysis, the reduction and recover of etching damage by re-annealing was effective in the additive O_2 into Ar/CF_4 rather than additive O_2 into Ar/Cl_2 plasma.

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DI+EL-WeP12 Etching Characteristics of (Pb,Sr)TiO$_3$ Thin Films Using Cl$_2$/Ar Inductively Coupled Plasma, ***G.H. Kim***, *D.P. Kim, K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

Recently, ferroelectric thin films have received great attention for the application to high density memory devices. Among the various ferroelectric films, the BST thin film was noticed as the most promising material due to its high dielectric constant and paraelectricity at normal operating temperature. Although BST possesses a satisfactorily high dielectric constant, it was known that a post heat treatment at a high temperature was essential to obtain good electrical property. The heat treatment at high temperature can cause deleterious effects on an electrode, barrier metal, and contact plug. Strontium titanate (SrTiO$_3$) is one of the few titanates which is cubic at room temperature. But, the dielectric constant is lower than BST. The addition of lead into strontium titanate makes its dielectric constant(ε_r=1377) higher and the temperature of crystallization lower. Therefore, PST thin film can be a promising material due to its high dielectric constant and paraelectricity at normal operating temperature. However, there is no report on the characteristics and mechanism of PST thin films during etching process. In this study, Inductively coupled plasma etching system was used for etching PST because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of PST thin films were investigated in terms of etch rates and selectivity as a function of gas mixing ratio, rf power, dc bias voltage and chamber pressure. The Cl$_2$/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 and secondary ion mass spectrometry. Scanning electron microscopy was used to investigate the etching profile.

Acknowledgement:This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

DI+EL-WeP13 Etching Characteristics of Bi$_{4-x}$Eu$_x$Ti$_3$O$_{12}$ Thin Films Using Inductively Coupled Plasma, *K.T. Lim, D.P. Kim, K.T. Kim,* ***C.I. Kim***, Chung-Ang University, Korea

In recent years, some Bi-layered perovskite oxide such as SrBi$_2$Ta$_2$O$_9$ (SBT) and Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (BLT) have been intensively studied for use in FRAMs because of its low leakage current, low coercive field, and fatigue-free with simple Pt electrode. The fatigue-free behavior of SBT and BLT thin film was due to the charge compensating effect of Bi$_2$O$_2$ layers resulting in the reduction of space charge and from domain wall unpinning that happens at least as rapidly as domain pinning. However, SBT and BLT thin films have a disadvantage of low remanent polarization for the high-density integration of FRAMs. From the viewpoint of the general formula of Aurivillius compounds, radii of Europium ion (0.95 Å), similar to Bi ion (0.93 Å) in the Bi$_4$Ti$_3$O$_{12}$(BIT), occupies the A site in the perovskite unit BIT. The europium-substituted BIT(BET) thin films resulted in a large 2Pr, whose value (60.99µmC/cm^2) is much larger than that of Sm-modified BIT thin film (2Pr = BSmT: 49µmC/cm^2) and BLT thin film (2Pr = 27µmC/cm^2) at an applied voltage of 10V. For this advantage, BET thin films have emerged as new ferroelectric materials. However, there is no report on etching BET thin films. Inductively coupled plasma source was used for etching BET because of its high plasma density, low process pressure and easy control bias power. BET thin films were etched with using CF$_4$/Ar plasma. The experiments were carried out with measuring etch rates and selectivities as a function of gas mixing ratio, rf power, dc bias voltage. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate the surface morphology of BET thin films exposed in plasma and etching profile.

DI+EL-WeP14 Etching Characteristics of YMnO$_3$ Thin Films in Cl Based Inductively Coupled Plasma, ***J.H. Park***, *D.P. Kim, K.T. Kim, C.I. Kim, E.G. Chang*, Chung-Ang University, Korea

YMnO$_3$ thin films are excellent dielectric materials for high integrated FRAM because YMnO$_3$ have a relatively low permittivity (ε_r=20) and do not include volatile materials such as Pb and Bi which easy diffuse into the Si substrate and lead to point defects. To apply the YMnO$_3$ thin films on the highly integrated FRAMs, high-density plasma systems should utilized because it provides high degree of anisotropy and good selectivity. In this study, we etched YMnO$_3$ thin films in Cl based inductively coupled plasma (ICP). Etching characteristics of YMnO$_3$ thin films were investigated in terms of etch rate and selectivity as a function of gas mixing ratio, RF power, and substrate temperature. The diagnostics of the plasma were estimated using optical emission spectroscopy (OES). To investigate etching mechanisms of YMnO$_3$ thin film, chemical reactions on the etched surface of YMnO$_3$ thin films were investigated by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). Etching profile was investigated by scanning electron microscopy (SEM).

DI+EL-WeP15 The Effect of Cr Doping on the Microstructural and Dielectric Properties of (Ba$_{1-x}$,Sr$_x$)TiO$_3$ Thin Films for Tunable Microwave Device Applications, ***C.I. Lee***, Ansan College of Technology, Korea, *K.T. Kim, C.I. Kim, D.H. Kang*, Chung-Ang University, Korea

(Ba$_{1-x}$, Sr$_x$)TiO$_3$ (BST) thin film is a very attractive material for the tunable microwave device applications such as electronically tunable mixers, delay lines, filters and phase shifters. We have investigated the structural, compositional and dielectric properties of BST thin film as a function of Cr dopant concentration from 0 to 15 mol% and analyzed using X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The dielectric constant of the 300 nm Cr-doped BST thin film decreased as the Cr concentration increased. The loss tangent of 15% Cr doped BST thin film was higher than that of the pure film, but the 1~10 mol% Cr doped thin film was lower than that of the undoped BST thin film.

Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

DI+EL-WeP16 Cyclic-CVD of Strontium Tantalate for Alterantive Gate Dielectric Applications, *H.S. Choi,* ***Y.M. Jang***, *M.J. Kang, I.H. Choi*, Korea University

As gate oxide thickness in SiO$_2$-based MOS device decreases, new high-k dielectric materials are demanded to substitute for silicon dioxide. In this presentation, we will discuss our work on developing strontium tantalate for use as alternative gate dielectrics. We have grown strontium tantalate thin films on p-type Si substrate by cyclic chemical vapor deposition technique using Sr[Ta(OC$_2$H$_5$)$_5$(OC$_2$H$_4$OCH$_3$)]$_2$ as precursor. Our studies have included substrate temperatures between 250 and 400°C and post annealing temperatures 600 and 800°C. We have studied the surface and interface image, the structural properties and film compositions by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Rutherford Backscattering Spectrometry (RBS). Also we have investigated the applicability to MOS device through the capacitance voltage (C-V) measurement and leakage current measurement.

DI+EL-WeP17 Surface Preparation of Si (100) Substrates Prior to Deposition of High K Dielectrics, ***V. Pawar***, *Z. Song, D.W. Crunkleton, B.R. Rogers*, Vanderbilt University

We have investigated different fluoride based reagents for etching of native oxide on silicon surfaces prior to chemical vapor deposition of high K dielectrics. We have also investigated different cleaning agents (water and organic based) to see the effect on the native oxide growth and surface cleanliness. The native oxide growth was monitored by spectroscopic ellipsometry and x ray photoelectron spectroscopy. We have shown that time logarithmic model can be used to model the data and useful information about the characteristic time (incubation time) can be obtained for different treatments.

DI+EL-WeP18 Comparison of Reactive Sputtered Oxide Films from Zr and Hf Metal Targets with Poly-Si or Poly-SiGe Gate, ***J.-H. Yoo***, Yonsei University, Korea, *S.-W. Nam*, Samsung Electronics Co., Ltd., Korea, *S. Nam, D.-H. Ko*, Yonsei University, Korea

As CMOS devices are being continuously scaled down, gate oxides with EOT < 15Ã… will be required. Key process issues in conventional SiO$_2$ scaling are with boron penetration, gate leakage for very thin gate oxides and depletion effects in the polysilicon electrodes. Therefore, dielectric materials with higher dielectric constant than SiO$_2$, possibly large band-gap, low interface state density, and good thermal stability have drawn a lot of attention as alternative gate dielectric materials. Recently, ZrO$_2$, HfO$_2$ and their silicates have been considered as promising alternative materials due to their high dielectric constant and good thermal stability with Si substrates. We investigated the microstructures and electrical properties of reactive sputtered ZrO$_2$ films and HfO$_2$ films on Si (100) substrate. And the thermal stabilities and compatibilities between the films with poly-Si gate electrode were compared. The films as a gate dielectric were deposited by reactive dc magnetron sputtering, followed by thermal annealing in N$_2$ gas ambient using furnace and subsequently the microstructures of the films were investigated by Ellipsometry, XRD, AFM, TEM and XPS. The interfaces with poly-Si or Si substrate were carefully observed by HR-TEM, XPS/AES and SIMS with annealing temperature. Also, the properties of the films with poly-SiGe as alternative gate electrode were investigated. The electrical properties were assessed and compared by C-V and I-V measurements of Metal-Oxide-Semiconductor capacitor structure.

DI+EL-WeP19 Mechanical and Optical Properties of Low Dielectric Constant Silicon Containing Fluorocarbon Films by Plasma Enhanced Chemical Vapor Deposition, ***Y.Y. Jin***, Louisiana State University, *G.S. Lee*, The University of Texas at Dallas

Silicon containing fluorocarbon (SiCF) film for use as low-k interlayer dielectrics (ILD) has been investigated on mechanical and optical properties. The preparation of SiCF films is carried out by plasma enhanced chemical vapor deposition (PECVD) using precursors 5% disilan in helium (5%Si_2H_6/He) and tetrabluorocarbon (CF_4). Hardness and residual stress in the films subsequently measured using an atomic force microscopy (AFM) and the curvature method via Stoney's equation, respectively. The SiCF film samples were deposited on quartz plates to investigate the characteristics of optical transmission and optical energy gap. The optical transmission data were obtained in the wavelength range of 200 nm to 800 nm by the NIR-UV-VIS spectrophotometer at room temperature. The optical energy gaps of the films are calculated from a plot of Tauc extrapolations.

DI+EL-WeP20 Effect of Low Pressure Annealing for Low Temperature Crystallization of $SrBi_2Ta_2O_9$ Ferroelectric Thin Films, *H.S. Choi*, ***K. Lee***, *G.S. Lim*, Korea University, *Y.T. Kim, S.I. Kim*, Korea Institute of Science and Technology, *I.H. Choi*, Korea University

A new low pressure annealing method for low temperature crystallization of $SrBi_2Ta_2O_9$ thin films is proposed. SBT films were prepared on IrO_2 bottom electrode by metalorganic decomposition (MOD) method and annealed under low oxygen pressure by a modified rapid thermal annealing process. Under an oxygen pressure as high as 30 torr, the crystallization temperature inducing the ferroelectric SBT phase can be lowered to 650°C. Those films processed at 650°C showed satisfactory ferroelectric properties, that is, the remanent polarization (P_r) and the coercive electric field (E_c) were 5.68 µmC/cm^2 and 61 kV/cm at an applied voltage of 5 V, respectively. The films also showed fatigue-free characteristics: no fatigue was observed up to about 10^{10} switching cycles.

Electronic Materials and Devices
Room: Exhibit Hall B2 - Session EL+SC-WeP

Poster Session

EL+SC-WeP1 Mechanistic Aspects of SiC Oxidation, *C. Radtke*, ***F.C. Stedile***, *I.J.R. Baumvol*, UFRGS, Brazil, *I.C. Vickridge, I. Trimaille, J.-J. Ganem, S. Rigo*, Universite de Paris 6 et 7, France

SiC is the material of choice in the field of high band-gap semiconductors used in high-power, high-frequency, high-voltage, and/or high temperature applications. The possibility of obtaining an oxide film with good electrical characteristics (SiO_2) by thermal oxidation is one of its major advantages. In order to develop an oxidation model, the knowledge of the oxidation mechanism is of great importance. We investigated the incorporation of oxygen in surface and interface regions during different stages of the oxidation process of the Gface of 6H-SiC(0001) wafers as well as its dependence with the gas pressure. Oxidations in natural ultra dry O_2 followed by oxidations using isotopically enriched oxygen ($^{18}O_2$) were performed. Different times of oxidation in the natural gas and chemical etching of grown oxides were used to obtain samples representing different starting conditions. Amounts of incorporated ^{18}O and depth profiles were determined using nuclear reactions in plateau and resonance regions of their cross-section curves, respectively. The results evidence that in the whole range of oxidation times studied, the oxidation process was limited by the reaction rate of diffusing oxygen with SiC. These results present a new dynamical mechanism with remarkable differences from the oxidation of Si.

EL+SC-WeP2 Comparison of the Decomposition of Metacarborane and Orthocarborane, ***A.N. Caruso***, *P.A. Dowben*, University of Nebraska, Lincoln

It is now recognized that there are several different polytypes of B_5C (boron carbide) for which the electronic structure has remained obscure. We present a novel B_5C polytype that is radically different from previous polytypes in that it forms an n-type semiconductor. Decomposition of closo-1,7 dicarbadodecaborane (metacarborane) and closo-1,2 dicarbadodecaborane (orthocarborane) due to adsorption of photons (32eV soft x-rays) has been observed. We compare adsorption and decomposition for these molecules and attempt to address why molecules with the same basic structure create materials that are wildly different in their electronic (semiconducting) properties.

EL+SC-WeP3 Non Destructive Evaluation of Alternative Substrate Quality Using Glancing Incidence X-Ray Diffraction and Raman Spectroscopy, ***H.J. Haugan***, *A.M. Cain, T.W. Haas, K.G. Eyink*, Air Force Research Laboratory, *C.J. Eiting*, Uniroyal Optoelectronics, *D.H. Tomich, L. Grazulis, J.D. Busbee*, Air Force Research Laboratory

Alternate substrate technology holds promise for the growth of high quality lattice mismatched epitaxial films. Unfortunately, the technology has been plagued by difficulties in reproducibility of results. Some of this problem resides in a lack of characterization of the thin, twist bonded layer used as the template for subsequent epitaxial growth. In this work, grazing incidence diffraction (GID) and micro-Raman spectroscopy were used to characterize the alternative substrate prior to growth. The 14 nm and 50 nm thin GaAs layers were bonded to (100) GaAs substrates and subsequently exposed by standard thinning and etching techniques. The crystalline quality of the thin bonded substrates was studied by GID. The full widths at half maximum (FWHM) of the 004 peaks were used to monitor optimum bonding condition. The measured FWHM varied from 29 to 601 arcseconds with smooth surfaces exhibiting the lowest values. The effect of bond pressures on template layers were studied for a series of 50 nm alternative substrates prepared using pressures ranging from 75 psi to 25 psi with a constant bonding temperature of 450 °C. All transferred template layers prepared within this pressure range showed poor quality (FWHM ranged from 324 to 601 arcseconds) when compared to the bulk-GaAs of 12 arcseconds. Micro-Raman measurements were also carried out on these samples. A transverse optical (TO) phonon line is seen and the intensity ratio of the TO to longitudinal optical phonon were much higher than that of GaAs substrate, confirming that the bonding process is causing damage to the thin template layer.

EL+SC-WeP4 Design and Simulation of AlGaN/GaN Heterojunction Bipolar Transistors, ***K.P. Lee***, *S.J. Pearton, F. Ren*, University of Florida, *J.-I. Chyi*, National Central University, Taiwan, *A. Dabiran, P.P. Chow*, SVT Associates

The progress in developing AlGaN/GaN HBTs has been very limited compared to HEMT devices in the same materials system.HBTs would have advantages of better linearity,higher output power,better radiation resistance and more uniform threshold voltage compared to field effect transistors.To date,dc current gains in HBTs have been limited to <30 at room temperature and the rf performance is poor.The high base resistance is one of the limiting factors in npn structures.We have used a drift-diffusion model to simulate the dc characteristics of a variety of structures designed to improve the HBT performance.These include a superlattice base to enhance the hole concentration due to incomplete ionization of the Mg acceptors,base grading and a regrown base contact structure.The anisotropy in transport properties of the superlattice base have been taken into account.Base transport enhancement is predicted by the introduction of a quasi-electric field in the base layer.The minority carrier lifetime in the base is also a critical parameter determining the HBT performance.A comparison will be given of the relative strengths of the different device structures and their prospects for realizing a high gain,high speed,robust AlGaN/GaN HBT technology.

EL+SC-WeP6 Growth of Gallium Nitride on Silicon Substrate by MOCVD Using Multiple Buffer Layers, *M.A. Al-Tamimi*, ***D.A. Gulino***, Ohio University

An attempt has been made to improve the crystalline quality of MOCVD-grown gallium nitride on silicon (111) substrate by the insertion of a second aluminum nitride buffer layer. The conventional method for growing GaN on heterosubstrates has been to first grow a thin, low-temperature layer of typically aluminum or gallium nitride to act as a compliant, or "buffer," layer to reduce the degree of crystalline defects and threading dislocations in the subsequently-grown GaN epilayer. In the work reported here, a second, low-temperature AlN buffer layer was grown on top of the first GaN epilayer, and this was followed by a second GaN epilayer. We have found improvement in the crystalline quality of the second GaN epilayer as measured by x-ray diffraction rocking curves. We also experimented with ramping the temperature during growth of both the first and second AlN buffer layers, and we discovered that the best quality GaN film obtained in this work occurred when the first buffer layer was grown as the temperature was ramped from 800 to 1060°C and the second buffer layer grown at a fixed temperature of 800°C.

EL+SC-WeP7 Edge Termination Design and Simulation for Bulk GaN Rectifiers, ***K.H. Baik***, University of Florida, *Y. Irokawa*, Toyota Central Research Laboratories

GaN bulk rectifiers show excellent on-state resistances (in the milli-ohm.cm-2 range) forward turn-on voltages of ~1.8V and reverse-recovery times of <50ns. A key requirement is to develop effective edge termination techniques in order to prevent premature surface-induced breakdown. We have performed a simulation study of the effects of varying the dielectric passivation material(SiO2,SiNX,AlN,Sc2O3 or MgO),the thickness of the this material, the extent of metal overlap onto the dielectric and the ramp oxide angle on the resulting reverse breakdown voltage(VB) of bulk rectifiers. We find that SiO2 produces the highest VB of the materials investigated, that there is an optimum metal overlap distance for a given oxide thickness and small oxide ramp angles produce the highest VB. Initial experimental results on small-area devices show good agreement with the trends identified by the simulations. The dc characteristics are still dominated by the defect density in the substrate for large-area rectifiers.

EL+SC-WeP8 Photoelectrochemical Oxidation of GaN and Fabrication of Metal-oxide-semiconductor Structures using Ga-oxide Dielectrics, ***D.J. Fu***, *T.W. Kang*, Dongguk University, Korea

GaN metal-oxide-semiconductor (MOS) capacitors were fabricated by using Ga oxide formed by photoelectrochemical oxidation of GaN. The electrical properties of the MOS structures as characterized by capacitance-voltage measurement were found to be dependent on the oxidation time and post-treatment. Positive flatband voltage was observed in devices with thin oxide layers indicating the existence of negative oxide charge. Very thin oxide exhibits high capacitance and reverse leakage, which can be reduced by rapid thermal annealing. Passivation of the interface by the annealing is partially responsible for the improvement. Thicker oxide layers exhibit improved electrical properties. Low density of interface states was obtained in the Ga-oxide/GaN structure grown under optimized conditions.

EL+SC-WeP9 Relating Interfacial Structure and Composition of Pt/CdZnTe to Radiation Detector Device Performance, ***D.J. Gaspar***, *M.H. Engelhard, V. Shutthanandan, S. Thevuthasan,* Pacific Northwest National Laboratory, *A.A. Rouse, C. Szeles, J.-O. Ndap, S.A. Soldner*, eV PRODUCTS

The interfacial structure and composition of platinum/CdZnTe interfaces was examined to establish correlations between surface and interfacial stoichiometry and radiation detector device performance. X-ray photoelectron spectroscopy (XPS), including depth profiling, and Rutherford backscattering spectroscopy (RBS) were used to determine surface and Pt/CdZnTe interfacial composition. The ^{57}Co spectral response of five CdZnTe detector devices formed by deposition of Pt contacts on a CdZnTe crystal was correlated to the interfacial stoichiometry and the ideality factor. Non-ideal contact behavior was correlated to interfacial oxidation and to the bulk series resistance of the diode. XPS depth profiling revealed differences in the formation of the rectifying contacts, which correlated to device electrical performance.

Microelectromechanical Systems (MEMS) Room: Exhibit Hall B2 - Session MM-WeP

Poster Session

MM-WeP1 Metallization Schemes for RF MEMS Switches, ***K. Leedy***, *R. Cortez, W. Cowan, J. Ebel, J. McFall, R. Strawser, A. Walker*, Air Force Research Laboratory

A series of surface micromachined MEMS switches with composite metal bridges were fabricated by standard photolithographic techniques. The study was conducted in order to assess the influence of film stress and composition on the released shape of cantilever and fixed-fixed beam structures. A 1 µm thick evaporated Au film was the basis for all bridge materials with additional 20 nm layers of evaporated or sputter deposited Ti, Pt, or Au on the top or bottom surface of the thick Au. The planarity and stress gradient of cantilever beam structures and the planarity of fixed-fixed beam structures were measured with optical interferometry. Au-only bridge structures displayed the best planarity of those examined while structures including Ti layers displayed the least planarity. Tensile cantilever stress gradients were calculated using both cantilever tip deflection and radius of curvature techniques. The thin film biaxial moduli used in stress gradient calculations were measured with a wafer curvature technique and were slightly higher than the bulk Au value. Results of this study show that thin metal layers (2% of total beam thickness) have substantial influence on released beam curvatures but that beam planarity can be achieved with a suitable combination of materials.

MM-WeP2 Inorganic Electret Using SiO_2 Thin Films Prepared by r.f. Magnetron Sputtering, *T. Minami,* ***T. Yamatani****, T. Utsubo, T. Miyata,* Kanazawa Institute of Technology, Japan, *Y. Ohbayashi*, Hosiden Corporation, Japan

The ability to fabricate inorganic thin-flim electrets on low temperature substrates is necessary for applications such as electret actuators and sensors in MEMS. In this paper, we describe the fabrication of silicon dioxide (SiO_2) thin-film electrets that exhibit a highly stable surface potential in tests at high temperatures as well as high relative humidities in air. The SiO_2 films were prepared on various conductive substrates at a temperature of 250 to 400°C by rf magnetron sputtering using a fused quartz target. It was found that operational stability in highly humid atmospheres can be considerably improved by postannealing in a highly humid atmosphere at a high temperature. In addition, the obtained surface potential stability also proved to be dependent on the deposition conditions. The surface potential of SiO2 films postannealed in a highly humid atmosphere at 350 to 450°C for 10 to 180 min was found to be highly stable even when tested at a relative humidity of 90% and a temperature of 60°C. In addition to the postannealing conditions, the deposition conditions were optimized: substrate temperature, about 350°C; sputter gas pressure,0.3 Pa; and O_2 partial pressure, 20%. As a result, the surface potential of SiO_2 electret films prepared under optimized deposition and postannealing conditions exhibited no decay when tested over a long term at a temperature of 60°C and a relative humidity of 90%. SiO_2 thin-film electrets with a thickness of 2 to 5 µm maintained a surface potential above 300 V when tested at temperatures above 250°C in air or at 60°C with a relative humidity of 90%. It was concluded that highly stable thin-film electrets can be realized by SiO_2 thin films prepared on various conductive substrates at a temperature of about 350°C and postannealed at 400°C in a highly humid atmosphere.

MM-WeP3 MEMS Electrostatically Actuated Vertical Mirror Switch for Optical Transceiver, ***M.W. Lee***, *K.C. Lee, S.B. Jo, B.H. O, S.G. Lee, S.G. Park, E.H. Lee*, Inha University, Rep. of Korea, *H.S. Lee, H.G. Ryu*, Neoptek, Rep. of Korea

We have developed a simple structured MEMS vertical mirror switch for optical transceivers. As the optical characteristics and mechanical stability of MEMS switches is sufficient for excellent performance in communication networks, it is necessary to lower the fabrication cost by simplifying or eliminating processes of manual assembly or alignment. Here, novel structures for mirror assembly and stopper are proposed and fabricated to satisfy simplicity and accuracy of a vertically-assembled mirror, made with only three layers by deposition, polysilicon, silicon-oxide, silicon-nitride layers on a silicon substrate. Poly-silicon layer is to build a cantilever and a mirror. The silicon-oxide layer is a sacrificial layer and the silicon nitride layer is for electrical isolation. Fabrication processes of semiconductor micromachine offers accurate position due to it's nature. PR-pads are also used for the technique of photoresist(PR) applied self-assembly (the works of R.R.A. Syms[1]). The characteristics of fabricated devices will be discussed in detail. Low actuation voltage and other performances are considered to be enough for the application in optical communication systems.

[1] Richard R.A. Syms, Surface Tension Powered Self-Assembly of 3-D Micro-Optomechanical Structures, Journal of Microelectromechanical Systems, Vol. 8, No. 4, Dec. 1999.

MM-WeP4 Development of Microfluidic Devices for Gas Centrifuge Separation, ***S. Li***, *R. Ghodssi*, University of Maryland

A mass spectrometer on a chip (MSOC) is suited for environmental monitoring with the advantages of fast response, low power consumption and portability. Gas centrifuge separation (GCS) is capable of concentrating the minor constituents in a gas mixture and increasing the sensitivity of MSOC. An integrated MEMS fabrication method is presented for developing GCS devices as the front-end for MSOC. A hybrid device that incorporates silicon, plastic and glass is realized by utilizing a combination of deep reactive ion etching (DRIE) and low temperature wafer bonding techniques. Inlet and outlet ports (500 µm in diameter and depth) are created in the silicon substrate by DRIE. Using standard photolithography, micro converging-diverging nozzles with throats as small as 3.2 µm wide and 5 µm deep are formed in EPON SU-8 supported on the silicon substrate. The second SU-8 layer, coated on a pyrex wafer, is bonded with the first SU-8 layer to form sealed micro nozzles. Macroscale capillary needles (400 µm in diameter) and quick-setting glue are used to interface the microfluidic device to the macroscopic world (i.e., the pressure measurement setup). Measures are taken to prevent the glue from seeping through the gaps and blocking the microfluidic channels. Calibration results demonstrate the feasibility of the test setup for measuring pressure distributions of gas flow in the micro nozzles. Preliminary measurement results and a detailed fabrication process will be presented.

MM-WeP5 Characterization of the Residual Stress in Titanium/Platinum and Tantalum/Platinum Thin Film Electrodes used in the Processing of PZT MEMS Devices, ***R.G. Polcawich**, J.P. Clarkson, J. Pulskamp, A. Wickenden, M. Wood, K. Kirchner, M. Ervin, E. Zakar, M. Dubey*, U.S. Army Research Laboratory

Residual stress in freely suspended MEMS devices is critical for optimal performance. The high temperature anneals required to crystallize lead zirconate titanate (PZT) thin films create stress gradients within the piezoelectric stack yielding non-planar released structures. From our previous studies, tantalum/platinum (200 Å / 1700 Å) metallization used as bottom electrodes for PZT MEMS has contributed the largest residual stress (~850 Mpa) to the multilayer stack. This research focused on using the sputter deposition parameters as a means of producing low stress (~<450 Mpa) Ta/Pt and Ti/Pt metal layers. Ti, Ta, and O diffusion were investigated with Auger electron spectroscopy by using O^{18} as a tracer during the anneal process. Additionally, x-ray diffraction and scanning electron microscopy were used to identify the presence of second phase compounds within the Pt metal layer. From this combined analyses, oxygen diffusion and the subsequent formation of TiO_2 and Ta_2O_5 compunds within the Pt matrix was the primary cause of reducing the residual stress in metal stacks with Ta and Ti thin films greater than 200Å.

MM-WeP6 Mitigation of Residual Film Stress Deformation in Multi-Layer MEMS Devices, ***J. Pulskamp**, B. Piekarski, R.G. Polcawich, A. Wickenden, M. Dubey*, U.S. Army Research Laboratory

An approach to compensate for the residual thin film stress deformation of multi-layer MEMS devices is presented based upon analytical modeling and in-process thin film characterization. Thermal and intrinsic deposition stresses can lead to the warping of released MEMS structures. This detrimental phenomenon in many cases can prevent proper device operation. Ellispsometric and laser wafer bow measurements yield thickness and film stress values that are used to update the deflection model during device fabrication; allowing for the compensation of the fabrication process variability. The derivations of linear and nonlinear residual film stress induced deflection models are presented. These models are based upon Bernoulli-Euler beam theory and are thus restricted to the associated geometric constraints. The models are initially validated by comparison with surface micro-machined sol-gel PZT (Lead-Zirconate-Titanate) cantilever structures; with initial experimental results agreeing well with both models.

MM-WeP7 Epitaxial Growth and Characterization of the Ferromagnetic Shape Memory Alloy Co_2NiGa on (001) GaAs, ***T.C. Shih**, J.W. Dong, J.Q. Xie, X.Y. Dong, S. McKernan, R.D. James, C.J. Palmstrom*, University of Minnesota

Recently Wuttig and his coworkers[1] reported a new ferromagnetic shape memory alloy Co_2NiGa, using bulk samples. This present study focuses on the growth of (001) Co_2NiGa thin films on (001) GaAs substrate by molecular beam epitaxy. In-situ reflection high energy electron diffraction, ex-situ X-ray diffraction, and cross-sectional transmission electron microscopy indicate the single crystal growth of Co_2NiGa on (001) GaAs. X-ray diffraction data from bulk samples[2] indicate that the Heusler alloys $Co_2Ni_{1+x}Ga_{1-x}$ ($0<x<0.3$) order in the B2-phase (CsCl structure) with doubled its lattice parameter close to 5.75 Å, which corresponds to a 1.8 % mismatch to GaAs. The X-ray diffraction data from the Co_2NiGa thin films indicate an out-of-plane lattice parameter of 6.10 Å, which suggests that the Co_2NiGa thin film may grow in a strained epitaxially stabilized tetragonal structure. Vibrating sample magnetometry and superconducting quantum interference device magnetometry measurements have been performed for the Co_2NiGa film with magnetic fields applied in-plane. The room temperature magnetic moment versus applied field curve shows a hysteresis loop with a coercivity of 170 Oe and a saturation magnetization ~250 emu/cm^3. The Curie temperature is above room temperatures which is comparable to the bulk measurement (Tc=326K).[2] In this talk, the crystal structure as a function of growth conditions as well as the mechanical properties of released films will be presented.

[1] M. Wuttig, J. Li, and C. Craciunescu, Scripta Mater., 44, 2393 (2001).

[2] J. G. Booth, R. Cywinski, and J. G. Prince, Journal of Magnetism and Magnetic Materials, 7, 127 (1978).

MM-WeP8 Micromirror Coatings with Low-stress, High Reflectivity, ***Y.N. Picard***, University of Michigan–Ann Arbor, *D.P. Adams, O.B. Spahn*, Sandia National Laboratories, *S.M. Yalisove*, University of Michigan–Ann Arbor, *D.J. Dagel*, Sandia National Laboratories

While thin film coatings can greatly improve the reflectivity of micromirrors used in optical MEMS devices, such coatings can yield a moderate compressive or tensile stress, leading to a significant change in the micromirror curvature. This work seeks to develop highly reflective optical coatings exhibiting near-zero average film stress and minimal through-thickness stress. In this study, multilayer thin films consisting of Cr, Ti, Au, Si and Si_3N_4 are deposited on blank Si (100) substrates using DC planar magnetron sputtering. Au is greater than 90% reflective over a range of infrared wavelengths, and either Cr or Ti can be employed as an adhesion promoter between Au and Si. The residual stress of multilayer films is determined through curvature based measurements using laser-scanning and applying Stoneys equation. The influence of sputter gas pressure and deposition rate on residual film stress is assessed for a variety of multilayer systems. Also assessed is stress aging at room temperature over a period of one year. Using optical interferometry, we have already demonstrated that low stress Au/Ti films deposited on micromirrors 125-500 µm in size induce less than $\lambda/40$ change in bow. This work seeks to extend these initial results by combining low stress Au/Ti films with Si_3N_4/Si Bragg reflectors to achieve a near-zero stress multilayer exhibiting both a ~99% reflectivity for a target wavelength of radiation while inducing minimal curvature changes when deposited on pre-released polysilicon micromirrors. Since thin film microstructural defects and interfacial roughness can contribute to optical absorption, examination of both is conducted using cross-sectional transmission electron microscopy. Surface roughness is also measured using atomic force microscopy. Spectral reflectivity of thin film coatings is measured using an optical spectrum analyzer.

MM-WeP9 Deep Reactive Ion Etching of Silicon Using an Aluminum Etching Mask, ***W. Wang**, P. Reinhall*, University of Washington

A novel double-sided micromachining process for the silicon based device fabrication has been developed that allows the use of capacitively coupled RIE equipment for high aspect ratio etching. The resulting etch rates in Si of 2.2 µm/min is comparable to 1 to 3 µm/min from the standard ICP deep reactive ion etching process. Although a lower anisotropy (~0.5) and lower selectivity to thermal oxide (Si: SiO_2 = 10:1) and to photoresist (Si: +PR = 9:1) resulted, the proposed process is much simpler and requires only the use of an aluminum mask. Based on the experimental results, a 1000 Å thick Al film sufficiently protects the unexposed substrate while allowing the etching of a 350µm deep hole with an area of 3x3mm^2 when etching with SF_6 /CHF_3/O_2 plasma. A 2000µm long and 100µm wide (with layers of Al/SiO_2/Si and thicknesses of 0.1µm/2.2µm/40µm respectively) cantilever is also achieved. The technique was developed mainly for bulk micromachining of silicon or composite silicon cantilever structures.

Nanometer Structures
Room: Exhibit Hall B2 - Session NS-WeP

Nanometer Structures B

NS-WeP1 Electrostatic Force Spectroscopy of Pure InP and Self-assembled InAs/InP Quantum Dots Studied by Non-contact Atomic Force Microscopy, ***R.-P. Stomp***, McGill University, Canada, *S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada, *P. Grutter*, McGill University, Canada

The purpose of this work is to develop a low-temperature, non-contact Electric Force Microscope (EFM) technique to image semiconductor dots embedded in a dielectric matrix. Non-contact Atomic Force Microscope (nc-AFM) is a very versatile tool to study conductive as well as non-conductive surfaces without damaging them. Our microscope operates at 4.5K with a built-in heater and the possibility of applying a magnetic field up to 8T.[1] In this study we use samples of self-assembled InAs quantum dots embedded in InP grown by chemical beam epitaxy.[2] In the present study, we are investigating the change in resonance frequency of the AFM tip as function of tip-sample bias voltage, or electrostatic force spectroscopy, of bare InP and InAs/InP quantum dot. In case of bare InP an asymmetric frequency-voltage dependence was observed that enabled us to determine the charge sign of the carrier and to deduce the work function potential of the material. This is an on going work, and results on the quantum dot samples will be presented and discussed. It has been previously demonstrated that quantum dot spectra can be measured by EFM, where we can observe the filling of energy levels at low temperature.[3]

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NS-WeP2 Defects in Cylindrical Multi-shell Copper Nanowires, ***J.W. Kang**, J.J. Seo, H.J. Hwang*, Chung-Ang University, Korea

We have performed atomistic simulations for cylindrical multi-shell (CMS)-type Cu nanowires containing defects. Our investigation has revealed some physical properties that have not been detected in previous studies that have considered defect-free nanowires. Since the vacancy formation energy is lowest in the core of a CMS-type nanowire, a vacancy formed in the outer shell of a CMS-type nanowire naturally migrates toward the core. The maximum of the formation energy of an adhered atom on the surface of a CMS-type nanowire was modeled using a 16-11-6-1 nanowire. The formation energy of an adhered atom decreased when the diameter of the CMS-type nanowire was either above or below the diameter of the peak energy maximum. This investigation found three recombination mechanisms for the vacancy-adhered atom pairs: (i) by direct recombination, (ii) by a kick-in recombination, and (iii) by a ring recombination. Vacancy formation energy calculations show that an onion-like cluster with a hollow was formed, and molecular dynamics simulations for various CMS-type nanowires found that vacancies migrated towards the core. From these, we obtained basic information on the formation of hollow CMS-type metal nanowires (metal nanotubes).

NS-WeP3 Dispersion Relation of the Electromagnetic Waves in the Strong-coupling Superconductive Nano-disk, *V.Z. Lozovski, **D.V. Reznik***, Institute of Semiconductor Physics NAS of Ukraine

The investigated system consists of the superconductor disk on the surface a dielectric substrat. We study the dispersion relations of the electromagnetc waves which can be excitated in the system. The dimensions of the disk is order of 100-1000 Å. We take into account the strong coupling of the superconductor in the framework of the enhanced u-v- transformations method which was developed in.[none 1] The dispersion relation are determine by the pole part of the effective susceptibility. The susceptibility is calculated by solution of Lipman-Shwinger self-consistent equation. This equation is solved by exact summation of iteration procedure series proposed in.[2] The initial receptivity was written in terms of u-v-coefficients. One takes into consideration strong-coupling. We take into account the despersion of the phonon energy and perturbation of the electron energy spectrum at Fermi level by electron-phonon interaction. The proposed approach allows us to calculate the effective nonlocal susceptibility for the both weak and strong coupling superconductors. As it is shown in[2] the effective susceptibility can be rewritten as the tensor product of the initial susceptibility and inverse mass operator. Then the electromagnetic waves dispersion relations are determined by the roots of the real part of the determinant of the effective susceptibility inverse matrix. The dispersion curves depend on the electromagnetic properties of the substrate and disk material, the strength of the coupling in superconductor and the geometry of the system (thickness and radius of the disk). Moreover, dispersion depends on coordinate in which electromagnetic field is investigated.

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NS-WeP4 Zinc Sulfide Coating on Carbon Nanotubes, ***H.S. Kim***, University of Florida

Mophological study on zinc sulfide (ZnS) synthesized by a solid state reaction on the outermost shells of multiwalled nanotubes (MWNT) is presented. It was found that ZnS coats the surface of CNTs in the forms of ultrathin films, quantum dots, and nanorods. ZnS nanorods were grown on the surface of MWNTs without the presence of catalyst suggesting the vapor-liquid-solid (VLS) mechanism is not applicable for the here shown growth process. The average diameter of nanorods on MWNTs is about 140 nm and the length is around 250 nm.

Zinc Sulfide Coating on Carbon Nanotubes.

NS-WeP5 Gas Sensor Based on Metal and Metal Oxide Individual Nanowires and Nanowire Arrays, ***Y. Zhang**, A. Kolmakov, G. Cheng, M. Moskovits*, University of California, Santa Barbara

We report on the approach, which can constitute a novel versatile platform for micro- and nanosensor application. Arrays of nanowires with tunable diameters and length in the range of 10-100 nm and 5-200 micrometers, respectively, were fabricated from the catalyticaly active materials inside close-packed nanochannel alumina templates. Electrodes deposited on the surfaces of these nanostructures provides electrical contacts which with the incorporated heaters determines the device architecture. In particular, metal (Cu, Ag, Pb, Pd) and metal oxide (SnO_2) individual nanowires and their arrays were tested using HRTEM, XPS and Auger spectroscopy. Chemical reactivity and gas sensitivity toward hydrogen and carbon monoxide of individual and assemblies of Pd and SnO_2 nanowires were assessed using conductivity measurements and TPD analysis. These structures based on single nanowires and nanowire arrays offer full range of options useful to gas sensing, including robustness, high surface-to-volume ratio, small size if required, functionalization via doping, integrability into other devices.

NS-WeP6 Switching Behavior of Plasma Polymer Thin Films Containing Metal Nanoparticles, ***A. Kiesow***, Fraunhofer-Institute for Mechanics of Materials Halle, Germany, *J.E. Morris*, Portland State University, *C. Radehaus*, Technical University Chemnitz, Germany, *D. Katzer, A. Heilmann*, Fraunhofer-Institute for Mechanics of Materials Halle, Germany

The nanostructures of plasma polymer thin films containing silver-particles are characterized by particle size and particle shape distribution and have been investigated by means of transmission electron microscopy (TEM). The electrical properties have been determined and correlated with the nanostructures. Three different nanostructural types could be observed: metallic, percolation, and dielectric region. While for the metallic and dielectric regions, respectively, metallic conduction and thermally activated tunneling can be identified as the dominant conduction mechanisms, a switching effect was observed for the region near percolation. These drastic abrupt changes in the current (I) -voltage (V) behavior (of up to 6 orders of current magnitude) are reversible, and can be defined as threshold bistable switching. The threshold voltage is dependent on the switching frequency.

NS-WeP7 Frequency Dependence of Local Electronic Properties: Nanoimpedance Spectroscopy, *S.V. Kalinin, **R. Shao**, D.A. Bonnell*, University of Pennsylvania

Progress in nanoelectronics necessitates an understanding of the structure and properties of materials on the local level. While substantial advances have been made in local property measurement particularly based on scanning probes, they have accessed either dc properties or ac properties at a single frequency. The ability to probe the frequency dependence of local electronic properties would lead directly to mechanistic considerations of trap states at defects, scattering at interfaces, etc., in nano or molecular electronics. We have developed a local spectroscopy that determines tip-surface impedance directly over a wide frequency range (40 Hz - 110 MHz) with nanometer spatial resolution. This approach is generalized to spatially resolved nanoimpedance spectroscopy and imaging. The technique will be illustrated on 2-D structures, an atomically abrupt interface and a nano wire; and a 3-D structure, a nano particle on a substrate.

Organic Films and Devices
Room: Exhibit Hall B2 - Session OF+EL-WeP

Organic Films and Devices

OF+EL-WeP1 Cycloaddition of Silyl-disila-cyclopentene on Si(001) Surface, ***B.-Y. Choi**, Y.-J. Song, Y. Kuk*, Seoul National University, South Korea

It is known that π bonds of unsaturated organic molecules can easily react with Si=Si dimers of the reconstructed Si(001)-2x1 surface, resulting in two new Si-C σ bonds. Through such a cycloaddition, densely-packed molecules on hybridized Si(001) surface are highly ordered both translationally and rotationally over macroscopic length scale. However, in spite of much effort, the mechanism of cycloaddition on surface is not known clearly. We investigated the reaction of 2-silyl-1,3-disilacyclopent-4-ene (SDC) with the Si(001) surface using scanning tunneling microscopy. STM images show that the SDC molecules are slightly elongated parallel to the dimer direction, suggesting that the molecules bond in a manner of typical [2+2] cycloaddition. It can be noted that there exists a preferred bonding site of SDC molecule. However, the analysis of the observed structure suggests that there is more than one way for SDC to bond to the Si(001) surface. Some molecules place perpendicular to dimer direction and even complex absorbates are shown. We suggest that the several reactions occur nearly as frequently.

OF+EL-WeP2 Nanolithography Technique Based on Dynamic Mode Atomic Force Microscopy and Organosilane Self-Assembled Monolayers, ***K. Hayashi**, N. Saito, H. Sugimura, O. Takai*, Nagoya University, Japan

Organosilane self-assembled monolayer (SAM) is a candidate for resist material in future nanolithography techniques. Although several techniques have been applied to patterning of the SAMs, scanning probe lithography using an atomic force microscope (AFM) is promising since the method has a high potential in archiving nanometer scale resolution. However, there has been a serious problem, that is, damages of the AFM-tip, when the AFM is operated in the contact mode. Here we report on nanopatterning of organosilane SAMs using a dynamic mode AFM in which tip damages are expected to be reduced. We observe AFM-tip induced chemical changes on the SAM surfaces by Kelvin-probe force microscopy (KFM) working in the dynamic mode as well. Onto cleaned silicon (Si) substrates covered with native oxide (SiO_2), a SAM was formed from n-octadecyltrimethoxysilane

[ODS: CH$_3$(CH$_2$)$_{17}$Si(OCH$_3$)$_3$]. Thickness of this ODS-SAM was ca. 1.8 nm. While scanning a AFM-tip (Au coated Si tip), operated in the dynamic mode, on an ODS-SAM/Si sample, a DC bias voltage was applied between the conductive tip and the sample. After the patterning, the sample surface was characterized by KFM. Due to electrochemical reactions induced by the injected current, the modified region where current had been injected from the tip was found to show a more positive surface potential than the surrounding unmodified region. Through the surface potential images acquired by KFM, chemical changes of ODS-SAM could be detected, while such changes could hardly be confirmed in topographic images. KFM is a powerful means to characterize nanoscale patterns on the SAMs drawn by scanning probe lithography.

OF+EL-WeP3 Photoemission Study of Dodecanthiol on Au (111), *H. Geisler, S. Sales,* Xavier University of Louisiana, ***J.M. Burst**, S.N. Thornburg, C.A. Ventrice Jr.,* University of New Orleans, *Y. Losovyj, P.T. Sprunger,* Louisiana State University

The adsorption of alkanethiols on various single-crystal metal surfaces results in the formation of self-assembled monolayers (SAMs). Typically, SAMs are grown on surfaces that are immersed in aqueous solutions, and adsorption times of 15 hours or more are necessary to obtain well-ordered, defect free structures. In this study, 1-dodecanethiol was vapor deposited on Au (111) in ultra high vacuum, which produces a SAM in a period of only a few minutes. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) was used to determine the orientation and the electronic structure of the thiol. Deposition at room temperature gave no signature of thiol adsorption at the surface with either ARUPS or low energy electron diffraction (LEED). Deposition at ~100 K resulted in an ordered monolayer, as indicated by the dispersion of the thiol valence band emissions. A comparison between clean gold and the SAM spectra indicate that the 1-dodecanethiol adsorbs upright at a 20° angle to the surface normal. Deposition of multilayers of thiol at ~100 K produced a disordered overlayer with no dispersion of the valence band emissions. The onset of emission from the thiol valence band for the multilayer films was measured to be 3.5 eV below the Fermi level.

OF+EL-WeP4 XPS Studies of Brilliant Green Doped Conducting Polymer Polythiophene Films, ***H.K. Kato**, S.T. Takemura, M.H. Hirayama*, Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule brilliant green (BG) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between the dye molecule and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that BG molecules were injected into polymer matrix in the hybrid films prepared by electrochemically reduced method and BG diffused method. S 2p lines were observed split indicates simultaneous doping of BG cation and HSO4-. 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, A-type and B-type by the difference of S 2p core-level energy shift. In the sample of A-type, the energy shift of the lower peak of S 2p suggest the charge transfer between BG molecules and polymer backbone creating a n-type polymer backbone state. In the case of electrochemically as-grown films, both BG and HSO4- doping were not observed because S 2p line was single and no N 1s signal was observed.

OF+EL-WeP5 XPS Studies of Initial Stage of Conducting Polymer Film Growth on Si Substrate, *H.K. Kato, **S.T. Takemura***, Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) film growth on Si substrate was investigated by XPS. PT/Si interface fabricated by electrochemical method was closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. At the initial stage of electrochemical polymer growth, affinity between a deposited polymer PT film and Si substrate was strong compared with the case of PT film growth on ITO substrate expecting bondings between polymer chains and Si substrate layers. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different Gaussian components correspond to different valence states of Si in contrast to the core-level spectra of non-deposited Si substrate. The lower binding energy peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Strong affinity between a deposited polymer PT film and Si substrate and variation of the XPS spectral profile suggest that Si-C and Si-F bondings are created at the PT/Si interface.

OF+EL-WeP6 Formation and Characterization of Ferrocene and Porphyrin Monolayers on Si and Ge Surfaces : Towards a Hybrid Molecular/CMOS Electronic Device, ***A.A. Yasseri**, Z. Liu, R. Dabke,* University of California Riverside, *V. Malinovskii, K.H. Schweikart, J.S. Lindsey,* North Carolina State University, *W.G. Kuhr, D.F. Bocian, K.M. Roth*, University of California Riverside

Construction of a novel hybrid molecular based device may provide the most tractable approach in bridging the gap between modern day semiconductor materials and molecular based devices. Toward this goal, we have examined functionalized monolayers of ferrocene and porphyrin terminated alcohols and thiols covalently linked to mono-crystalline Si and Ge (100) and (111). Electrochemical communication with the surface immobilized molecules was achieved through a covalently anchored Si-O, Si-S or Ge-O and Ge-S tether to photlolithographically patterned surfaces. Silicon microelectrodes were fabricated on heavily doped silicon masked with a thermally grown oxide to define the active electrode area for monolayer assembly. Surfaces were activated via a two-step process. Chemically stable hydride-terminated surfaces, using HF or ammonium fluoride, were reacted with a solution of iodine yielding an iodide functionalized surface. XPS measurements confirm the mechanism for the displacement of surface iodine atoms via a base catalyzed reaction with alcohol terminated iron and zinc-centered ferrocene and porphyrin respectively. Iodide derivitization prior to film deposition chemically facilitates the formation of more densely packed monolayer of porphyrins. Fast scan voltammetry performed on monolayers demonstrate the chemical stability of the films over millions of cycles in an inert atmosphere. Modified AC voltammetry was used to probe the redox kinetics of the semiconductor film junction in order to measure the rate for film oxidation and reduction under an applied potential. Monolayers formed from solution phase assembly reactions were further characterized using scanning probe microscopy.

OF+EL-WeP7 Characterization of OLED Degradation by Emission Microscope, ***N. Miura**, Y. Luo, K. Takagi*, ITES Co. Ltd., Japan

The purpose of this study is to investigate how an emission microscope has been applied to evaluation for the degradation mechanism of organic light-emitting devices (OLED). One of the most effective ways to characterize OLED degradation is to study a physical and chemical phenomenon that occurs with an exact point of interest. The problem, however, is one of isolating the exact point of degradation. Thickness of a luminescent layer is around 0.1 microns. Consequently, a less-than-0.1-micron foreign matter can become a cause of an electrical short failure. On the other hand, a size of a pixel is the approximately one hundred microns. Therefore pinpoint detection of a failure location is extremely difficult. In order to solve this problem, an emission microscope used for a failure analysis of Si-based LSIs has been applied to detect a degradation point in plane luminescent devices. An emission microscope is a tool to detect a faint light emitting at a failure point with PMT or CCD camera and to find out a point of interest by adding an optical image and a detected one. This study describes a method for applying emission microscope in the failure analysis of OLED and demonstrates the effectiveness of this method. It is confirmed that an observation under sub-threshold bias condition is effective to find out a failure point. Although no electro-luminescence is observed under this condition with an optical microscope, an emission microscope can get detect a photon emission at a failure location. Some case studies are described to demonstrate the effectiveness of this method. Cross sectional TEM observations of defects located with this technique are also included.

OF+EL-WeP8 Polyatomic Ion Deposition of Thiophenic Thin Films, ***Y. Choi**, E.R. Fuoco, L. Hanley*, University of Illinois at Chicago

Oligo- and polythiophenes are utilized as conducting polymers in many applications. 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.[1] We demonstrate here the growth of thiophenic thin films on aluminum and silicon substrates by mass-selected <200 eV C$_4$H$_4$S$^+$ ion beams. Thiophenic films are also grown by non-mass selected ion beams containing <200 eV C$_4$H$_4$S$^+$ and fragment ions. Our non-mass selected ion deposition method permits rapid film growth over wide substrate areas and it is described here for the first time. X-ray photoelectron spectroscopy and atomic force microscopy are used to compare the film chemistry and morphology for the two methods. Oxidation of the films during aging in air is observed.

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OF+EL-WeP9 Mg-Phthalocyanine Thin Films with High Sensitivity for Chlorine Gas, ***T. Miyata**, S. Kawaguchi, T. Minami*, Kanazawa Institute of Technology, Japan

There has been considerable interest in the study of organic substances such as phthalocyanines in thin film form for use as the active layer in gas sensor devices. In particular, the electronic properties of metal phthalocyanine (MPc) thin films are known to be affected by the presence of a foreign gas. Recently, we have demonstrated newly developed high-sensitivity chlorine (Cl_2) gas sensors using Cu-phthalocyanine (CuPc) thin films. However, these CuPc thin film gas sensors still have several unsolved problems such as low sensitivity at operating temperatures above 150ºC and the necessity of a heat treatment process for repeated operation. In this paper, we introduce newly developed chlorine gas sensors that can be operated at high temperatures using Mg-phthalocyanine (MgPc) thin films. The Mg-phthalocyanine thin films (thickness from 30 to 180 nm) were evaporated onto substrates; Au thin films were deposited as electrodes. The substrate temperature was varied from RT to 180ºC. Gas sensitivity is defined as ratio $(I-I_0)/I_0$. Here, I_0 and I are the currents through the sensors before and after gas introduction, respectively. The sensor resistance decreased when exposed to chlorine gas; MgPc thin film gas sensors exhibited high sensitivity at the operating temperatures as high as 230ºC. The characteristics of MgPc thin film sensors were strongly dependent on the preparation conditions of the MgPc thin films. For example, sensitivity increased as the substrate temperature of the MgPc thin films was increased from RT to 180ºC: maximum sensitivity at a thin film deposition temperature of 180ºC. At an operating temperature of 200ºC, the sensitivity of the optimized MgPc thin film gas sensor linearly increased with the Cl_2 gas concentration in the range of 0.35 to 35 ppm.

OF+EL-WeP10 The Surface Stress under Ion Irradiation on Si and SAM-coated Si, ***A.N. Itakura**, M. Kitajima*, Institute for Materials Science, Japan, *R. Berger*, IBM Deutschland Speichersysteme GmbH, Germany

Evaluation of stress in the Si stencil mask is very important for ion projection patterning or ion lithography technology, because the stresses would cause a deformation of the projected patterns. Ar ion irradiation makes a compressive stress on Si(001) surfaces.[1] Stencil masks often become folded during the ion projection patternings, which should be owing to this ion induced compressive stress. In this paper, we have studied the stress evolution of Si membranes under ion irradiation. Bare Si and alkanethiol-coated-Si were examined during ion irradiation from ion energies of 5 to 50eV. The stresses were in-situ real-time monitored by using a microcantilever sensor technique combined with ion irradiation system in UHV. Self-assembled monolayers (SAM) such as alkanethiol, $HS-(CH_2)_{n-1}-CH_3$ for n=4,6,8,12, on gold induced compressive stresses.[2] In contrast to the compressive stress during SAM growth, a strong tensile surface stress of about -0.7 N/m was found when the sensor is exposed to Ar ions. This value is 3-4 times larger than the compressive stress. The constant value of the tensile stress for an Ar-ion dose higher than 4×10^{14} ions/cm^2 indicates that a stable monolayer forms during Ar-ion irradiation. Stable protective monolayers featuring tensile stress can play a key role in micro-machining and as protective overlayers for silicon mask lithography.

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OF+EL-WeP11 Controlled Growth of Ultrathin Molecular Films, ***E.J. Kintzel, Jr.***, Florida State University, *D.-M. Smilgies*, Cornell High Energy Synchrotron Source, Cornell University, *J.G. Skofronick, S.A. Safron, D.H. Van Winkle*, Florida State University

Controlled growth of the aromatic p-phenylene oligomer molecules adsorbed onto KBr(001), KCl(001), NaCl(001), and NaF(001), has been investigated by x-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis provides evidence that the substrate temperature during deposition, substrate lattice constant, and molecular length affects the molecular orientations within these ultrathin films. AFM images contribute independent evidence for a surface microstructure evolution that is consistent with the XRD results. Oriented films can therefore be grown with the desired molecular orientations by careful selection of an appropriate combination of the above deposition parameters.

OF+EL-WeP12 Current Sensing AFM Study on Electric Property of Organic Monolayer Formed on Hydrogen Terminated Si(111) via Si-C Bond, *K. Uosaki, **J.-W. Zhao***, Hokkaido University, Japan

Current Sensing AFM was used to measure the conductivity of alkyl monolayer of various chain length formed on hydrogen terminated Si(111) via Si-C Bond. Conductance was dependent on chain length, bias and force. The current increased exponentially with the bias. Based on the chain length dependence of the Log(current) - bias relation, the conduction mechanism is discussed. The force dependence of the conductance at a given bias was well explained by the bending of the monolayer and the chain length dependence of the mechanical property of the monolayer will be discussed.

OF+EL-WeP13 Surface Structure and Surface Properties of Organosilane Monolayers Selectively Assembled on the Si-wafer Substrate, ***A. Takahara**, T. Koga, M. Morita, H. Otsuka*, Kyushu University, Japan

Three-component micropatterned organosilane monolayers were successfully fabricated on Si-wafer substrate by stepwise vacuum ultraviolet-ray (VUV) photolithography technique with a rotation of line-type photomask. The introduction of different organosilanes was confirmed by X-ray photoelectron spectroscopy (XPS). Atomic force microscopic and lateral force microscopic observations revealed that the line-widths of micropatterned surface corresponded to those of photomask. Micropatterning of the surface functional groups influenced the magnitudes of surface free energy.

Plasma Science
Room: Exhibit Hall B2 - Session PS+TF-WeP

Plasma Etching & Deposition

PS+TF-WeP1 Expanding Thermal Plasma Deposition of UV Filters and Abrasion Resistant Coatings, ***C.D. Iacovangelo**, M. Schaepkens*, General Electric Global Research Center

Use of plastics in large area applications such as automotive glazing require deposition of abrasion resistant and inorganic UV filter coatings for protection. These coatings must be hydrolytically stable and weather able. We have developed expanding thermal plasma (ETP) deposition processes for high rate, large area deposition of ZnO and doped-ZnO UV filters and organo-silicon based inter-layers and abrasion resistant layers on polycarbonate (PC) substrates. This paper will describe the ETP processes used to deposit these materials and the effect of processing parameters on the deposition rate, UV absorbency, hydrolytic stability and weather ability of these materials and multi-layer packages. ZnO was deposited from diethylzinc, dimethlyzinc, and by thermal evaporation of metallic Zn into the ETP Ar/Ox jet. Abrasion resistant coatings and inter-layers were formed from TMDSO, HMDSO, and D4. Using these processes, highly stable, weather able coatings at deposition rates of 20 microns/minute on PC substrates were obtained. Processing parameters, degree of doping, and precursor selection were critical to achieving ZnO with high UV absorbency and hydrolytic stability. ZnO coatings of 0.5 microns thick provided UV absorbency at 350 nm of 4.0. ZnO coatings from metallic zinc were crystalline and resulted in superior stability to deposits from either diethyl or dimethylzinc. Highly abrasion resistant coatings, Taber abrasion of 2 at 1000 cycles, were obtained with all of the organo-silicone materials examined, however, UV absorbency of the coatings limit the practical application of all but D4. Equivalent 10-year life of multi-layer packages has been demonstrated in accelerated weathering tests.

PS+TF-WeP2 Tuning the Material and Electrical Characteristics of ZrO_2 Film Obtained by Plasma Enhanced Chemical Vapor Deposition, *B. Cho, **J.P. Chang***, University of California, Los Angeles

ZrO_2 was investigated as a dielectric to replace SiO_2 for dynamic random memory (DRAM) capacitor. ZrO_2 films were deposited on p-Si (100) wafers by ECR-PECVD using zirconium tetra-tert-butoxide ($Zr(OC_4H_9)_4$)) as an organometallic precursor, Ar to carry the precursor vapor, and O_2 as oxidant. We used optical emission spectroscopy (OES), Langmuir probe, and quadrupole mass spectrometry (QMS) to characterize the gas phase. Atomic force microscopy results showed that the ZrO_2 surface was very smooth with rms=1.4 Å as long as O_2/Ar was set to over one. X-ray diffraction showed that the films were amorphous. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry indicated that stoichiometric ZrO_2 film was obtained with various amount of carbon incorporation depending on the electron temperature and the O_2 /Ar. We obtained a linear dependence of the carbon content determined by XPS upon the OES intensity ratio of molecular carbon and atomic oxygen. High resolution transmission electron microscopy was used to observe the interfacial layer formation between the deposited ZrO_2 and the substrate Si. Fourier transform infrared spectroscopy was used to investigate the hydrocarbon composition in the film. The electrical properties of the as-deposited ZrO_2 were assessed by forming Al/ZrO_2/Si capacitor structures. We obtained the maximum dielectric constant of 16 at O_2/Ar=1. C-V curves shifted to higher bias voltage with increasing O_2 /Ar, which indicated more negative fixed charges were introduced into the film as we add more O_2 in the gas phase. We observed that the leakage current density decreased drastically with increasing O_2/Ar. ZrO_2 film at O_2/Ar=4 showed $3.3x10^{-6}$ A/cm^2 at equivalent oxide thickness of 25 Å.

PS+TF-WeP3 RF Inductively Coupled Plasma Assisted Re-sputtering Techniques for Step Coverage Control in sub 0.13µm Structures, *P. Gopalraja, S. Rengarajan,* ***J. Forster****, X. Tang, R. Jauhari, U. Kelkar, A. Chan, M. Schweitzer, K. Miller, A. Bhatnagar, N. Maity, J. Van Gogh, S. Parikh, Z. Xu*, Applied Materials Inc.

A sputter deposition source has been developed that allows the bottom coverage in small structures to be made arbitrarily small, while retaining significant sidewall coverage. This ability is becoming increasingly desirable as copper based back-end metallization schemes in integrated circuits shrink to 0.13µm and below. The reduction in bottom coverage is made possible by utilizing a process, which combines deposition onto and re-sputtering of material from the wafer. The deposition occurs via a partially ionized PVD process, and the re-puttering occurs via a RF inductively coupled plasma assisted re-sputtering process. The hardware components for both deposition and re-sputtering have been integrated into a single chamber. The data presented in this paper will include simulations of plasma characteristics for the re-sputtering process for varying power and pressure conditions, and the correlation of these simulation results with the properties of the thin films deposited. Transmission electron micrographs show bottom coverage arbitrarily close to zero can be achieved in both via and dual damascene structures. Electrical testing on dual damascene structures shows that minimal bottom coverage improves via resistance, and that substantial sidewall coverage improves stress migration and electro-migration properties.

PS+TF-WeP4 Plasma Enhanced Chemical Vapor Deposition of SiO_2 Films from Tetramethylcyclotetrasiloxane and Dimethyldimethoxysilane, ***J. Zhang****, E.R. Fisher*, Colorado State University

The deposition of SiO_2 films from novel alkoxysilane/O_2 and alkoxysilane/N_2O plasmas has been investigated using tetramethylcyclotetrasiloxane (TMCTS) and dimethyldimethoxysilane (DMDMOS). The films were analyzed with Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy, and spectroscopic ellipsometry. For both the precursors, deposition rates and hydrocarbon incorporation in the SiO_2 films decrease with addition of O_2 or N_2O. High quality SiO_2 films can be deposited when the ratio of oxygen atom to precursor is equal or higher than the reaction stoichiometric ratios, i.e., 20:1 for TMCTS and 14:1 for DMDMOS. The effects of rf power and substrate position in the reactor on film quality are also examined. Gas phase species in these plasmas were studied with mass spectrometry and correlated with film characteristics. Moreover, with the imaging of radicals interacting with surfaces (IRIS) method, the surface reactivity of OH in these plasmas was measured as a function of O_2 or N_2O addition and rf power. The role of OH in deposition of SiO_2 films from TMCTS and DMDMOS based plasmas will be presented and compared to previous results for OH in TEOS/O_2 plasmas.[1]

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PS+TF-WeP5 Evaluation of PFC Emission Reduction for PE-CVD Chamber Cleaning with Measurement and Simulation, ***E. Wani****, K. Kosano, T. Sunada, S. Okura, Y. Mitsui, K. Sakai, T. Beppu,* Research Institute of Innovative Technology for the Earth (RITE), Japan, *A. Sekiya*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of perfluorocarbons and other fluorinated compounds (PFCs) emission from PE-CVD chamber cleaning is one of the urgently required issues in the semiconductor manufacturing for the prevention of global warming. There are mainly three approaches such as the optimization of traditional cleaning processes, the development of alternative gases and the development of alternative cleaning processes. In our recent study, COF_2 has been suggested as a potential alternative cleaning gas.[1] Various methods for the emission reduction have been investigated from the aspects of the alternative gas, process and tools. The process condition optimization is a common requirement to induce best performance for all these investigations. Recently, a simulation tool for the Capacitively Coupled Plasma (CCP) source has been developed and is now commercially available. In this study, the emissions from CCP of C_2F_6 as well as COF_2 have been simulated and the results have been compared with the ones measured by Fourier transform infrared spectroscopy (FT-IR) and Quadrupole mass spectroscopy (QMS), which were equipped after the dry pump. Both results showed that CF_4 emission from COF_2 is less than that of C_2F_6. The discharge in the CVD chamber was also observed using optical emission spectroscopy (OES) and FTIR. The results have been also compared with the ones simulated. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

[1] Y. Mitsui et al., ISESH 2001, June 17-21, 2001.

PS+TF-WeP6 Eliminating the Hysteresis Effect for Reactive Sputtering Processes, *T. Nyberg,* ***S. Berg***, Uppsala University, Sweden, *U. Helmersson*, Linkoping University, Sweden

Despite that reactive sputtering has existed for more than 50 years, increasing the pumping speed to unrealistically high values is so far the only reported way of eliminating the hysteresis effect for planar magnetrons. The cause of the hysteresis effect is a complex interaction between target sputter erosion and the gettering of the reactive gas on the target and coated surfaces. These relations are not yet fully understood. By computer process modeling, however, we have developed a theoretical model capable of predicting the complex correlations between these involved parameters. By process modeling it is possible to carry out ”virtual processing” to predict processing results for unexplored ways of carrying out processes. By reducing the size of the target sputter erosion zone below a critical value, simulations predicted that it should be possible to completely eliminate the hysteresis. This was also experimentally verified for the reactive sputtering of Al in an argon/oxygen atmosphere. Moreover, there is almost no loss in compound deposition rate as compared to sputtering from a traditionally designed target. Notice that an increase of the total target current using a large sputtering erosion zone will not eliminate the hysteresis. The fundamental explanation to this behaviour as well as experimental verification will be presented.

PS+TF-WeP7 In situ Measurement of C_2 Radical Density in Microwave-Enhanced Methane/Hydrogen Plasma Used for Nanocrystalline Diamond Film Growth, ***M. Hiramatsu****, K. Kato, K. Ito,* Meijo University, Japan, *C.H. Lau, J.S. Foord*, University of Oxford, UK

Conventional plasma-enhanced chemical vapor deposition (CVD) methods for diamond fabrication normally employ high-pressure (≥10 Torr), and methyl (CH_3) radicals are generally known to be important species for diamond formation. On the other hand, nanocrystalline diamond films were grown using fullerenes in a microwave argon plasma without addition of hydrogen. It was suggested that carbon dimer (C_2) radicals also might play an active role in conventional hydrogen-activated CVD. In the present work, C_2 radical density at the lowest excited state was measured in an ASTeX style conventional microwave plasma reactor with a CH_4/H_2 mixture using absorption spectroscopy. The Xe lamp emitting a continuous spectrum was used as a light source, and transmittance spectra through the plasma ball were obtained around 516.5 nm of (v' =0, v'' =0) bandhead of C_2 Swan system. Measurement was carried out under the conditions where nanocrystalline diamond films can be formed. At the typical growth conditions for the microwave plasma-enhanced CVD reactor used for nanocrystalline diamond film formation, the C_2 radical density in the plasma ball was of the order of 10^{12} cm^{-3}. The emission intensity of (0, 0) bandhead of C_2 Swan system was also measured. It was found that the emission intensity correlated linearly with C_2 radical density. C_2 radical density in the plasma ball under the condition where predominantly diamond can be formed was estimated to be 10^{10} - 2 x 10^{11} cm^{-3}.

PS+TF-WeP8 Effect of NO Radical Produced by Additives to PFC on Global Warming during PECVD Chamber Cleaning Using a Remote ICP Source, ***J.H. Kim****, C.H. Oh,* Sungkyunkwan University, Korea, *S.S. Yoon,* Jusung Engineering Co., Ltd., Korea, *N.-E. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

N_2, N_2O, and NO were added as additive gases producing NO radical to C_4F_8/O_2 during PECVD(plasma enhanced chemical vapor deposition) silicon nitride chamber cleaning and the effects of these additive gases to the PECVD silicon nitride cleaning have been investigated. For plasma cleaning, a remote ICP(inductively coupled plasma) source was used and cleaning rate, DRE(destruction efficiency), and MMTCE(million metric tons of carbon equivalent) were investigated as a function of gas mixture ratio, working pressure, rf source power, and flow rate. Using this ICP source, high DRE more than 95% could be obtained for all of the investigated conditions due to the high dissociation of the feed gases. Adding N-based additive gases and O_2 to C_4F_8 not only significantly increased the cleaning rate by the surface reaction of NO radical generated by these additive gases but also decreased the MMTCE by decreasing the emitted CF_4 concentration which has the highest concentration among the emitted PFCs (perfluorocompounds) in addition to the high global warming potential. C_xF_y is believed to decrease through the reaction between nitrogen from the additive gases and fluorine or carbon in C_xF_y from the dissociated PFCs. In this experiment, remaining feed gas and emission species such as CF_4, C_3F_8, C_2F_6, COF_2, etc. were detected at the exhaust line during silicon nitride cleaning by FT-IR(fourier transform - infrared spectrometer). Also, F and NO radicals were observed by OES(optical emission spectroscopy) and QMS(quadrupole mass spectrometer) at the chamber.

PS+TF-WeP9 TaN Diffusion Barriers by Chemical-Enhanced Physical Vapor Deposition (CEPVD), ***N. Li**, J.P. Allain, D.N. Ruzic,* University of Illinois, Urbana-Champaign

Ta and TaN films deposited by physical vapor deposition (PVD) or ionized PVD (iPVD) are widely used as a conducting diffusion barrier layer in ultra-large scale integrated (ULSI) devices to prevent migration of Cu into adjacent dielectrics. While PVD films lack the highly conformal sidewall coverage of chemical vapor deposition (CVD) or metalorganic CVD (MOCVD), they offer high density and low resistivity desired for optimum barrier performance. Since the parameter space of PVD is quite different from CVD, getting the best attributes of both methods is problematic. We describe a novel process called chemically-enhanced physical vapor deposition (CEPVD) that, by the addition of a proper amount of precursor in the vicinity of the substrate, has the potential to deposit films with PVD quality and CVD step coverage. A Ta target is sputtered in a magnetron system with the Ta-containing metal-organic precursor vapor, TBTDET, in combination with a reactive (N_2) carrier gas and an RF-powered secondary ionization plasma. In this preliminary experiment, planar films were deposited on silicon wafers at different pressure, RF incident power, substrate temperature and bias voltage. The ionized metal deposition conveys significant energy to the surface through bombardment, promoting film adhesion and generating films of stable crystallographic orientation. In addition the ion bombardment enhances the impurity volatilization and reduces the substrate temperature needed for chemical decomposition. Deposition rate and ionization fraction are measured using a gridded energy analyzer and a quartz crystal microbalance (QCM). Surface morphology are visualized using SEM and AFM; film composition and microstructure are characterized by XPS and XRD, respectively. Resistivity is evaluated by a four-point probe. Extension of the method to patterned structures is also discussed.

PS+TF-WeP10 Two-dimensional Modeling of Charged Particles Transport in Capacitively Coupled Radio-frequency Discharges, ***A. Salabas**,* Instituto Superior Técnico, Portugal, *G. Gousset,* Univ. Paris-Sud, France, *L.L. Alves*, Instituto Superior Técnico, Portugal

Plasma enhanced chemical vapour deposition is often employed to produce chemical active species, using capacitively coupled radio frequency (ccrf) glow discharges driven at 13.56 MHz. Predictions over film deposition rates necessarily pass through the description of charged particle transport in the discharge. The present work describes the transport phenomena in a ccrf reactor using a two dimensional fluid model. The description of charged particle transport is made by solving the continuity and momentum transfer equations for electrons and ions, coupled with Poisson and the electron mean energy equations.[1] The physical model adopts the local mean energy approximation i.e. it computes the electron and energy transport parameters as well as the electron impact collision rates as functions of the electron mean energy. The model writes the electron and energy fluxes in the drift diffusion approximation, including the variation with position of the diffusion coefficient. Ion inertia terms are also considered by generalising the earlier concept of effective electric field.[2] Adequate flux boundary conditions have been employed. The convergence criterion checks the main plasma parameters and assumes steady state solution when relative changes between two subsequent periods are less then 0.001. The model is solved for He, H_2 and SiH_4-H_2 discharges produced within a cylindrical ccrf reactor similar to GEC reference cell, for 68 mTorr - 3 Torr pressures and 100 V - 500 V applied rf voltages. Results concerning non-local phenomena, the influence of silane dilution and reactor geometry are pointed out. In general, comparisons with experimental data indicate that the model improves earlier reported results for some electrical benchmark parameters.

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[2] J. D. P. Passchier and W. J. Goedhee J. Appl. Phys. 74 (6) (1993) 3744.

PS+TF-WeP11 Effect of N-based Additive Gases to C_4F_8/O_2 on Global Warming Gas Emission during Silicon Nitride PECVD Chamber Cleaning Process Using a Remote Plasma Source, ***C.H. Oh**, N.-E. Lee, J.H. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea, *S.S. Yoon*, Jusung Engineering Co., Ltd., Korea

PFCs have been used for CVD chamber cleaning and oxide etching processes. During cleaning and etching processes, the emission of perfluorocompounds(PFCs) into the atmosphere has caused growing concern in the semiconductor industry because of their potential global warming effects. Therefore, the semiconductor industry is proactively seeking ways to reduce PFCs emissions through alternative process chemicals, process optimization, and different abatement technologies including destruction and recovery. In this study, N-based additive gases were added to C_4F_8/O_2 for silicon nitride plasma enhanced chemical vapor deposition(PECVD) chamber cleaning and their effects on the perfluorocompounds(PFCs) emission properties were investigated. We determined an optimum cleaning condition of C_4F_8/O_2 chemistry as a function of processing condition such as additional gas mixture ratio, total gas flow, and working pressure. Under the optimum condition, we quantified the net emission of PFCs during cleaning of silicon nitride using Fourier transform-infrared spectroscopy (FT-IR) and then compared the effects of adding N-based additive gases to C_4F_8/O_2 by evaluating the destruction removal efficiency (DRE) and the million metric tons of carbon equivalent (MMTCE). DRE and MMTCE were calculated by evaluating the volumetric emission. Ar/NF_3 gas mixtures, which are commercially used for PECVD chamber cleaning, were also investigated with the remote plasma source to compare with the results of C_4F_8/O_2/N-based additives gas mixtures. Comparing MMTCE with C_4F_8/O_2/N-based additives and NF_3/Ar in optimum condition, we could obtain similar MMTCE values for each gas mixture. Therefore, it is believed that Ar/NF_3 can be replaced by C_4F_8/O_2/N-based additive gas chemistry using a remote plasma source for the silicon nitride PECVD chamber cleaning.

PS+TF-WeP12 Low-temperature PECVD Thin Film Optical Waveguides, ***G.T. Dalakos**, E.M. Breitung*, General Electric Global Research Center

The ability to process inorganic thin film optical waveguides at low deposition temperatures (room temperature to <200C) allows compatibility with a large range of different material types. Notably, these include low-melting point optical polymers. However, most work in inorganic waveguide fabrication has been at high processing temperatures or involved high-temperature post-processing anneal steps which is incompatible with low-melting point materials. We offer insight into performance degradation, especially in regards to the processing of silicon alloy materials at low substrate temperatures in a conventional Plasma-enhanced Chemical Vapor Deposition (PECVD) setup. Optical loss due to interfacial surface roughness and bulk material absorption are focused on and processing methods to reduce both of these are presented.

PS+TF-WeP14 Feature Profile Evolution during Cl_2 and HBr Plasma Etching of Silicon, *M.O. Bloomfield, T.S. Cale,* ***Y.H. Im***, Rensselaer Polytechnic Institute

As demands for improved IC manufacturing continue to increase, topography simulation of the plasma etching process can help engineers develop easier and less costly process recipes. One of the barriers in achieving this goal is the lack of fundamental understanding of the behavior of energetic ions and reactive neutrals at the plasma-solid interface. We present a simulation study of feature topography evolution under Cl_2 and HBr plasma etching using a deteministic approach. In this work, we use the ballistic transport and reaction model that was presented by Cale and Raupp.[1] Fluxes from the plasma directly to the feature surface, from diffuse re-emission of neutrals from the surface, and from both specular and non-specular reflection of ions are considered. To consider the angular and energy dependence of the etch rate, we use the work of Chang and co-workers.[2] In order to capture the bimodal shape of ion energy distribution, we regard the bombarding ions as the sum of independent monoenergetic species. We consider the ion angular distribution of each monoenergetic species, so that the effect of ion energy distribution on the shape of feature profile can be investigated. We compare the shape of etched feature profiles, some of which exhibit microtrenching, to experimental data for Cl_2 and HBr plasma etching. Our simulations show that the difference in etched profiles can be regarded as due to the different characteristics of the specular reflection and the dependence of the etching yield on incident angle for Cl_2 and HBr plasma. Simulation results are compared with experimental data and Monte Carlo based simulation from the literature.

[1] T.S. Cale and G. B. Raupp, A Unified line-of-sight model of deposition in rectangular trenches, J. Vac. Sci. Technol. B 8 (6), 1990

[2] Jane P. Chang, Arpan P. Mahorowala, and Herbert H. Sawin, Plasma-surface kinetics and feature profile evolution in chlorine etching of polysilicon, J. Vac. Sci. Technol. A 16, 1998

PS+TF-WeP15 Plasma Damage Reduction in PZT Thin Films Etched by Inductively Coupled Plasma, ***K.T. Lim**, D.P. Kim, K.T. Kim, C.I. Kim,* Chung-Ang University, Korea

Ferroelctric lead zirconate titanate (Pb(Zr,Ti)O_3) thin films have been known for their applications in memory devices such as nonvolatile ferroelecric random access memory (FRAM) because of their high dielectric constants and bistable polarization. It is expected that PZT will improve the limitations in storage density encountered in conventional Si memory technology. During the dry etching, the defects, such as physical damage and chemical residue contamination and decomposition, will change the near surface region of the material that is exposed to the plasma and degrade ferroelecric and electrical properties. In this study, PZT thin films were prepared on Pt/Ti/SiO_2/Si substrates by sol-gel processes. Pt top electrodes were deposited on PZT thin films by using rf magnetron sputtering. SiO_2 was deposited on Pt top electrodes. SiO_2 layer was etched in CF_4/Ar inductively coupled plasma with PR mask. We continued etching Pt/PZT/Pt layer without removing PR and SiO_2 patterns. PZT thin films were etched with Ar/Cl_2 inductively coupled plasma. The etch rate is observed by various parameters. We also observed the effect of etching damage in PZT thin films during etching in Cl_2/Ar 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_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 transmission electron microscope (TEM) and x-ray diffraction (XRD). The chemical deformation of etched surface was surveyed x-ray photoelectron spectroscopy (XPS), electron probe micro analyzer (EPMA), auger electron spectroscopy (AES) and TEM-EDS.

PS+TF-WeP16 Effects of Substrate Temperature on the Etching of Silver Films using Inductively Coupled Halogen-based Plasmas, ***S.D Park***, *Y.J. Lee,* Sungkyunkwan University, Korea, *S.G. Kim, H.H. Choe, M.P. Hong,* Samsung Electronics, Korea, *G.Y. Yeom*, Sungkyunkwan University, Korea

Silver(Ag) is one of the potential materials in thin film transistor liquid crystal display (TFT-LCD) because of its lowest bulk resistivity of all metals at room temperature and high reflectivity. Also, it is one of the attractive candidates for the intergrated circuit(IC) manufacturing. Currently, Ag etching is performed using wet etching methods, however, for the fabrication of the high resolution display devices, the use of plasma etching process is indispensable. In reality, there are several problems to be solved before Ag plasma etching to be applied to TFT-LCD processing. The main problems are the formation of involatile etch products, low etch rates, and high surface roughness after removing the etch products. For example, many works on Ag etching using halogen-based plasma have been studied, however, slow etch rates lower than 100nm/min and a thick involatile Ag etch products remaining during the etching were reported. Therefore, in this study, using an inductively coupled halogen-based plasma, the effects of substrate temperature were investigated to obtain higher Ag etch rates without remaining any involatile etch products. The results showed that when the substrate temperature was increased above 70°, the etch rate higher than 250nm/min could be obtained and, when Ar is added to halogen plasma, Ag etch products were effectively removed during the etching because of the increase of sputtering effect of etch products. To understand have the Ag etching characteristics, the optical emission spectroscopy(OES) and X-ray photoelectron spectroscopy(XPS) have been used and measured as a function of gas combination and substrate temperature. Also, a scanning electron microscope(SEM) was used to observed as-etched Ag surfaces.

PS+TF-WeP18 A Study of Sapphire Etching Characteristics using Magnetized Inductively Coupled Plasmas, ***C.H. Jeong***, *D.W. Kim, H.Y. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

Sapphire substrate is attractive material because of its superior mechanical and corrosion property. It has been widely used as the substrate for GaN epitaxial growth and as insulating layer due to its high chemical stability, thermal stability, and dielectric property. On the other hand, it is known to be difficult for other processing such as etching and cutting due to the chemical and high thermal stability, the high hardness of sapphire itself, and the differences in the crystal orientation for GaN on sapphire. In this study, (0001) sapphire wafers were etched using magnetized inductively coupled plasmas(MICP) and their etch characteristics were compared with those by non-magnetized conventional inductively coupled plasmas(ICP). The use of Helmholtz type axial electromagnets around the chamber wall increased the sapphire etch rates while decreasing etch uniformity. By using both multi-dipole permanent magnets and axial electromagnets around the chamber wall, the etch uniformity could be improved while maintaining high sapphire etch rates. The sapphire etch rates close to 700nm/min which are higher than those etched using the conventional ICP could be obtained with optimized MICP conditions. The effects of etch parameters such as axial electromagnetic field(0 - 40Gauss), inductive power(600 - 1600Watts), and bias voltage(-100 - -300Volts) on the sapphire etch characteristic such as etch rates and etch selectivity over photoresist were investigated. The gas chemistry were maintained at 81%BCl_3/9%HBr/10%Ar, respectively. The etch mechanism of sapphire in MICP was investigated by plasma diagnostics using optical emission spectroscopy(OES) and quadrupole mass spectrometry(QMS) during the sapphire etching and by surface analysis using X-ray photoelectron spectroscopy(XPS) after the etching. The etch profile was observed as a function of process parameters by scanning electron microscopy(SEM) before and after etching the samples.

PS+TF-WeP19 Improvement of Etching Sub-micron Photonic Structure by Enhanced-inductively Coupled Plasma (E-ICP), *S.B. Jo,* ***B.H. O***, Inha University, Rep. of Korea, *Y. Fainman,* University of California, San Diego, *S.G. Park, S.G. Lee, E.H. Lee,* Inha University, Rep. of Korea

Photonic crystals have attracted broad range of interests due to fascinating control power of light propagation in photonic devices. As it is important in photonic devices to have optical surface smoothness and high accuracy of critical dimensions, it is not simple to fabricate photonic crystals with sub-micron period. It is required to minimize surface smoothness and to have highly anisotropic etch profile in order to achieve high fidelity fabrication of photonic crystal structures. In this study, we have fabricated a silicon-oxide sub-micron grating for 1D-photonic crystal structure by plasma etching method. A simple periodic grating structure with a period of sub-wavelength of a light is a kind of one dimensional photonic crystal with a special purpose. The characteristics, such as etch profile and surface roughness, are improved in enhanced inductively coupled plasma (E-ICP) technique compared to normal ICP technique. PMMA as a mask of a fine-grating patterning is patterned by a E-beam lithography. Sub-micron grating patterns have been successfully transferred into silicon-oxide layer with high etch rate over 350 nm/min, at the optimized condition of an E-ICP mode. The vertical angles are about 90Â° and the surface roughness is less than 20 nm as seen in a scanning electron microscope (SEM) images.

PS+TF-WeP20 Inductive Coupled Cl_2/Ar Plasma: Experimental Investigations and Modeling, ***A.M. Efremov***, Ivanovo State University of Chemistry & Technology, Russia, *D.P. Kim, C.I. Kim*, Chung-Ang University, Korea

Inductively coupled plasma in Cl_2/Ar mixtures is a widely used in microelectronics technology. The main aim of the current work was to investigate the influence of external process parameters (gas pressure and flow rate, input power density, mixture content) on internal electro-physical properties (EEDF, electron drift rate and average energy) and on a kinetic characteristics of neutral and charged active particles formation and decay (kinetic and transport coefficients). Investigations were carried out in ICP 13.56 MHz system under such condition as: gas pressure 10 - 30 mTorr, total gas flow rate 10 - 20 sccm and input power density 0.1 - 0.2 W/cm^3). Analysis was carried out using both experimental and mathematical modeling technique. Experimental part included investigations using OES spectroscopy and actinometry, langmuir probe measurements and QMS analysis. Modeling algorithm was based on the simultaneous self-consistent solution of Boltzmann kinetic equation together with the balance kinetic equation of neutral and charged particles formation and decay in a quasi-steady-state approximation. A main mechanisms supporting chlorine atoms formation and decay both for volume and heterogeneous processes were analysed including a stepwise dissociation involving an excited "heavy" particles (Ar metastable atoms). A stationary mass content of plasma volume including neutral (ground-state and excited atoms and molecules) and charged (electrons, positive and negative ions) was determined under the various external process conditions.

PS+TF-WeP22 Improvement of ITO Etch Rate and Uniformity by Enhanced-ICP Technique, *C.W. Kim,* ***S.B. Jo***, *B.H. O, S.G. Park*, Inha University, South Korea

Indium-tin-oxide(ITO) is now being used widely as a transparent electrode with high optical transmittance and excellent electrical conductivity. As the wet etch technique of ITO has several problems, such as isotropic etch profile and etch rate dependent film characteristics, dry etch technique has been applied to form ITO film-electrodes. Although the dry etch technique of ITO with organic gas chemistry provides good anisotropic etch profile, it has the problem of low etch rate. And as the size of applicable substrate, such as for the flat panel display(FPD), increases, the uniformity of etch rate on large area becomes one of the most important issues. Here, we report improved etch characteristics of ITO on large area by applying the 'Enhanced-ICP'(Inductively Coupled Plasma) technique with an appropriate design of experiment (DOE), based on Taguchi method, to obtain better etch rate with organic gases. The unit ICP antenna for large area plasma source is arrayed to form 2x2. The etch rate of ITO with E-ICP operation showed improvement of about 50% than normal-ICP operation, as consistent to the previous report for the photoresist etch by E-ICP operation. A better etch uniformity is also obtained on 350x300mm substrate with E-ICP operation.

PS+TF-WeP23 Modeling of Etch Profiles in RF biased Inductively Coupled Plasma Etching Reactor, ***C.D. Wang***, *B. Markland, D. Malanaric, E. Brown, D. Galley,* ATMEL, *B. Abraham-Shrauner*, Washington University, *R. Hoekstra*, Sandia National Laboratories

Knowledge of the ion angular distribution at the wafer plane in an etching plasma is critical for modeling the etching profiles. The etching profile is an evolution of etch surface in time. The evolution equation can be expressed in terms of etch rate. This paper illustrates that the etching profile can be obtained by considering both the ion energy distribution (IED) and ion angular distribution (IAD). These distributions were generated using the Hybrid Plasma Equipment Model and Plasma Chemistry Monte Carlo Model for a Lam TCP plasma etching reactor. The points from the distribution function simulations are divided into different sets in terms of incident angles of ions. Due to the noisy characteristics of simulated data, a smoothing technique is implemented. Each set of smoothed data is fitted with multiple terms of the analytical expression for the drifting Maxwellian distribution functions. These etch rates manifest a proportional relationship with the ion energy flux of experimental evidences by Ding et al.. A statistical optimization technique is utilized here for extracting three parameters: ion temperature, ion density and ion drift energy from each set of the ion drifting Maxwellian distribution functions. By using these crucial parameters, an etch profile is obtained.

PS+TF-WeP24 Impact of Pattern Density on Characterization of Critical Dimension

X. Xu, *E. Croffie*, *M. Garza*, LSI Logic Corporation

The plasma etch of polysilicon is the most critical step in the fabrication of integrated circuits with submicron features since the critical dimension of polysilicon, which is typically used as gates, affects the speed performance of microelectronics devices. The characterization of polysilicon plasma etch can be varied by a global pattern density (called the loading effect) and a local pattern density (called the microloading effect). The etch variations, caused by the pattern density, depend on the specific plasma sources and tool configuration. In this work, silicon wafers patterned with photo resist on a stack of N-doped polysilicon and silicon dioxide have been etched on Lam 9400 DFM etching system in order to investigate the effects of pattern density on critical dimension (CD) and CD bias. The global density is obtained by varied dummy sizes and densities. The local effect is obtained by a large area with a certain polysilicon density and narrow isolated and dense lines at different distances from the large area. It has been found that the impact of global and local polysilicon densities with our new recipe on the tool is small compared to our old technology. In addition, the corresponding plasma chemistries have been studied by the Hybrid Plasma Equipment Model (HPEM).

PS+TF-WeP25 Effects of Ion Bombordment on Developed Photoresist during RIE Processes for sub 0.25 micron Semiconductor Devices

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The use of advanced resist systems has become necessary for lithography in processing of advanced (sub 0.25 Âµm) semiconductor devices to achieve acceptable image quality. These novel resist systems are more sensitive to both post exposure treatments as well as the ion bombardment component present in reactive ion etch (RIE) processes. We discuss the impact of resist interactions with low energy plasma and morphological changes in the resist profile. In particular, the effects of different photoresist constituents, post develop bake conditions, various RIE steps and RIE parameters in capacitively coupled plasma (CCP), magnetically enhanced RIE (MERIE) and inductively coupled plasma (ICP) systems on resist morphology and the quality of final etched images are presented.

PS+TF-WeP26 Characterization of RIE Lag Scaling In Oxides

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Recent advances in ultra large-scale integration (ULSI) have typically depended on reductions in etched feature size. This has motivated efforts to find etch processes that will precisely etch increasingly smaller features while retaining the ability to etch larger features. As feature sizes push below 0.25 µm, reactive ion etch (RIE) lag control becomes increasingly important. Knowing how RIE lag scales with feature size for a given process aids in determining if that process must be discarded and a new one developed. In those situations where a process cannot be discarded, an understanding of RIE lag scaling aids in predicting fabrication difficulties for a given device design. Using a minimal set of initial assumptions, it is shown that a relationship can be derived which relates etch rate to the time development of the feature aspect ratio. It is then shown that this relationship can be used to derive an expression for the etch depth as a function of time and feature size. The assumptions made are justified by phenomenological observation rather than by an assumed mechanism. This approach enhances the generality of the results obtained, thus making them useful for a variety of practical etch engineering applications.

PS+TF-WeP27 The Etching Mechanism of Au Thin Films in Cl$_2$/Ar High Density Plasma

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Au is employed extensively in the electrodes of high dielectric capacitors or in compound semiconductor devices, principally because of its high electrical conductivity and its property of relative chemical inertness. Since the report of Au thin film etching has a few, we studied the etch characteristics of Au thin films by using high density plasma etching system. In the study, Au thin films were etched with a Cl$_2$/Ar gas combination in an inductively coupled plasma. The experiment was done by controlling the etching parameters such as gas mixing ratio, radio frequency power, direct current bias, and chamber pressure. The surface reaction of the etched Au thin films was investigated with x-ray photoelectron spectroscopy (XPS) using narrow scan spectra. Ar ion bombardment is more dominant than chemical reaction between Au and Cl. The results of secondary ion spectrometer (SIMS) analysis were the same as results of XPS analysis. In addition, optical emission spectroscopy (OES) were investigated to analyze radical density of Cl and Ar in plasma. The profile of etched Au investigated with scanning electron microscopy (SEM).

PS+TF-WeP28 Reduction of Particle-contamination in Plasma Etching Equipment by Dehydration of Chamber Wall

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For reduction of particles sticking on the wafers in the poly-gate (WSi/poly-Si) etching by real transfer coupled plasma (TCP) equipment, we have investigated the behavior and the outbreak of particles above the wafers by using laser light scattering method. Numbers of particles on the wafers were also investigated by wafer-level inspection machines. Most particles were observed at rf power turned-off in case of the process gas containing fluoride. The main composition of particles were Al and F. And upside of the process chamber wall coated with Al$_2$O$_3$ was corroded. Therefore it was inferred that these particles were generated by a reaction of the fluoride gas and Al$_2$O$_3$ surface. Moreover, numbers of particles above and on wafers were drastically increased after the wet cleaning of the chamber wall . It showed that the reaction of generating particles was activated by moisture. From the knowledge, dehydration process inserted after wet cleaning of a process chamber achieved the particle-contamination reduction. In the conventional maintenance, it took 30 hours to reduce the number of particles until acceptable quantity after wet cleaning. However it was shorten to 2 hours by inserting dehydration process.

PS+TF-WeP29 Shallow Trench Isolation Etch for Sub 0.10 µm Applications

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As feature size continues to shrink to sub 0.10µm and below, photoresist thickness is becoming steadily thinner, and the migration to 193nm resist is beginning. We have developed resist mask and hard mask etch processes, which address the challenges posed by these small feature sizes. Both processes are in situ, with the mask open and trench etch performed in the same chamber, increasing throughput and lowering the cost of ownership. For customers who require near zero nitride loss, the resist mask approach allows the continuation of current integration schemes; by protecting the nitride throughout the trench etch. The process is tunable from 78-88 degrees, and incorporates both top corner and bottom corner rounding in order to minimize leakage current and stress related defects. The resist mask process will eventually run into limitations when resist thicknesses approach 3000Å, especially when 193 nm resist is used, driving STI etch toward the hard mask approach. For customers making a transition from a resist to a hard mask STI etch, it is important to maximize the selectivity to the nitride hard mask in order to minimize the impact on the integration scheme. We have developed a hard mask process, which is highly selective to nitride (>40:1) and tunable from 78-88 degrees. Bottom corner rounding and top corner rounding schemes are incorporated. In addition, the process is HBr free, eliminating the corrosion associated with Br condensation.

PS+TF-WeP30 Silcon Etching in High-Denisty Plasmas, Revisited

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The ECR-microwave plasma etching of silicon with chlorine is revisited using the enhanced capabilities of supersonic pulse, plasma sampling mass spectrometry. Using a new orthogonal injection time-of-flight mass spectrometer, it is now possible to measure the relative concentrations of both etch products, such as SiCl, SiCl$_2$, SiCl$_3$, and sputtered species, such as Si$_2$Cl, Si$_2$Cl$_2$, and distinguish them from species formed in the gas phase as a function of plasma conditions.

Surface Science
Room: Exhibit Hall B2 - Session SS-WeP

Surface Science Poster Session

SS-WeP1 Study of Polymethylmethacrylate Removers for Electron Beam Lithography through Quantitative Surface Roughness Characterization by AFM, ***Q. Hang***, *D. Hill, G.H. Bernstein*, University of Notre Dame

As nanotechnology approaches molecular scales,issues of surface contamination by unremoved resists will play an important role in device fabrication. Electron beam lithography (EBL) of polymethylmethacrylate (PMMA) resist is still among the most widely used nanofabrication techniques, so it is relevant to study its residual contamination on both exposed and unexposed surfaces using a variety of resist removers. Besides preventing good metal adhesion, the resulting contaminant-induced surface roughness reduces the ability to characterize deposited molecular patterns by atomic force microscopy (AFM). We are aware of no systematic, quantitative study of surface roughness after removal of PMMA by different solvents toward determining the least amount of residual resist. The ideal stripper exhibits high affinity for both the polymer (as quantified by the lowest Flory-Huggins interaction parameter) and the substrate, the latter aimed at reducing the solid-liquid surface energy. We characterized the effectiveness of several different strippers: acetone, dichloromethane (DCM), a mixture of acetone and DCM (volume ratio 1:1), 1,2-dichloroethane (DCE), a mixture of acetone and DCE (volume ratio 1:1), and the commercial PMMA remover Nano™ Acryl Strip (MicroChem), on two different molecular weights of PMMA. Environmental AFM was used to investigate SiO_2 surfaces before and after PMMA was applied and removed by those strippers. The effects of electron beam exposure of the PMMA will also be presented. Power spectral density and root mean square surface roughness analyses showed that DCM and DEC are the best PMMA removers, and can produce the same surface roughness as the original SiO_2 surface (i.e. no contamination). Estimates of the polymer-solvent, Flory-Huggins, interaction parameters and surface-solvent interfacial energy (from contact angle measurements) satisfactorily predict the effectiveness of the solvents.

SS-WeP2 Functionalization and Patterning of C-H Containing Surfaces Using Oxalyl Chloride, ***G. Husseini***, *E.T. Sevy, M.C. Asplund, M.R. Linford*, Brigham Young University

Functionalized and patterned surfaces are of great utility in a variety of areas of science and technology. One particularly useful functional group is the acid chloride, which readily reacts with amines and alcohols. Here we describe a facile gas-phase method of patterning acid chloride groups onto C-H containing surfaces. Basically, a surface that contains C-H groups, e.g., alkylated silicon or polyethylene, is introduced into a flow-through cell that has a quartz window. A mixture of N_2 carrier gas with a low concentration of oxalyl chloride then flows through the cell at room temperature. The surface is next illuminated with 365 nm light, which is known to cause dissociation of oxalyl chloride. Surface reactions then occur that introduce the -COCl group onto the surface where the surface was illuminated and nowhere else. In particular, clean silicon surfaces are first alkylated with dimethyloctadecylchlorosilane. Acid chloride groups are then introduced onto the surface as mentioned above, followed by characterization using XPS, FTIR, ellipsometry and contact angle goniometry. XPS confirms the presence of chemically shifted carbon. FTIR confirms the presence of carbonyl groups. Optical ellipsometry shows an increase in film thickness. Contact angle goniometry shows a decrease in water contact angles. The main advantage of this work is that silicon surfaces can be easily derivatized with an acid chloride in a one-step-photochemical-gas-phase reaction. We are in the process of extending this work to perform photolithographic patterning of surfaces. The resulting functional groups can be used to attach molecules, including biomolecules such as DNA and peptides.

SS-WeP3 Functional Group Effects on the Adsorption of Organics on Silicon Surfaces, ***S.M. Casey***, *L. Zhang, A.J. Carman*, University of Nevada

Computational studies have been undertaken using density functional theory and cluster models of the Si(100) surface in order to compare the adsorption pathways for small organic molecules that contain different functional groups. The efficiency of nitrogen-addition via the amine group can thus be compared to the efficiency of [2+2] cycloaddition via the alkene group or oxygen-addition via the alcohol group in this manner. By variation of the functional group, the relative reactivity of these groups with the silicon surface dimers can be surmised. Both nitrogen-addition and oxygen-addition appear to be favored adsorption pathways compared to the [2+2] cycloaddition pathway. A clear preference between the two addition channels is more difficult to determine, however. The results from these computations compare favorably with results from experimental studies of the adsorption of allyl amine, propanamine, allyl alcohol, propanol, propene, and 3-amino-1-propanol on this surface.

SS-WeP4 The Formation and Segregation of Carbon at a Ni(111) Surface, ***H. Nakano***, *J. Ogawa, H. Hirashima, J. Nakamura*, University of Tsukuba, Japan

The formation and segregation of carbon at Ni surfaces are important as initial processes for synthesis of carbon nanotube by Ni catalysts. We have studied the carbon formation by the Boudouard reaction (2CO --> C + CO_2) and the decomposition of ethylene (C_2H_4 --> 2 C + $2H_2$) using scanning tunneling microscopy (STM), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). It was found that the behavior of the carbon deposition was very different between the Boudouard reaction and the ethylene decomposition. As for the Boudouard reaction, the carbon was formed at step edges on Ni(111), which immediately diffused into the bulk at 400 - 500 K. The carbon dissolved in the bulk then segregated to the subsurface at low temperatures of 300 - 400 K. The segregation rate was greater at lower temperatures. A single domain of carbide islands located along the step edges was clearly observed by STM, which was explained by the growth of the island initiated at the step edge. On the other hand, no such segregation was found for the carbon formation by the decomposition of ethylene. The decomposition took place on the terrace leading to an isolated unit or carbide short strings without forming islands. The difference in the decomposition behavior was ascribed to that in the site of carbon formation. That is, CO should dissociate at the step edge on Ni(111), while ethylene should decompose to carbon at the terrace site. We have also examined the effect of sulfur upon the carbon formation on Ni(111). Interestingly, no significant poisoning effect was observed upon the formation rate of carbon for both Boudouard reaction and ethylene decomposition.

SS-WeP5 Surface Characterization of Dendrimer-Encapsulated Pt Nanoparticles, ***B.T. Long***, *F. Parsons, J. Gao, C. Murphy, D.A. Chen*, University of South Carolina

The ability to prepare metal nanoparticles with narrow size distributions has many potential applications in the field of heterogeneous catalysis. Platinum nanoparticles with uniform size distributions can be prepared from solution in the presence of poly(amidoamine) generation 4 starburst dendrimers. The resulting Pt nanoparticles have diameters of ~1.5 nm and are encapsulated by the dendrimers. These dendrimer-encapsulated metal nanoparticles have been spin-coated on mica and Au surfaces and imaged by tapping mode AFM and STM. At higher concentrations, the surface is covered by a single-layer dendrimer film while at lower concentrations, dendrimer aggregates are observed. Our goal is to remove the dendrimers from the Pt particles, which can then be used for catalytic studies. Thermal gravimetric analysis experiments have shown that the dendrimer begins to decompose at approximately 200°C, but decomposition is not complete at temperatures below 400°C. Ultrahigh vacuum studies will be used to further address the decomposition of the dendrimers. Specifically, the species that remain on the surface at various stages of dendrimer decomposition will be characterized by X-ray photoelectron spectroscopy. Gaseous products that desorb from the surface during decomposition will be monitored by temperature programmed desorption.

SS-WeP6 Dimethyl Methylphosphonate Reaction on Metal Nanoparticles Deposited on a TiO_2(110)-(1x2) Surface, ***J. Zhou***, *K. Varazo, D.A. Chen*, University of South Carolina

The thermal decomposition of dimethyl methylphosphonate (DMMP) on supported copper and nickel nanoparticles has been investigated under UHV conditions by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Our STM studies have shown that Cu particles grown on a TiO_2(110)-(1x2) surface at room temperature have a uniform particle size distribution. By annealing the surface to higher temperatures, the particle size can be increased while maintaining narrow size distributions. XPS studies of DMMP adsorbed on small Cu nanoparticles (35 Å diameter) indicate that molecularly adsorbed DMMP is the main species at room temperature. Heating to 350 K results in P-C and P-OCH3 bond scission and the formation of two distinct phosphorous-containing species on the surface. Between 350 K and 700 K, the molecular DMMP continues to decompose, producing methane and hydrogen as the major gaseous products as observed by TPD. Upon heating to 800 K, all of the carbon is removed from the surface, but 30% of the original phosphorous signal is still observed up to 1000 K. DMMP reaction on the titania surface has also been studied. The surface chemistry of DMMP on larger Cu particles (70-100 Å diameter) will be investigated in order to understand if the size of the

Cu particles affects DMMP chemistry. Furthermore, DMMP decomposition on Ni particles of various sizes will also be investigated.

SS-WeP7 S K-edge NEXAFS and S 1s XPS Studies of L-cysteine on Transition Metals, ***Y. Matsumura***, *S. Yagi, Y. Nakano,* Nagoya University, Japan, *E. Ikenaga, S.A. Sardar, J.A. Syed,* Hiroshima University, Japan, *K. Soda,* Nagoya University, Japan, *E. Hashimoto, K. Tanaka, M. Taniguchi*, Hiroshima University, Japan

We have paid attention to L-cysteine [$HSCH_2CH(NH_2)COOH$] and investigated the adsorption behavior on polycrystalline Cu, Mo and Ni substrates by S K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) and S 1s X-ray Photoelectron Spectroscopy (XPS) techniques. The sample was prepared by adsorbing L-cysteine molecules on clean metal surfaces in an aqueous solution at room temperature. Curve fitting of the S K-edge NEXAFS spectra reveals that there is a peak at around 2470eV. The NEXAFS spectra clarifies L-cysteine molecule dissociates for Ni. In the S 1s XPS spectra a sharp peak and a shoulder structure appear at around 2473eV and 2470eV, respectively. The peak deconvolution of the XPS spectra reveals the presence of three S chemical states, which are L-cysteine molecule, thiolate and atomic sulfur. The result of NEXAFS is consistent with that of XPS qualitatively. Keywords: NEXAFS, XPS, L-cysteine, adsorption behavior, Cu, Mo, Ni.

SS-WeP8 Structural, Electronic and Catalytic Properties of Clean and Overlayer-Covered Ir(210), ***I. Ermanoski***, *W. Chen, M.J. Gladys, J.S. Quinton, T.E. Madey,* Rutgers, The State University of New Jersey, *M.D. Ulrich, J.E. Rowe*, North Carolina State University

We report results on the structure, morphology, electronic and catalytic properties of the Ir(210) surface - clean as well as covered with gaseous and metallic overlayers. The atomically rough Ir(210) surface is morphologically unstable: When Ir(210) is covered with more than 0.6 ML of oxygen and annealed, pyramidal facets exposing {110} and {311} surfaces develop on the initially planar surface. We have used a variety of methods to characterize this surface, including LEED, STM and high resolution soft X-ray photoelectron spectroscopy (HRSXPS) using synchrotron radiation. To prepare an oxygen-free faceted surface, we use catalytic CO oxidation at ~500 K to react the oxygen off and "freeze" the surface in its pre-prepared faceted state. HRSXPS has been employed to investigate core-level features of all the surfaces mentioned. The Ir 4f7/2 core levels are fitted with Doniach-Sunjic lineshapes. Surface and bulk peak identifications are supported by measurements at different photon energies (different electron escape depths) and variable photoemission angles. All of the surface components (first, second and third layer peaks) are identified with core-level shifts positioned at higher binding energies with respect to the bulk. This result is in contrast to previous reports of binding energy inversion on the Ir(100) surface. Using TPD we find evidence for structural sensitivity in a surface reaction, i.e. differences in the chemical reactivity of on the planar and faceted surfaces. Overlayers of Pd and Pt exhibit structural changes upon annealing, and HRXPS measurements show changes in the core-level properties of the overlayers. Supported by US DOE and ARO.

SS-WeP9 Surface Stress Induced during the Formation of Alkanethiol Self-Assembled Monolayers on Gold-Coated Cantilevers, ***M. Godin***, *O. Laroche, V. Tabard-Cossa, B. Seivewright,* McGill University, Canada, *P Williams,* Acadia University, Canada, *B. Lennox, P. Grütter,* McGill University, Canada

Functionalized alkanethiol self-assembled monolayers (SAM) have proven to be quite versatile in producing sensing layers that are both selective and reactive to specific target molecules during chemical or biochemical sensing. By self-assembling these sensing layers onto the surface of standard atomic force microscope (AFM) cantilevers, we can design micromechanical sensors that are tailor-made to respond to very specific chemical signals. The surface stress induced at the sensing layer during chemical sensing is directly measured as a deflection of the cantilever.[1] We have developed a new method[2] of obtaining quantitative surface stress measurements from cantilever deflection signals that does not require the knowledge of the cantilever's Young's modulus, which is often difficult to estimate when different sensing layers are used or for commonly used SiN_x. We systematically investigated the self-assembly process of alkanethiol monolayers on gold in order to model the surface stress buildup during chemical sensing, ultimately aiming to optimize the sensor's response. In particular, we studied the kinetics of alkanethiol SAM formation by combining real-time, in-situ, surface stress and thickness measurements. A differential micromechanical sensor was used to measure the surface stress evolution during SAM formation on gold-coated cantilevers from the vapor phase, while thickness measurements were performed by ellipsometry with sub-monolayer sensitivity. Results clearly demonstrate that analyte introduction and cell geometry play a determinant role in the structural development of the SAM, which not only affects the final stress values achieved, but also the kinetics during SAM buildup. Such considerations are crucial when optimizing sensor response through modeling or when comparing results achieved with different sensor systems.

[1] R. Berger et al. Science 276, 2021 (2000)

[2] M. Godin et al. APL 79, 551 (2001).

SS-WeP10 Characterization of Functionalized Thiol-SA-Layers on Au using TP-SIMS and Polyatomic ToF-SIMS, *M. Schröder,* ***J.C. Feldner***, *S. Sohn, H.F. Arlinghaus*, Westfälische Wilhelms-Universität, Germany

Functionalized monolayer substrates provide the basis for biosensor chips and other biorecognition systems. Several factors, such as type of SA layer building molecules, their functional headgroups and the different parameters concerning the immobilization process, influence the physical, chemical and biochemical properties of these substrate surfaces. We investigated different thiol classes, such as alkanethiols, $C_nH_{2n+2}S$, alkanethiol derivatives and aromatic thiols, with different functional headgroups, e.g. NH_2, COOH or OH, immobilized onto Au-substrates. Thiols with functional headgroups could be linked to larger biomolecules such as DNA and proteins in order to design biosensor-chips for diagnostics. To link NH_2-terminated molecules to carboxyllated surfaces, we used 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) to catalyze the formation of an amide bond. Another possibility for linking such molecules to a surface is to bind an NH_2-terminated thiol to the gold and use di-(n-succinimidyl)-carbonate (DSC) as a crosslinking mediator. The different reaction steps were monitored using time-of-flight secondary ion mass spectrometry (ToF-SIMS). We carried out ToF-SIMS measurements on SA-layers of different alkanethiols to investigate the time, concentration, and chain length dependence of the layer formation. Also, the influence of primary ion mass and of primary ion constituents on the secondary ion yield was investigated. With temperature-programmed SIMS (TP-SIMS), we were able to compare the desorption temperatures of different thiols, e.g. alkanethiols and their derivatives, and to investigate the influence of functional headgroups on the surface binding energy. From the obtained data it can be concluded that ToF-SIMS and TP-SIMS are useful techniques for investigating physical properties of SA-layers and for controlling crosslinking reactions to optimize e.g. binding conditions of DNA or PNA.

SS-WeP11 Low Temperature STM Investigation of Halosubstituted Biphenyls on Copper Surfaces, ***L. Bartels***, *B.V. Rao, Q. Zhang*, University of California at Riverside

4,4'-Di-bromo-biphenyl was adsorbed on a Cu(111) single crystal surface in ultra-high vacuum at 25K. The preferred adsorption site and the mobility of the species were investigated. 4,4'-Di-bromo-biphenyl was found to adsorb primarily at step edges on the surface with the long axis of the molecule aligned parallel to the step edge. High-resolution images reveal the individual, substituted benzene rings. Their separation is in good agreement with the value expected from the literature. In contrast, adsorption at nitrogen temperatures does not permit STM investigation of the unreacted species on the surface. STM images are poor and high fluctuations in the tunneling current point to a mobility of the adsorbate beyond the time-scale of the feedback loop. Retracting the tip several nanometers from the sample, the tunneling current does not vanish completely in a reliable fashions. This points to the spontaneous polymerization of 4,4'-di-bromo-biphenyl to long tethers on the surface.

SS-WeP12 Adsorption Behavior of L-cysteine on Transition Metals (Ni, Cu) in Aqueous or Methanol Solution Studied by S K-edge NEXAFS and XPS, ***S. Yagi***, *Y. Matsumura, Y. Nakano,* Nagoya University, Japan, *E. Ikenaga, S.A. Sardar, J.A. Syed,* Hiroshima University, Japan, *K. Soda,* Nagoya University, Japan, *E. Hashimoto, K. Tanaka, M. Taniguchi*, Hiroshima University, Japan

Adsorption behavior of a sulfur-containing amino acid molecule on transition metal surface has been interested in a bio-catalytic and surface reaction fields. In this study, we have studied the adsorption behavior of the L-cysteine amino acid [$HSCH_2CH(NH_2)COOH$] on polycrystalline Ni and Cu surfaces by sulfur K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) and sulfur 1s X-ray Photoelectron Spectroscopy (XPS) techniques. The sample was prepared by scratching the substrate in the aqueous or methanol solution of the L-cysteine at room temperature. In the NEXAFS spectra, a significant difference of the first peak (1s-to-σ^*(S-C)) shape was obtained between two kinds of Ni samples, which were prepared in the aqueous and methanol solutions. Curve-fitting results of the NEXAFS spectra indicates that the L-cysteine on Ni in the aqueous solution dissociates. On the other hand, the L-cysteine in the methanol solution on Ni does not dissociate. Keywords: NEXAFS, XPS, L-cysteine, adsorption behavior, Ni, Cu, aqueous solution, methanol solution.

SS-WeP13 LEED and HREELS Study of Methane Physisorbed on Ag(111), ***M. Sakurai***, *T. Nanba*, Kobe University, Japan

The structure of methane monolayer physisorbed on a Ag(111) surface was observed by LEED. The picture was recorded with suppressed electron current using cooled CCD camera in order to minimize the electron stimulated desorption of adsorbed methane. We have observed that the anomalous feature in the IV curve of very low energy electron scattered from this system at 40K depends on the ambient pressure of methane, with which the physisorbed layer is in equilibrium. By the present measurement, the LEED pattern indicated that the lattice of methane molecules forms hexagonal structure with rotationally commensurate drection with the substrate lattice. The LEED spots were somewhat obscure and had broadened nature in azimuthal direction at the equilibrium conditions; however, they became sharp ones when the substrate was cooled to 25K. We have also performed vibrational spectroscopy of adsorbed methane molecules by HREELS and anomaly in the vibrational excitation cross section (i.e. inelastic IV curve) has been observed. The relation between the IV curve and structure will be discussed.

SS-WeP14 Adsorption and Reaction of NO, CO and O_2 on Cu(100) at Low Temperatures Studied by Infrared Reflection Absorption Spectroscopy, ***C.-W. Yi***, Texas A&M University, *C.M. Kim*, Kyungpook National University, Korea, *D.W. Goodman*, Texas A&M University

The adsorption and reaction of NO, CO, and O2 on Cu (100) have been investigated in the temperature range 21 - 200 K using infrared reflection absorption spectroscopy (IRAS). NO forms dimers within the monolayer and multilayer regime at 21 K. The dimer, in turn, converts to N2O above 60 K. A strong lateral interaction between coadsorbed NO and CO at 21 K results in the NO and CO molecules tilting from the surface normal by approximately 45 degree. CO interacts strongly with chemisorbed dioxygen on Cu(100) within the temperature range 50 - 100 K resulting in the vibrational frequency of CO being blue-shifted by 25 cm-1. These studies provide new insights into the molecular interactions that are precursors to reactions between CO and NO/O2.

SS-WeP15 Artificial Control of Reaction Selectivity in Methanol Oxidation and Ethanol Decomposition on Pt, Pd and Ag Catalysts by Dynamic Lattice Displacement of Thickness Extension Mode Resonance Oscillation, ***Y. Yukawa***, *N. Saito, H. Nishiyama, Y. Inoue*, Nagaoka University of Technology, Japan

Selectivity is a very important factor in heterogeneous catalysis, and it is highly desirable to precisely control it in an artificial manner. We have employed the thickness extension mode resonance oscillation (TERO) of acoustic waves. In the present work, the TERO effects on the selectivity of methanol oxidation and ethanol decomposition on Pt, Ag and Pd catalysts were studied. To change the resonance frequencies of the TERO, four z-cut $LiNbO_3$ single crystals with different thickness of 0.3, 0.5, 1.0 and 2.0 mm were used: the first resonance frequencies were 11.2 MHz for 0.3 mm thick crystal, 7.3 MHz for 0.5 mm, 3.6 MHz for 1.0 mm and 1.8 MHz for 2.0 mm. A Pt, Ag or Pd film was deposited at 100 nm on the crystals. For methanol oxidation on Pt, the major products were CO_2, HCHO and $HCOOCH_3$. The TERO of 3.6 MHz accelerated the production of CO_2 and HCHO, but little $HCOOCH_3$. With increasing rf power, the selectivity for HCHO production increased from 9% without TERO, reached a maximum level of 18% at 0.5 W, and decreased. For the same reaction on Pd, the selectivity increased monotonously with increasing rf power. For ethanol decomposition on a Ag catalyst, the TERO accelerated the ethylene production without affecting acetaldehyde production. With increasing resonance frequencies, the selectivity for ethylene production increased, passed through a maximum at 7.3 MHz and decreased. Laser Doppler measurements showed that the magnitudes of standing waves (lattice displacement) caused by the TERO attenuated monotonously with frequency, whereas the number of the standing waves per area increased remarkably. The dependence of selectivity on the resonance frequency is discussed based on the contribution of the magnitudes and density of lattice displacement.

SS-WeP16 Oxygen Adsorption on Cu-9%Al(111) Studied by LEED and AES, ***M. Yoshitake***, *S. Bera, Y. Yamauchi, W. Song*, National Institute for Materials Science, Japan

Cu-based alloys have been used for electric cables for long time. In the field of microelectronics, Al had been used for electrical wiring. However, it became clear that electro-migration occurs in Al that causes breaking of wires in minute wirings. Due to this problem, Cu wiring is used in most-advanced microprocessors. Cu metal is more corrosive than Al and Cu-based alloys with a small amount of Al is expected to solve problems both on electro-migration and corrosion. The initial stage of corrosion is oxygen adsorption. We studied surface segregation of Al on Cu-9%Al(111) and oxygen adsorption on the surface with/without Al segregation in UHV by LEED and AES. It was found that Al segregates on the surface to form (√3x√3) structure and the structure vanishes above 320C to give (1x1) structure while Al still segregates. The specimen was exposed to oxygen at different temperatures. The amount of oxygen uptake was not structure dependent but temperature dependent. Below 320C, only a small amount of oxygen adsorbed. Between 325 and 600C, oxygen adsorbed surface showed amorphous LEED pattern. The specimen was annealed at 800C after oxygen exposure. When the specimen was exposed oxygen below 600C, the oxygen Auger intensity decreased significantly by annealing and the annealed surface showed (√3x√3) structure at room temperature. When the specimen was exposed to oxygen at 600C, diffused spots developed newly in LEED pattern but the pattern disappeared after 800C annealing while oxygen Auger intensity stayed almost constant. Exposing the specimen to oxygen at 725C resulted in clear spots in LEED pattern, which were attributed to (7/√3x7/√3) structure.

SS-WeP17 The Diffusion of Single CO Molecules and Dimers on Pd(111), *T. Mitsui*, Lawrence Berkeley National Laboratory, ***M.K. Rose***, *E. Fomin*, Lawrence Berkeley National Laboratory and University of California, Berkeley, *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

The diffusion of individual CO molecules on Pd(111) has been studied by scanning tunneling microscopy in the temperature range 40-50 K. By following the random walk motion as a function of temperature an activation energy barrier of 0.116 ± 0.005 eV and a pre-exponential factor of $10^{-3.5}$ cm^2-sec^{-1} were determined. Attractive interactions between CO molecules give rise to the formation of dimers that diffuse as a unit. Diffusion rates for dimers and energy parameters for the pair potential between CO molecules were also obtained. Coadsorbed hydrogen more than doubles the diffusion barrier of CO monomers.

SS-WeP18 Pd adatom-Adatom Interactions on the W (211) Surfaces, ***T.-Y. Fu***, *Y.-J. Hwang*, National Taiwan Normal University, ROC, *T.T. Tsong*, Academia Sinica, Taiwan

Adatom-adatom interactions play an important role in controlling the formation of surface layers, thin film growth and catalysis. Direct observations in the field ion microscope make it possible to determine the probability P(R) of finding two atoms at a separation R at equilibrium on a surface at temperature T. The free energy of interaction F(R) can be obtained from the relation: P(R) is proportional to exp[-F(R)/kT]. On W (211) planes, the interactions of two Pd atoms are studied in following cases: two Pd atoms in the same channel, in two nearest neighboring channels, in two next nearest neighboring channels, and so on. When two Pd atoms are in the same channel, they combine easily to form a dimer of bond length 2.74 Å and the dimer can diffuse along the channel. In the other cases, the oscillatory behaviors of interactions along the channel direction are observed. The more is the number of the separate channels, the smaller is the interaction energy maximum. The energy maximum in the same channel, two nearest neighboring channels, and two next nearest neighboring channels are 37.5 meV, 23.0 meV, and 9.0 meV, respectively.

SS-WeP19 Temperature Dependence of Self-Assembled Pb Domains on Cu(111), ***R. van Gastel***, *N.C. Bartelt, G.L. Kellogg*, Sandia National Laboratories

Pb deposited on Cu(111) organizes into self-assembled domain patterns. [1] It has been hypothesized that stress differences between the Pb/Cu surface alloy-phase and the Pb overlayer phase stabilizes the domains.[1] The domain patterns can be ordered arrays of dots (``droplet" or ``inverted droplet" phase) or alternating rows (``striped" phase). Their structure evolves as a function of Pb coverage. The feature size, area fraction and degree of long range order of the domain patterns also show a strong dependence on temperature. To understand this behavior, we have investigated the temperature dependence of the domain boundary energy by studying the thermal fluctuations of striped patterns. We observed an increase in thermal fluctuations with increasing T. Our measurements show that the boundary energy decreases by a factor three in the temperature range 570 K to 640 K. Since theory predicts that the stripe width decreases with decreasing boundary energy, this observation can explain the observed T dependence of the stripe pattern. The absolute value of the boundary energy provides an estimate of the surface stress - we discuss this number in the context of first principles calculations. We have also measured the change in area fraction with temperature of the surface alloy and overlayer phases. We observe a decrease in area fraction of the surface alloy phase with increasing T. We attribute this change in area fraction mainly to a change in the Pb-density of the alloy phase. This work was performed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

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SS-WeP20 Using Ti Interlayers as an Interface Stabilizer to Promote Epitaxial Growth of Fe on Al(100) Surfaces[1], *C.V. Ramana,* ***R.J. Smith***, Montana State University, *B.S. Choi*, Jeonju University, Korea

An approach is described to promote epitaxial growth of thin metal films on single-crystal metal substrates by stabilizing the interface with an extremely thin metallic interlayer. A single atomic layer of a metal is deposited at the interface prior to the growth of the metal film of interest to produce an abrupt, epitaxial interface in a system that is otherwise characterized by interdiffusion or chemical roughness. The stabilized interface prevents interdiffusion and serves as a template for ordered film growth. Using high-energy He+ backscattering and channeling techniques along with low-energy electron diffraction and low-energy He+ scattering, it is demonstrated that an atomically thin layer of Ti metal deposited at the Fe-Al interface, a system well known for considerable intermixing at room temperature, prevents interdiffusion and promotes the epitaxial growth of Fe films on the Al(100) surface. The resulting structure is observed to be stable for temperatures up to about 200 C.

[1] Work Supported by NSF Grant DMR-0077534.

SS-WeP21 Surface Structural Studies of Epitaxial Ag/Ni/Pt(111) and Ni/Ag/Pt(111) Ultrathin Films, ***C.W. Su***, *Y.W. Chu, H.Y. Ho, C.S. Shern*, National Taiwan Normal University

The introduction of Ag films on the epitaxial x ML Ni/Pt(111) metal surface, x=1-5, as the capping layer Ag/Ni/Pt(111) or the buffer sandwich Ni/Ag/Pt(111) was investigated by means of Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UPS) in UHV. The evidences from monitoring the initial annealing temperature of the Ag/Ni/Pt(111) corresponded to the signals began to decrease in AES show that 1 ML overlayer of Ag retards the bulk diffusion of the Ni atoms toward the Pt substrate. Compared with our previous study,[1] the initial temperatures of the system capped with Ag are higher than those capped without it. As for the behavior of atomic exchange, from Ni/Ag to Ag/Ni, has been observed on the annealed Ni/Ag/Pt(111) surface. Ag atoms migrate to the top at about 400 K and then reach an exchanging equilibrium at a high temperature. The thicker the Ni films, the higher the equilibrium temperature. The variations of electronic valence band by UPS though the annealing processes also attracted ours attention. In additional to the variations of the Fermi edge intensities and of the Ag-Ni hybrid d-band peaks during annealing, an extra peak in UPS appears gradually with the binding energy at about 11 eV on either the spectra of the Ag/Ni/Pt(111) or the Ni/Ag/Pt(111) even the temperature up to 825 K. The heating brought about the changes was contributed to additional chemical adsorption emerged from the surface. The most interesting case was the density of state (DOS) unexpectedly affected by an extra positive or negative bias on the sample. The shift of the UP spectra and the variation of the DOS were also remarkable. Finally, the possible explanations of the phenomena are to be discussed.

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SS-WeP22 The Importance of Pb-Vacancy Attraction on Diffusion in the Pb/Cu(001) Surface Alloy, ***M.L. Anderson***, *B.S. Swartzentruber*, Sandia National Laboratories

Vacancy-mediated diffusion has recently been shown to be a dominant mass transport mechanism on the Cu(001) surface. [1] Not only are vacancies responsible for self-diffusion of surface-layer Cu atoms, but also for diffusion of impurity atoms such as Pd, In, and Pb, embedded in the surface layer. We use atom-tracking STM to measure the diffusion of embedded Pb atoms directly as a function of temperature to extract the diffusion energies. We find a Pb-vacancy attraction that dramatically affects the diffusion statistics. A diffusion event consists of a "burst" of a series of rapid exchanges between an embedded Pb atom and a surface vacancy. The population density of surface vacancies and their migration energy in the Cu surface layer govern the burst-to-burst time interval statistics. Because a single diffusion event entails a number of Pb-vacancy exchanges, the net displacement of Pb is often much more than a single lattice constant. The details of this displacement distribution are measurably affected by the Pb-vacancy interaction. The long length scale of the displacement distribution due to Pb-vacancy attraction is in stark contrast to Pd, which has a repulsive interaction. The energetics extracted from the measurements in comparison with first-principles calculations lead to a better understanding of the driving forces responsible for surface alloy formation and kinetics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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SS-WeP23 Bias Voltage Dependence of Apparent Local Barrier Height at Constant Tip-Sample Separation, ***S. Yagyu***, *M. Yoshitake*, National Institute for Materials Science, Japan

The bias voltage dependence of apparent local barrier height (LBH) corresponding to "work function" at nanometer-scale has been measured by STM on Au (111) surface with Au tip at constant tip-sample separation (CS). The obtained main result is that in the bias voltage range of I-V curve showing nearly straight (ohmic), the LBH does not depend on the bias voltage and beyond this range the LBH decrease with increasing the bias voltage. The bias voltage dependence has been reported at relatively high bias voltage above 1.5 V. However, these reports had been measured at constant current (CC) conditions generally used in STM / LBH measurements. To measure its dependence under CC, the bias voltage is varied, which causes change in separations. In this situation, the measured results contain both effects (bias voltage and separation). Therefore, to measure the effect of bias voltage on LBH truly, the separation effects have to be eliminated. We have measured bias voltage dependence of LBH at CS using the current on I-V curve, and have compared results at CS with CC. At CS measurements, in the ohmic range (below 0.1V), LBH does not depend on bias voltage within the experimental error. Beyond this range, that is off ohmic, LBH decrease with increasing the bias voltage. On the other hand, at CC measurements, the range of I-V curve showing the ohmic and a slightly off the ohmic, the LBH increase with increasing the bias voltage, because of the increasing in separation. Beyond this range, LBH decreases with increasing the bias voltage as CS case, indicating that separation does not affect any more.

SS-WeP24 Electronic Friction at the High T_c Superconductor-Adsorbate Interface, ***X.F. Hu***, *P. Guptasarma,* University of Wisconsin-Milwaukee, *R.W.C. Hansen,* Synchrotron Radiation Center, *C.J. Hirschmugl*, University of Wisconsin-Milwaukee

Electronic friction at a substrate-adsorbate interface can be examined using grazing incidence Infrared Reflection Absorption Spectroscopy (IRAS). Adsorbed molecules provide extra scattering sites for substrate electrons in metallic substrates with electron mean free paths longer than the skin depth. This electron energy loss is observed as a broad absorption feature in the change in reflectivity with and without adsorbates. In superconductors, substrate electrons have varying mean free paths above and below the superconducting transition temperature. We will present IRAS results for CO adsorbed on surfaces parallel to and perpendicular to the ab-plane in near-optimal doped (Tc ~ 95K) large single crystals of $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO). The single crystal was grown by the float-zone technique in an infrared image furnace. Measurements were taken both above and below the superconducting transition temperature at the Synchrotron Radiation Center.

SS-WeP25 An UHV Analytical Tribometer to Evidence Tribochemistry, ***T. Le-Mogne***, *J.M. Martin*, Ecole Centrale de Lyon, France

Increasing demands in the mechanisms of lubricant additives and thin films have resulted in the development of new tribometers coupled with surface analysis techniques. In this paper the so-called AES/XPS analytical tribotester is presented. In-situ surface analyses inside and outside wear scars without air exposure are possible thanks to a tribometer directly installed in the UHV analytical chamber. Two experimental approaches are developed to study the tribochemical reactions of lubricant additives. The first one consists in UHV friction experiments on tribological films previously formed. Thanks to AES and XPS mapping, the good friction reducing properties of molybdenum dithiophosphate (MoDDP) are explained by the formation of MoS2 in the sliding contact. The second one studies the reactivity of fresh surfaces with gaseous compounds which are chemically representative of lubricant additives. Interesting results have been obtained by comparison between 1-hexene and n-hexane on steel at different partial pressures.

SS-WeP26 Coupling of XPS and XANES to Characterize Sulfides in Films Formed from Lubricant Additives, ***M.I. De Barros***, *J. Bouchet, T. Le-Mogne, J.M. Martin*, Ecole Centrale de Lyon, France

The nature and properties of each species formed in both the antiwear action of zinc dithiophosphate (Zndtp) and in the friction reduction of molybdenum dithiocarbamate (Modtc) are investigated. Special attention was carried out to the advantage of coupling two surface analytical techniques on the Zndtp, Modtc and Zndtp/Modtc combination tribofilms: XPS and XANES spectroscopies. XANES is a bulk analysis of the film compared to XPS which is much more surface sensitive. A Cameron-Plint friction machine was used to generate large tribofilm areas in mild/severe tribological conditions. First XANES spectroscopy at the P K-edge, Mo K-edge and S K-edge was carried out in order to investigate any differentiation between phosphate and sulfides. Afterwards, an XPS analysis was performed in the same location of the tribofilm. Special attention has been paid to the deconvolution of Fe2p, Zn2p, S2p, Mo3d and O1s photopeaks and Auger ZnLMM lines. Analytical results are discussed and compared with theoretical predictions from the Chemical Hardness model for Zndtp, Modtc and Zndtp/Modtc tribofilm formation.

SS-WeP27 Scanning Tunneling Microscopy Studies of a $Cu_3Pt(111)$ Surface and Its Dependence on Preparation Conditions, *K.T. Rim, T. Müller, G.W. Flynn,* Columbia University, ***A.V. Teplyakov***, University of Delaware

A single crystal Cu_3Pt (111) sample was studied using Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). The preparation conditions in ultrahigh vacuum have been analyzed by varying annealing temperatures following Ar^+ sputtering on the alloy surface. The STM study reveals that, despite a sharp 1x1 LEED pattern at three different annealing temperatures (825, 845, and 855K), the alloy surface changes from very corrugated to atomically flat over a relatively narrow temperature range. When the sample is annealed at 845K following Ar^+ sputtering, 10-20nm wide terraces are formed and an ordered 2x2 phase is observed. The atomically resolved STM image of the ordered 2x2 surface shows that bright protrusions correspond to Pt atoms surrounded by Cu atoms that appear dark. This ordered 2x2 phase covers approximately 10 - 15% of the surface, and a chemically mixed, disordered 1x1 phase covers approximately 85 - 90% of the surface. The 2x2 ordered phase also exhibits some defects and antiphase boundaries. Along the step edges of terraces, Pt atoms alternate with Cu atoms, and very few Pt-Pt pairs are observed on the terraces. The chemical reactivity of these two distinct surface phases with respect to HCl and 1-hexene will also be described.

SS-WeP29 Studies of Ballistic Electron Emission Microscopy on p-n Junction Structures, ***E.R. Heller**, J.P. Pelz, C. Tivarus*, The Ohio State University

One class of experiments using Ballistic Electron Emission Microscopy (BEEM) makes nm-scale studies of hot-electron transport through a deposited film[1] or 'stack' of metal films (e. g. magnetic multilayers)[2] and/or insulating layers (e. g. magnetic tunnel junctions).[3] For this class of experiments, a high quality (non-leaky) metal/semiconductor Schottky has been required to block thermal electrons. However, desired film deposition techniques (e.g. sputtering) and non-ideal surface preparation often produce very leaky and non-uniform Schottky barriers, making BEEM studies complicated or impossible. We will discuss an alternate approach for such studies which uses a buried pn junction in the semiconductor as the thermal electron blocking layer. We find this permits much higher signal-to-noise for sample structures which are incompatible with good Schottky barriers. By putting the blocking layer inside the bulk of the semiconductor, a leaky or non-ideal metal/semiconductor interface becomes largely irrelevant. A well-designed pn junction still can have low hot-electron attenuation[4] and extremely good rejection of thermal electrons. We will also discuss related on-going approaches which can permit BEEM studies at reduced temperatures with sensitivity down to the aA (10^{-18} amp) level. This work was supported by NSF Grant No. DMR-0076362.

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SS-WeP30 Monolayer Functionalization of Atomic Force Microscopy Tips for Chemical Sensitive Imaging, ***L.W. Zilch**, A.T. Woolley, M.R. Linford*, Brigham Young University

While atomic force microscopy (AFM) provides nanoscale information of surface topology, it is often incapable of detecting chemical differences between regions on surfaces. Thus, the usefulness of this technique increases when the AFM tip is chemically modified so as to perform chemical force microscopy. It is then possible to relate tip forces to both surface topology and chemical interactions between the tip and the surface. We are currently working on modifying silicon AFM tips with a variety of organic monolayers using gas and liquid phase silanes (on silicon oxide) or using 1-alkenes (on hydrogen-terminated silicon). Monolayers are advantageous because they do not substantially degrade the resolution of the technique by increasing the radius of curvature of the tip. After coating the tip with a monolayer we then intend to perform a variety of gas phase reactions in the presence of these coated tips to introduce useful functional groups onto them. Ultimately we intend to create an all gas-phase process for functionalizing AFM tips. We will use the resulting AFM tips to study surfaces that have regions of different hydrophobicities and chemical functionalities. Two suggested substrates for testing these tips are silicon and gold surfaces microcontact printed with silanes and thiols, respectively.

SS-WeP31 Contrast Mechanisms of Secondary Electron Images from Electron, Ion and X-Ray Excitation, ***Y. Sakai**, T. Tazawa, Y. Iijima,* JEOL Ltd., Japan, *C. Nielsen,* JEOL Inc., *T. Ichinokawa,* Waseda University, Japan

The atomic number (Z2) effect of the secondary electron yields for metals was compared by using secondary electron microscope (SEM), secondary ion microscope (SIM) imaging and X-ray photoelectron spectroscope (XPS) imaging. The atomic number (Z2) effect of the secondary electron yields for metals has recently experimented in secondary electron microscope (SEM) and secondary ion microscope (SIM) imaging (1). The Z2 dependence of the secondary electron yields is opposite to each other and the brightness of the secondary electron image by electron bombardment increases with increasing Z2, while the brightness of the secondary ion image by Ga+ or Ar+ ion bombardments decreases with increasing Z2. In this experiment, the Z2 dependence of the secondary electron yields in electron and X-Ray excitation are the same and opposite to that in ion excitation. The brightness of the secondary electron images by X-Ray bombardment increase with increasing Z2. These phenomena have been found by this experiment and compared with a difference of emission mechanisms for electron, ion and X-Ray bombardment for metal. The experiment was carried out by using an X-ray photoelectron spectroscope (JPS-9010MC). A photoelectron analysis for XPS has become a well- recognized in surface chemical analysis. The secondary electron peak at about 1 to 20eV was not used for the chemical analysis. But this peak will use for imaging observation, because the intensity of its is higher than the photoelectron peaks. A scanning secondary electron images by X-Ray excitation were measured by a stage scanning imaging method. The analyzing area was selected with the 200um aperture and scanned with a motor controlled stage. A specimen is the plate of Al, Cu, Ag and Au. The secondary electron energy from each metal as excited Mg-Ka(1253.6eV) and monochrometored Al-Ka(1486.6eV) was measured with a hemi-spherical electron analyzer at a constant retarding method (0.6%). For metal, the Z2 dependence of the secondary electron yields in X-Ray excitation increases with increasing Z2.

SS-WeP32 How Old is Surface Science?, ***E. Paparazzo***, Consiglio Nazionale delle Ricerche, Italy

Some philosophical and literary testimonies from the Classical World on solid surfaces are reviewed, and their implications discussed in the light of Surface Science. While Plato (V-IV century BC) thought the surface to be a real, material entity, Aristotle (IV century BC) considered it but a merely conceptual abstraction having no existence of its own. Subsequently, the Stoic philosopher Posidonius (I century BC) regarded plane surface as existing both in thought and in reality, although the implications involved in his view were remarkably different from those of Plato's. While Aristotle's view enjoyed a virtually unanimous consensus in antiquity, some passages in book 34 of the Elder Pliny's Naturalis Historia (I century AD) make a notable exception, as they refer to the surface of metal objects as to a region whose nature and behavior are quite different from those of the bulk: in other words, this bears witness to what appears to be an "ante litteram" example of Surface Science. Indeed, Pliny records the peculiar and dramatic ways in which these surfaces are affected by physico-chemical agents from the environment, and he also describes the remedies which best mitigate the effects of such phenomena. Further analogies between "old" and "modern" Surface Science are considered: purely-geometrical Plato's surface is found to compare favorably to a single-crystal surface, whereas the "corporeal" surface involved in Posidonius' view is best likened to an air-oxidized, or otherwise ambient-modified surface. I shall finally argue that the long-standing dominance of Aristotle's view from antiquity onwards has greatly delayed theoretical speculation into solid surfaces.

Thin Films
Room: Exhibit Hall B2 - Session TF-WeP

Poster Session

TF-WeP1 Effects of Starting Material of Aluminum Doped Zinc Oxide Under-layer on the Electric Properties of Palladium Doped Silver Film, ***T. Oyama**, M. Maekawa, T. Yanagisawa*, Asahi Glass Co., Ltd., Japan

Silver-based multilayer has been widely utilized as heat mirror for Low-E coating or transparent conductor for electromagnetic shielding. In this study, deposition conditions of the AZO(Aluminum doped zinc oxide) film were investigated to show how they affected the crystallographic property of the film and the electric property of palladium doped silver layer formed on the film in the layer system of Glass/AZO(42nm)/AgPd(1%Pd:10.5nm) deposited by DC magnetron sputtering. Starting material for AZO was aluminum doped zinc metal or aluminum oxide doped zinc oxide. Metal target was sputtered in oxygen atmosphere or carbon dioxide atmosphere whereas oxide target was sputtered in argon or argon/oxygen atmosphere. AgPd layer was deposited under the same condition. The effects of the over-layer were also investigated. Electrical resistivity was changed by up to 17% according to the deposition process of the under-layer. AgPd film deposited on AZO showed the lowest resistivity of 7.1x10E-6 Ωcm in the case of metal target with oxygen. On the contrary, the highest resistivity of 8.3x10E-6 Ωcm was observed in the case of oxide target with argon/oxygen. XRD patterns showed the most developed Ag(111) peak coupled with ZnO(002) peak in the case of metal target with oxygen and AFM observation revealed the smallest surface roughness in this case. Deposition of thin metal(Zn-Al) over-layer increased the resistivity implying the diffusion of zinc atom into silver-based layer, however the resistivity decreased with storage time. Optical constants of the films determined by spectroscopic ellipsometry(SE) and surface roughness of the films estimated by SE will be discussed.

TF-WeP2 The Synthesis and Characterization of Indium Tin Oxide Films by Cesium Assisted Sputtering System at Low Temperature, ***D.Y. Lee****, H.K. Baik,* Yonsei University, Korea, *S.J. Lee,* Kyungsung University, Korea, *K.M. Song*, Konkuk University, Korea

In this study, we investigated the properties of indium tin oxide (ITO) thin films synthesized by using a cesium assisted sputtering method. Cesium assisted sputtering enables to supply a cesium vapors on the target surface of sputter and generate the negative ions of target materials. The flux and energy of negative ions are independently controlled by the changing target voltage and cesium contents. ITO target (SnO2: In2O3 = 1: 9) was sputtered by mixture gas of argon and oxygen. Oxygen partial pressure, working pressure and other deposition parameters were optimized. RF coupled DC was used as a power source and its voltage was changed from 45 V(only RF) to 350 V(only DC). The temperature of cesium reservoir was varied from 80 to 200 Â°C. Negative sputtered particles including In, Sn, O and electron were generated from the target surface and accelerated to the substrate by target voltage. We applied additional substrate bias to control deposition energy and flux. The main object of our study is the fabrication of ITO films with low resistivity and high transparency at room temperature by negative ion beam process. The effects of cesium addition not only enable to generate the negative ions by lowering the target work-function but increase the plasma density. From the result of XRD, we concluded that the ion beam effects induced by positive and negative ion enhance the crystallinity of ITO films. In the case of positive bias, negative ions and electrons play a main role in improvement of ITO crystallinity. For the negative bias, argon ions, which fluxes were increased by cesium, promote ITO crystallinity by enhancing the mobility of adatoms on the substrate surface. Also we found that the preferred orientation of ITO films was changed with applied bias. The characterization of deposited ITO films was performed by XRD, four point probe, AFM.

TF-WeP3 Deposition of ZnO Films by Reactive Sputtering in CO$_2$ Atmosphere, ***N. Aomine****, K. Sato, E. Shidouji, J. Ebisawa*, Asahi Glass Co., Ltd., Japan

Transparent oxide films are often deposited by reactive sputtering from metal target in Ar/O$_2$ atmosphere because of cheep target cost. It is well known that deposition rate and absorbance of obtained films change drastically with a ratio of O$_2$ flow to total gas flow, and a transparent film can be obtained with a maximum deposition rate in the transition region from metallic to oxide mode. However, it is difficult to keep sputtering process in the transition region without monitoring plasma state e.g., emission, impedance, gas fraction, feed-backing to the process. In this work, reactive sputtering using CO$_2$ gas instead of Ar/O$_2$ gas was studied. ZnO films were deposited by reactive sputtering of a 10 cm-diameter Zn metal target. Process-film property relationship such as discharge voltage, deposition rate, film absorbance, and carbon content was investigated. Furthermore, gas fraction of CO$_2$ sputtering atmosphere was analyzed by quadrupole mass spectrometer (Q-mass). It was found that CO$_2$ sputtering has advantage to enable reactive sputtering in the transition region by only simply adjusting CO$_2$ flow rate. Films obtained with small CO$_2$ flow rate were absorptive, while films, with increasing CO$_2$ flow rate, became transparent and deposition rate finally began to decrease. Result from Q-mass spectra, showing CO$_2$ was partially decomposed into O$_2$ and CO by glow discharge, was analyzed based on gas supply and consumption balance model. It was concluded that CO$_2$ sputtering was advantageous owing not only to low O$_2$ partial pressure but also to deoxidation effect by CO. The advantage of CO$_2$ sputtering will be detailed.

TF-WeP4 Fabrication of ZnO Thin Films by Pulsed Laser Ablation with Remote Radical Source, ***T. Suzuki****, M. Hiramatsu, N. Shimizu,* Meijo University, Japan

Zinc oxide (ZnO) is a II-VI compound semiconductor with wide direct bandgap of 3.3 eV at room temperature. ZnO exhibits good piezoelectric, photoelectric and optical properties, and might be a good candidate for an electroluminescence device such as ultra-violet (UV) laser diode. ZnO films also have potential applications for surface acoustic wave devices and low loss wave-guides. In this study, ZnO thin films have been fabricated on Si (100) substrate at temperatures of 300 - 400°C by pulsed laser ablation using a KrF excimer laser with the wavelength of 248 nm. During the deposition, a remote microwave O$_2$/N$_2$ plasma as a radical source was used in order to improve the optical quality of the film. We have investigated the effect of the radical source on the optical and structural properties of ZnO films using photoluminescence (PL). From the PL measurement, all the films fabricated with and without using radical source showed a typical luminescence behavior with the two emissions of a narrow UV and a broad visible band. It is reported that the visible luminescence of ZnO was caused by the defects, such as oxygen vacancies and zinc interstitials in the films. As the partial pressure of N$_2$ in the microwave O$_2$/N$_2$ plasma increased, the intensity of UV luminescence increased and that of visible luminescence decreased. From this result, it was suggested that the injection of the nitrogen radicals into plasma plume might be effective to reduce the visible luminescence of ZnO and to improve the optical quality of the film.

TF-WeP5 XPS Study of First Stages of ZnO Growth and Nano-structure Dependence of the Polarisation Effects at ZnO/SiO$_2$ and ZnO/Al$_2$O$_3$ Interfaces, ***A.I. Martin-Concepcion****, F. Yubero, J.P. Espinos, A.R. Gonzalez-Elipe,* CSIC-Univ. Sevilla, Spain, *S. Tougaard*, University of Southern Denmark

A critical characteristic of nanoparticles and, in general, nanomaterials, is the overweighing importance of the surface and interface layers in respect to the bulk because of the small size of the aggregates (in 3D) or thickness of the layers (in the case of 2D) that constitute the nanomaterial. The present paper reports about the characterization of these interface layers in the particular case of ZnO/MO (MO: Al$_2$O$_3$ and SiO$_2$) interfaces by using X-ray photoelectron spectroscopy (XPS). Careful experiments have been performed consisting in the deposition of ZnO material on SiO$_2$ and Al$_2$O$_3$ substrates. Several samples were produced and characterized in situ. The nanostructure of the first stages of growth of the ZnO deposited was determined by Tougaard -peak shape analysis of several photoelectron peaks from both substrate and overlayer to check the consistency of the determined growth mechanisms. Thus the actual nanostructure of the growing ZnO films were carefully determined. In addition, the chemical interaction at the ZnO/MO interface was monitored by following the variation of the Auger parameter of the Zn atoms, as the amount of ZnO deposited was increased. Thus, the changes of the Auger parameter of the ZnO atoms have been correlated with the actual nanostructures formed by the ZnO deposits. From this information, a model is presented that accounts for the changes in the electronic parameters determined by XPS as a result of bonding and polarization interactions at the interface.

TF-WeP6 Fabrication of CuIn$_{1-x}$Ga$_x$Se$_2$ Thin Film Solar Cells by Two-step Process, ***H.K. Song***, Seoul National University, Korea, *S.G. Kim,* Kyungwon University, Korea, *H.J. Kim,* Seoul National University, Korea, *S.K. Kim, K.H. Yoon*, Korea Institute of Energy Research, Korea

Photovoltaic (PV) modules based on CuIn$_{1-x}$Ga$_x$Se$_2$ polycrystalline thin films have been promising candidates as an effective absorber material for solar cells. It has been reported that solar efficiency over 17% by co-evaporation of elemental sources (Cu, In, Ga, and Se) through three-stage process. But this process is difficult to scale-up for a large-manufacturing system. So we prepared CuIn$_{1-x}$Ga$_x$Se$_2$ thin films by 2-step process that can be easily scaled-up to industrial process. Metallic precursors were deposited on Mo coated soda-lime-silicate glass by DC magnetron sputtering followed by selenization process using Se vapor in an evaporation system. Ga was incorporated by using a Cu-Ga(23 at.%) alloy target. CdS buffer layer, intrinsic and n-type ZnO layer and Al top contact electrode were deposited by CBD (chemical bath deposition), RF sputtering system, and E-beam evaporator system, respectively. Fabricated CuIn$_{1-x}$Ga$_x$Se$_2$ thin film solar cells have relatively smooth surface morphology and mono-crystalline chalcopyrite phase. The efficiency of solar cell are measured by solar simulator and the characteristics of CuIn$_{1-x}$Ga$_x$Se$_2$ films are analyzed by X-ray diffraction (XRD), Auger Electron Spectroscopy (AES), Electron Probe Micro Analysis (EPMA), and Field Emission Scanning Electron Microscope (FESEM).

TF-WeP8 Structural and Optical Properties of the Novel Semiconducting Alloy Films Cu$_x$Cd$_{1-x}$Te:O Grown by rf Sputtering, *J. Santos-Cruz, G. Torres-Delgado, R. Castanedo-Pérez, O. Jiménez-Sandoval,* CINVESTAV, Mexico, *B.S. Chao,* Energy Conversion Devices, ***S. Jiménez-Sandoval***, CINVESTAV, Mexico

Current efforts towards understanding the degradation processes in CdS/CdTe heterojunction solar cells are strongly focused on the role of copper and oxygen in these two materials. We have studied the effects of incorporating both Cu and O in a controlled manner, during growth, on the structural and optical properties of CdTe films. When only Cu is introduced up to a concentration of around 3 at.%, the obtained material has a composition of the form $Cu_xCd_{1-x}Te$ which does not present significant changes in its physical properties as compared to those of CdTe. However, when oxygen is incorporated in the chamber during the growth of the $Cu_xCd_{1-x}Te$ films, the structural and optical properties may be varied significantly: depending upon the oxygen partial pressure, the structure of the films may be changed from polycrystalline to amorphous, and the optical band gap may present values between 1.4 and 2.8 eV. These results are addressed in terms of the chemical composition, structural properties and on the known behavior of copper and oxygen in the CdTe host.

TF-WeP9 Properties of Co-deposited ITO and ZnO Films Using a Bi-polar Pulse Power Supply and a Dual Magnetron Sputter Source, ***M.S. Hwang***, *H.S. Jeong, Y.W. Seo*, ITM, Inc., Korea

Multilayer coatings consisting of metal layers sandwiched between transparent conducting oxide(TCO) layers are widely used for flat panel display electrodes and electromagnetic shield coatings for plasma displays, due to their high electrical conductivity and light transmittance. The electrical and optical properties of these multilayer films depend largely on the surface characteristics of the TCO thin films. A smoother surface on the TCO thins films makes it easier for the metal layer to form a continuous film, thus resulting in a higher conductivity and visible light transmittance. ITO and ZnO films were co-deposited, using a dual magnetron sputter and a bi-polar pulse power supply, to decrease the surface roughness of the TCO films. The symmetric pulse mode of the power supply was used to simultaneously sputter an In2O3 (90wt%) : SnO2 (10wt%) target and a ZnO target. We varied the duty of the pulses to control the ratio of ITO : ZnO in the thin films. The electrical and optical properties of the films were studied, and special attention was paid to the surface roughness and the crystallinity of the films.

TF-WeP10 The Effects of Substrate Temperature and Ion Flux on the Opto-electronic Properties of dc Magnetron Sputtered Aluminum-doped Zinc Oxide, ***N.W. Schmidt***, *T.S. Totushek, W. Kimes, J.R. Doyle*, Macalester College

We present a study of the effects of substrate temperature and ion flux on the opto-electronics properties of reactive dc magnetron sputtered aluminum-doped zinc oxide (AZO). Near-substrate plasma density is varied using an unbalanced magnetron with external coils which allow variation of the ion-to-neutral ratio from 0.2 to 2. The substrates are electrically floating with a floating voltage of about -10 V, implying that the ions have 10 eV of energy upon arrival at the growing film. The ion flux is measured using cylindrical and flat plasma probes. Film quality is characterized by conductivity, visible transmission, x-ray diffraction, scanning electron microscopy, and Hall effect measurements. Film quality is found to be very sensitive to substrate temperature in the range of room temperature to 120 C, with transparency increasing and resistivity decreasing with increasing temperature. Film quality is also improved with increasing near-substrate plasma density up to 120 C. The best films have resistivities less than 0.0004 Ohm-cm with average transmission above 85% in the visible. Film quality maximizes in the range 120 - 150 C and then becomes independent of ion flux. The improvement in film quality observed with increasing ion flux at lower temperatures is similar to that found with increasing temperature. However, careful calibration of the substrate temperature indicates that the beneficial effect of increased ion flux is not simply due to substrate heating, implying that kinetic or momentum transfer effects are also important during ion bombardment.

TF-WeP11 Electronic Properties of Cu(In,Ga)Se2 (CIGS)-Based Solar Cells, ***J. AbuShama***, Colorado School of Mines

We examined the electronic properties of CIGS-based polycrystalline thin-film solar cells by Deep Level Transient Spectroscopy (DLTS) and Capacitance-Voltage (C-V) measurements. We prepared four CIGS thin films (by Physical Vapor Deposition) in the region where the film transitions from Cu-rich to In(Ga)-rich. Cu-rich sample exhibits a shallow majority carrier trap with an activation energy of 0.12 eV and another deeper trap with an activation energy of 0.27 eV. The shallow trap with a concentration of about 2.1x10^14 cm^-3 yields the dominant emission in Cu-rich CIGS in the observed temperature and frequency range. The In-rich sample has a shallow minority carrier trap with an activation energy of 0.12 eV. This trap with a concentration of 6x10^14 cm^-3 yields the dominant emission in In(Ga)-rich CIGS in the observed temperature and frequency range. The two samples show evidence of a deeper trap at higher temperature. C-V measurements showed that the carrier concentration around the junction of the cell changed as the film transitions from Cu-rich to In-rich. We see that the acceptor (donor)-like traps are dominant in the Cu(In)-rich samples. The transition from the Cu-rich to the In(Ga)-rich compositions causes an extensive transformation of intrinsic defects from acceptor-like traps (e.g. Cu on In(Ga) sites) to donor-like traps (e.g. In(Ga) on Cu sites).

TF-WeP12 Low Temperature Indium Tin Oxide Films Using Dual Magnetron Sputtering, ***H.S. Jeong***, *M.S. Hwang, H.J. Lee, Y.W. Seo*, ITM Inc., Korea, *S.J. Kwon*, Kyungwon University, Korea

Recently, the needs of low temperature deposition processes for transparent conducting oxide(TCO) films on a plastic substrate are increasing. Flexible plastic substrates have been used in liquid crystal displays, organic lighting-emitting diodes, and organic EL displays. Indium tin oxide films were deposited in a horizontal in-line sputter system equipped with a pulsed dual magnetron sputter source[DC ~50kHz]. An ITO target of In_2O_3(90 wt%):SnO_2(10 wt%) has been used. The substrates(glass and flexible plastic) were cleaned by an O_2 plasma processes. The properties of ITO films such as electrical resistivity, optical transmission, and surface roughness were investigated with respect to O_2 partial pressure, pulse frequencies, and substrate temperature(room temperature ~ 150°C). Also, we will investigate the film structure and plasma contamination difference between the pulsed single magnetron and the pulsed dual magnetron sources by XRD and RGA, respectively.

TF-WeP13 High Rate Deposition of ZnO Thin Films by Vacuum Arc Plasma Evaporation, *T. Miyata*, ***S. Ida***, *T. Minami*, Kanazawa Institute of Technology, Japan

Present requirements for zinc oxide (ZnO) thin films in various applications call for achieving further preparation cost reductions and higher deposition rates on larger area substrates. Recently, a newly developed vacuum arc plasma evaporation (VAPE) method providing high-rate film depositions on large area substrates has attracted much attention. In this paper, we describe the preparation of undoped and impurity-doped ZnO thin films on large area substrates by a VAPE method using oxide fragments as a low-cost source material. For example, the difficulty of preparing FZO thin films by sputtering deposition is well known. However, fluorine-doped ZnO (FZO) thin films suitable for transparent and conductive thin-film applications could be prepared. The film depositions were carried out under the following conditions: substrate, large area glass; substrate temperature, RT to 450°C; oxide fragments, sintered mixture of ZnO and ZnF_2 powders; pressure, 0.08 to 1 Pa; Ar and O_2 gas flow rates, 10 to 50 and 0 to 10 ccm; and cathode plasma power, 2.5 to 10 kW. A deposition rate of 150 nm/min and a resistivity on the order of $10^{-4}\Omega$cm as well as a uniform distribution of resistivity and thickness on the substrate surface were obtained for FZO films deposited at a pressure of 0.15 Pa, an Ar gas flow rate of 20 ccm, a cathode plasma power of 4.5 kW and a substrate temperature of 250°C. In film depositions by VAPE, the rate was easily controlled by varying the cathode plasma power. It should be noted that deposition rates from 55 to 375 nm/min were obtained in ZnO films deposited at a deposition pressure of 0.25 Pa with a cathode plasma power that ranged from 2.5 to 10kW.

TF-WeP14 Photocatalytic Properties of TiO_2/WO_3 Bilayers Deposited by Reactive Sputtering, ***T. Takahashi***, *H. Nakabayashi, J. Tanabe, N. Yamada*, Toyama University, Japan

Titanium dioxide (TiO_2) has attracted considerable attention because it is known to have strong activity as a photocatalyst under irradiation of ultraviolet rays. However, TiO_2 photocatalyst can only react slightly to solar energy because of its optical band gap E_G smaller than 3.2 eV (λ of 380 nm). So, it is desirable for most solar energy applications to have new materials that can highly react strongly to visible-light. In this study, the bilayers composed of TiO_2 and WO_3 films have been prepared by reactive sputtering at room temperature. At first, TiO_2 films with a thickness of about 1.4 µm have been deposited on glass-slide substrates at working gas pressure P_W of 1 mTorr and a mixed atmosphere of Ar and O_2, using the facing targets sputtering with dc power supply. Then WO_3 films have been deposited onto as-deposited TiO_2 ones at various P_W ranging from 1 to 8 mTorr in an atmosphere of mixture gas of 80%Ar and 20%O_2, using RF magnetron sputtering. The gaseous methyl alcohol by using the bilayers have been decomposed under irradiation with artificial sunrays of wavelength λ ranging from 330 to 750 nm for 2 h at room temperature. The bilayers were successful in carrying out a photocatalytic reaction of the decomposition of CH_3OH into CO_2 and H_2O from measurement of infrared transmittance spectra. Its decomposition rate using the bilayers significantly increases, as compared with that using the monolayers of TiO_2 films. It is found that the bilayers can decompose CH_3OH under irradiation of only slight visible-light. Consequently, the bilayers deposited in this study have a good photocatalytic reaction and activate the decomposition of gaseous methyl alcohol.

TF-WeP15 Influence of Preparation Conditions on Structure and Properties of WO_3Films Reactively Deposited by RF Magnetron Sputtering, *T. Takahashi, **J. Tanabe**, H. Nakabayashi, N. Yamada*, Toyama University, Japan

TiO_2 photocatalyst can only react slightly to solar energy because of its optical band gap E_G smaller than 3.2 eV (λ of 380 nm). So, it is desirable for most solar energy applications to have new materials that can highly react strongly to visible-light . Therefore, WO_3 films with E_G of 2.5 eV are very useful for the underlayer of TiO_2 photocatalyst. In this study, WO_3 films with thickness of 0.9-6.7 µm have been deposited on glass-slide substrates, using RF magnetron sputtering in an atmosphere of mixture gas of 80%Ar and 20%O_2. The crystallographic and the surface structures and the optical properties of WO_3 films deposited at the working gas pressure P_W ranging from 1 to 8 mTorr have been investigated in detail. The as-deposited films showed dark metallic color as like as target at P_W of 1 mTorr. The as-deposited films were yellow at P_W of 3 mTorr. With further increase of P_W, the color of the films changed to pale yellow. From the X-ray diffraction patterns, the as-deposited films were polycrystalline crystallizing in the monoclinic or the triclinic crystal structure with high c-axis orientation perpendicular to the film plane. The optical transmittance of the films deposited at P_W of 1 mTorr is nearly zero. However, the transmittance of the films deposited at other P_W are larger than 70 % in the wavelength λ ranging from 500 to 900 nm. With decreasing λ to 400 nm, the transmittance steeply become zero. The λ at this absorption edge is longer than that in TiO_2 and comes in the visible region. The surface morphology of the films depends on P_W. As P_W increased, the surfaces of the films become rougher and grain sizes of the films also become larger. The WO_3 films deposited in this study may be available for the underlayer of TiO_2 photocatalyst.

TF-WeP16 Ti Target Characteristics of Medium Frequency Reactive Sputtering: Process Modeling Improvement and Experimental Verification, ***Lai Zhao***, Tsinghua University, China, *S. Xu, C. Fan, W. Gao,* HIVAC Technology (Group) Co. Ltd., China, *X. Hou, Liangzhen Cha*, Tsinghua University, China

Deposition of TiO2 with reactive dual magnetron sputtering (DMS) is difficult to control due to its critical transition region of hysteresis curve caused by the high metallicity of Ti target. To stabilize the sputtering process, electrical characteristics of the Ti target is investigated in an on-line experiment. An improvement to the sputtering process modeling developed by S.Berg is proposed based on these experimental data. To better explain the hysteresis curve, it is found that the accumulation of positive argon ion charges on the oxidized target surface affects the electrical field and argon ion incident current density. Hence, the coverage of oxide component on the target will change correspondently. The changing argon ion current density due to charge accumulation is introduced to the equations. The simulated result fits well with the measured hysteresis curve.

TF-WeP17 Effects of Deposition Conditions on Step Coverage Quality in Metal-organic Chemical Vapor Deposition of TiO_2, ***S.Y. No**, J.H. Oh, C.S. Hwang, H.J. Kim*, Seoul National University, Korea

Dielectric thin films including Ti element such as (Ba,Sr)TiO_3(BST), $SrTiO_3$(STO) have been investigated intensively by many researchers for next generation DRAM capacitor. Recently, the problem of cationic composition non-uniformity was reported when these multi-component films were deposited on patterned structure by metal-organic chemical vapor deposition(MOCVD) method. To understand the problem of composition non-uniformity in multi-component films, it needs to know the step-coverage variation of each component film. In this study, the step coverage of TiO_2 thin films were investigated, which were grown on patterned Si substrates by liquid-injection MOCVD using $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ at substrate temperature ranging from 410°C to 500°C. The effects of various deposition parameters such as the chamber-wall and gas-line temperature, the source injection rate, the substrate temperature, solvents and deposition atmosphere on the step coverage quality were investigated and activation energy of deposition was also evaluated in each case. As the chamber-wall temperature increased from 230°C to 400°C, the step-coverage improved while degraded when gas line temperature was changed from 230°C to 400°C. With increasing the partial pressure of Ti source, the step-coverage improved slightly. When the substrate temperature was changed from 470°C to 410°C, the step-coverage quality enhanced, and the degree of variation in step-coverage was larger in oxygen-rich atmosphere than in Ar-rich atmosphere. Tetrahydrofuran(THF) and ethyl alcohol were used as solvents for Ti precursor dissolution and step-coverage is better when THF is used.

TF-WeP18 Raman Spectroscopy Measurement of TiO_2 Sputtered Films Changing Degree of Plasma Exposure, *T. Takahashi, H. Nakabayashi, J. Tanabe, **N. Yamada***, Toyama University, Japan, *W. Mizuno*, Toyama Industrial Technology Center, Japan

The relationship between the Raman spectra and the crystallographic orientation of the TiO_2 films deposited at different working gas pressures have been investigated in detail. The TiO_2 films with thickness of about 800-2300 nm have been reactively deposited on glass-slide substrates at an atmosphere of Ar and O_2 mixture, using the facing targets sputtering. The maximum deposition rate of the film was 12.8 nm/min. The Raman spectra, and the crystallographic orientation of the films were measured using Raman spectroscopy, and X-ray diffractometry, respectively. Most of films deposited in this study were transparent and had anatase crystal structure, while some of them were semitransparent. The anatase phase of as-deposited TiO_2 films has revealed in the Raman spectra with a Raman shift of 145 cm^{-1} and the X-ray diffraction patterns. When the TiO_2 films have been deposited at the working gas pressures of 3 mTorr with increasing plasma exposure, the highest peak intensity with a Raman shift of 145 cm^{-1} steeply increased, while the X-ray peak intensity of A(220) with preferential crystallographic orientation also steeply increased, where A shows the anatase phase of TiO_2. On the other hand, in the films deposited at the working gas pressures of 1 mTorr with decreasing plasma exposure, the Raman peak intensity at 145 cm^{-1} gradually decreased at the condition that the preferential crystal orientation changed from A(220) to A(101). This implies that the change in the Raman peak intensity at 145 cm^{-1} may be closely related to the change in the A(220) peak intensity. The A(220) peak was significantly higher than other peaks when the TiO_2 crystallites became larger regardless of the working gas pressure. Consequently, it was found that the Raman peak intensity at 145 cm^{-1} in as-deposited TiO_2 films were strongly affected by the plasma exposure related to the substrate position during film deposition.

TF-WeP19 Growth Morphology of Sputter Deposited Vitreous Titanium Dioxide Films, ***J.D. DeLoach***, Texas Instruments, *R.S. Sorbello,* University of Wisconsin-Milwaukee, *G. Scarel,* Laboratorio MDM-INFM, Italy, *C.R. Aita*, University of Wisconsin-Milwaukee

Room temperature growth of a ceramic film usually occurs by coalescence of three-dimensional nuclei. This initial morphology leads to column formation. The boundaries between columns can be open and can have a different physiochemistry than the column interior. In this study, we use high resolution transmission electron microscopy and electron diffraction to study the growth structure of TiO_2 films. The films were sputter deposited at room temperature on <111> Si substrates from which the nascent SiO_2 layer had not been removed. The film thickness ranged from 250 to 700 nm. The films' atomic structure was vitreous, that is, had no long range order. Most of the films' volume was amorphous with short-range order characteristic of anatase Ti-O nearest neighbor coordination. The remaining volume consisted of both anatase and rutile nanocrystallites. The most striking morphological feature observed by HREM was a network structure encompassing both amorphous and nanocrystalline regions in all films. Isolated regions within this network were on the order of tens of nanometers, increasing in size with increasing film thickness. Suboxide rings on electron diffraction patterns indicate that the network may be conducting. We suggest that this network has a profound effect on the properties of as-grown TiO_2 films, in particular on their ultraviolet and infrared optical absorption behavior. A recent[1] infrared absorption-reflection study showed that the model dielectric function which best fit the experimental data was obtained by averaging the dielectric functions of weakly interacting TiO_2 regions of different orientations. This result was surprising because of the large polarizability of TiO_2. Further analysis in the present study using a Maxwell-Garnett approach shows that this dielectric function is consistent with TiO_2 units embedded in a conducting network.

[1] G.S. Scarel et al. J. Appl. Phys. 91 1118 (2002).

Applied Surface Science
Room: C-106 - Session AS-WeA

High-k Dielectric Characterization
Moderator: B.R. Rogers, Vanderbilt University

2:00pm **AS-WeA1 Ultra-high Resolution AES Depth Profiling using a Masked Specimen Holder**, ***K. Satori***, *H. Kobayashi,* SONY Corporation, Japan, *K. Kimura, K. Nakajima*, Kyoto University, Japan

Auger electron spectroscopy (AES) using an instrument with coaxial geometry for an electron column and a cylindrical mirror analyzer (CMA) has the advantages of high sensitivity and accurate mapping capability. However, the analytical depth when using a coaxial CMA is larger than when using a hemispherical analyzer because the angle of the Auger electrons detected by a coaxial CMA ranges widely at any given tilt angle. This is a serious problem when we wish to evaluate ultra-thin films such as gate dielectrics. Some studies have been conducted using ion sputtering with low kinetic energy, to obtain high depth resolution. However, these studies have highlighted that one of the most important factors concerning depth resolution is the analytical depth. We designed angled and masked specimen holders to obtain a more shallow analytical depth using the coaxial CMA. We optimized the holder angle by calculating the distribution of the angle of the Auger electrons and the actual AES measurement to increase the intensity of the Auger electrons emitted at high angle from the surface normal. Next, we designed an electron shadow mask on a specimen holder to prevent the analyzer detecting the Auger electrons at low angle from the surface normal. Using the holder that we designed, the surface-sensitivity becomes three times higher than that of conventional methods. In addition, to improve depth resolution, we designed a new mask shape and obtained a low incident angle for the ion beam. Using the holder, the depth resolution was improved sufficiently to evaluate ultra-thin silicon oxynitride films (thickness 2.5nm). The shape of the AES depth profile was in good agreement with that obtained by means of high-resolution Rutherford backscattering spectroscopy. Our method is easy to use but useful for obtaining a shallow analytical depth and high depth resolution.

2:20pm **AS-WeA2 Sputtering Artifacts in Depth Profile Analysis of HfO_2 and $HfSi_xO_y$**, ***C.F.H. Gondran***, *J.A. Bennett, M.R. Beebe,* International SEMATECH

As electrical device sizes continue to shrink, thinner transistor gate oxides are required. Soon the required gate oxide thickness will be too thin to be obtained using SiO_2. Thicker gate oxides can be used to obtain the desired equivalent silicon dioxide thickness if the material used has a higher dielectric constant. HfO_2, ZrO_2 and their silicates are among the most promising candidates for alternative high-dielectric-constant gate materials. With these new materials, come a host of new challenges for both device processing and materials characterization. Preferential sputtering and other affects seen in the Auger and SIMS depth profiles of HfO_2 and $HfSi_xO_y$ result in the appearance of Hf deep into the Si Substrate. In mixed oxides the relative size of this artifact varies with the composition posing a challenge for quantitative analysis. The sputtering artifacts in HfO_2 and $HfSi_xO_y$ are characterized and practical approaches for analysis are discussed.

2:40pm **AS-WeA3 Challenges for the Characterization and Integration of High-k Gate Dielectrics**, ***R.M. Wallace***, University of North Texas **INVITED**

The integration of new high-k gate dielectric materials into advanced planar CMOS technology presents several significant challenges.[1] Moreover, the introduction of these materials is expected to occur at an unprecedented pace to meet industry technology forecasts[2] and will therefore mandate a rapid correlation of physical characterization with electrical performance. Although recent research has dwelled on the search for a material that yields a suitable (higher) dielectric constant, a more important problem is the actual integration of any new dielectric material in existing CMOS flows in a cost-effective manner. These integration issues include etching, control of phase segregation, dopant penetration, gate electrode compatibility, and many others that will influence the resultant electrical properties. This talk will examine several of these integration issues and the associated surface and thin film characterization challenges that must be addressed for successful high-k gate dielectric integration.

[1] For a review, see: G.D.Wilk, R.M.Wallace and J.M.Anthony, J. Appl. Phys. 89 (2001) 5243.

[2] See the International Technology Roadmap for Semiconductors at http://public.itrs.net/.

3:20pm **AS-WeA5 Quantitative Depth Profiling of Hafnium Films by Electron Spectroscopies**, ***P. Mrozek***, *H. Krasinski, D. Sarigiannis, B. Kraus*, Micron Technology Inc.

Surface analysis was performed by AES/XPS on hafnium oxide and hafnium oxy - nitride films grown on silicon. Depth profiles, using elastic peak intensities, aided estimates for inelastic mean free path ratios. Subsequent AES and XPS quantitative analysis was performed using matrix correction factors that incorporated these ratios. Linear least squares analysis was used to deconvolute the different chemical states from elastic peaks and to identify phases within multilayers. Auger parameter, based on hafnium high energy Auger transitions M4N6,7N6,7 and the deep 3d5/2 core level, was used to verify the presence of oxide and silicide layers that were detected by these hafnium chemical state profiles. The results were compared with those obtained from the usual AES quantitative analysis approach to demonstrate the value of supplemental elastic peak measurements.

3:40pm **AS-WeA6 Binding Energy Shifts in Soft X-ray Photoelectron Spectroscopy of $HfO_2/SiO_2/Si$ High-k Gate-dielectric Structures**, ***M.D. Ulrich***, *J.G. Hong, J.E. Rowe, G. Lucovsky*, North Carolina State University, ***T.E. Madey***, Rutgers, The State University of New Jersey

We have observed binding energy shifts for thin films of $(HfO_2)_x(SiO_2)_{1-x}$ on Si(111) substrates deposited as alternative high-k gate dielectrics in the film thickness range, 6-15 Å. Thin films of HfO_2 and $(HfO_2)_x(SiO_2)_{1-x}$ on Si(111) substrates were prepared by remote plasma enhanced chemical vapor deposition (RPECVD). This process results in a 6-10 Å layer of SiO_2 between the deposited dielectric and substrate. Samples were analyzed using high-resolution soft X-ray photoelectron spectroscopy (SXPS) with synchrotron radiation. Photoemission measurements were performed at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratories using beamline U4A which has a total instrumental resolution of better than 0.1 eV. The Si $2p_{3/2}$ [SiO_2] binding energy from SiO_2 films on silicon substrates decreases with decreasing (5-30 Å) film thickness due to core hole screening. This shift is well described with an image charge model of core hole screening.[1] According to this model, an overlayer above the SiO_2 layer should further increase Si $2p_{3/2}$ [SiO_2] core hole screening causing an additional decrease in binding energy. For the HfO_2 samples, SiO_2 thickness was determined to be ~10 Å. The Si $2p_{3/2}$ [SiO_2] binding energy was 0.3 eV lower than that of a SiO_2 film of similar thickness without the HfO_2 overlayer. The Si $2p_{3/2}$ single-component SXPS spectra indicate that interfacial silicate exists between the SiO_2 and HfO_2 with a signal strength less than one third that of the SiO_2 peak. The result of the Si $2p_{3/2}$ [SiO_2] binding energy matches the image charge model well.

[1] J. W. Keister, J. E. Rowe, J. J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Madey, and G. Lucovsky, J. Vac. Sci. Technol. A 17, 1250 (1999).

4:00pm **AS-WeA7 Chlorine and Oxygen Transport in ALD Grown ZrO_2 and HfO_2 Films on Silicon**, ***S. Ferrari***, *G. Scarel, C. Wiemer, S. Spiga, M. Fanciulli,* Lab. MDM - INFM, Italy

ZrO_2 and HfO_2 have received a lot of attention as possible candidates to replace SiO_2 as insulating layers in CMOS structures. Oxygen diffusivity in those materials may affect a number of properties. Among them, oxygen stoichiometry in the oxide, interfacial silicon oxide formation/reduction are critical parameters that need to be controlled in order to succesfully build high-k based devices with the desired properties. The growth of ZrO_2 and HfO_2 films by means of Atomic Layer Deposition (ALD) from $ZrCl_4$ And $HfCl_2$ percursors is known to cause significant incorporation of chlorine. Chlorine may have detrimental effects on the electrical properties of the films, by introducing positive charge in the film and possibly localized states in the band gap. In this paper we study oxygen and chlorine diffusion by means of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) in ZrO_2 and HfO_2 films as a function of annealing temperature in different environment gasses such as N_2 and O_2 . Preliminary results show that in oxygen deficient environment chlorine desorption in inhibited, demonstrating that chlorine can out-diffuse by exchange with the oxygen. HfO_2 shows a limited oxygen and chlorine mobility as compared to ZrO_2.

4:20pm **AS-WeA8 A Study of the Microstructure and Electrical Properties of the Reoxidized HfO_2 upon Annealing Methods**, ***D. Lee***, *H.-E. Seo, D.-H. Ko, M.-H. Cho,* Yonsei University, Korea, *C.-W. Yang*, Sungkyunkwan University, Korea

Hafnium oxide has been known as gate dielectric material to replace SiO_2 in MOS devices. First of all, for preparation of reoxidized HfO_2, Hf films were deposited on p-type Si(100) substrate by DC magnetron sputtering system. Next, Hf films were reoxidized by RTA(Rapid Thermal Annealing) and vertical furnace. They were analyzed by AFM, XRD, XPS, AES and HR-TEM. For ~50nm thick as-deposited Hf film, the HfO_2 layer was observed about ~5nm at the surface by HR-TEM. The HfO_2 layer increased to be ~15nm at 600°C in N_2 ambient. Especially, HfO_2 grains were shown not only at the surface of the Hf film but also at the silicide(Hf_5Si_4) grain boundaries. These grains of silicides on the Si substrate were not observed at the sample that annealed at 800°C for 30min in N_2 ambient, due to decompositing into HfO_2 and Si. And then the Si reacted with the oxygen that diffused from surface and accumulated on the interface of Si-substrate. For ~10nm thick as-deposited Hf films, it was observed that the HfO_2 films locally crystallized in the whole films and the interfacial layer between HfO_2 and Si substrate was about 8Å. After annealing by furnace as increasing anneal time and temperature in N_2 or O_2 ambient, also, the thickness of interfacial layer was increased to that of as-deposited film. As a result of measuring C-V and I-V, it was calculated that the value of CET was 51.5Å at -3V and dielectric constant was about 15.5 at 800°C for 5min in N_2 ambient. The leakage current of HfO_2 film decreased as the anneal temperature increased or time increased at constant temperature.

Biomaterials
Room: C-201 - Session BI-WeA

Polyelectrolyte Surfaces/Cell-Surface Interactions
Moderator: A. Chilkoti, Duke University

2:00pm **BI-WeA1 Polyelectrolyte Multilayers: Design of Biofunctional Surfaces**, ***G. Decher***, Université Louis Pasteur, France **INVITED**

Layer-by-layer (LbL) assembly@super 1@ is an easy to use method for the fabrication of multi-composite films and has kindled widespread interest in such nanohybrids.@super 1-@super 7@. Electrostatic interactions between anionic and cationic compounds (synthetic or natural polyelectrolytes, DNA or proteins) offer four major advantages: (1) layer-by-layer construction due to surface charge reversal in each layer (2) restriction to single layers due to repulsion between last layer and excess material (3) low steric demand for interaction between oppositely charged ions (4) deposition on almost any solvent accessible surface. As an introduction to the LbL-technique, the guiding principles of multilayer assembly will be presented and details of the film structure will be discussed. Since the technique allows to interface a wide variety of materials with predefined spatial arrangement, it has successfully been introduced to both materials science and applied bio-sciences. At this meeting we will focus on work relevant for surfaces in contact with biological materials or environments. This will include work on films composed of natural or semi-synthetic polyions such as charged polypeptides or polysaccharides some of which has been carried out in close collaboration with the groups of P. Schaaf (ICS) and J.-C. Voegel (INSERM U 424).

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2:40pm **BI-WeA3 Poly-(L-Glutamic Acid)/Poly-(L-lysine) Multilayers used as Biomaterial Coating**, ***P. Schaaf***, Institut Charles Sadron (CNRS), France, *J.C. Voegel, C. Picart, Ph. Lavalle*, Unite INSERM U424, France, *F. Boulmedais*, Institut Charles Sadron (CNRS), France

Polyelectrolyte multilayers constitute an easy tool for multi-functionalizing biomaterial surfaces. In this paper we will discuss biological and physico-chemical properties of poly-(L-glutamic acid)/poly-(L-lysine) (PGA/PLL) multilayers. We first discuss the response of cells in contact with (PGA/PLL) multilayers functionalized by embedding active peptides within the films. We then present results relative to the cellular response when the film is functionalized by embedding proteins in the architecture. In both cases we get a cellular response even when the active molecules are embedded under up the 20 (PGA/PLL) bilayers. We discuss also possible cell recognition mechanisms of the active molecules. But the system (PGA/PLL) is also interesting because it leads to films with internal secondary structures such as beta-sheets or alpha-helices. The relation between the secondary structure of the film and the secondary structure of (PLL/PGA) complexes in solution will also be presented.

3:00pm **BI-WeA4 Cellular Interactions with Multilayered Polyelectrolyte Films**, *C. Picart*, Université Louis Pasteur, France, *Ph. Lavalle*, INSERM Unite 424, France, *L. Richert, D. Vautier*, Université Louis Pasteur, France, *P. Schaaf*, CNRS, France, ***J.C. Voegel***, INSERM Unite 424, France

The short time interactions of chondrosarcomas cells with polyelectrolyte multilayered architectures built up by the alternated deposition of poly(L-lysine) (PLL) and poly(L-glutamic acid) (PGA) were estimated in the presence and the absence of serum. Film constructions with and without protein adsorption were first characterized by means of optical waweguide lightmode spectroscopy, quartz cristal microbalance and zeta potential determinations. In the presence of a serum containing medium, the detachment forces measured by the micropipette technique were about eight times smaller for PGA than for PLL ending films. For these later ones, the adhesion forces decreased also when the films increased in thickness. In a serum-free medium the differences between the negative and positive ending films become larger : adhesion forces on PLL-ending films were by 40 % to 100 % higher, whereas no cells adhered on PGA terminating films. Also, PGA ending films were found to prevent the adsorption of serum proteins whereas large protein amounts adsorbed always on PLL ending films. These data suggest that cell interactions with polyelectrolyte films can be tuned by the type of the outermost layer, by the presence of proteins, and the number of deposited layers.

3:20pm **BI-WeA5 Entrapment of Phosphate Ester Hydrolyzing Enzymes in Polyelectrolyte Multilayers Deposited on Glass Beads and Extended Retention of Their Enzymatic Activity**, ***A. Singh***, *Y. Lee, I. Stanish*, Naval Research Laboratory, *T.C. Cheng*, Edgewood Research Development & Engineering Center, APG, MD

Recent advances in multilayer technology involving layer by layer technique indicate its utility in solving complex problems of multidisciplinary nature. We have explored layer-by-layer technology for entrapping enzymes organophosphorus hydrolase and Organophosphorus acid anhydrolase in polyelectrolyte multilayers with a goal to sustain their biological activity for a long period of time under an environment, where native enzymes turned inactive. Thus, phosphate ester-hydrolyzing enzymes were immobilized in multilayers coated on glass beads (30-50 µm). Coatings on Glass beads consist of 3 alternating layers of branched poly (ethyleneimine) (BPEI) and polystyrene sulfonate (PSS) as precursor layers, followed by five alternative layers of BPEI and OPH. Immobilized enzymes were tested for their enzymatic activity and stability at different temperature and under different humidity conditions and found active. Surprisingly, in 15 percent relative humidity environment an enhancement in enzyme activity was observed. Stability of multilayers incorporating enzymes was further improved by laying additional poly (acrylic acid) (PAA) layer on top of the multilayer assemblies and endcapping the enzyme-PAA layer with monomers, such as trimethylsilyl propylethylenediamine (TMSPED), and vinyl benzyl solketol (VBS). TMSPED end-capped OPH enzyme performed better than VBS coated multilayers and was further evaluated through salt stress test (involving 1 M aq. NaCl). An improved performance of end-capped OPH glass beads was demonstrated than their uncapped counterpart. Efforts on the synthesis of novel support beads will also be presented.

3:40pm **BI-WeA6 In-situ Measurements of Polyelectrolyte Multilayer Build-up using Ellipsometry and QCM-D : 9**, ***T.J. Thurell***, *U. Elofsson*, YKI, Sweden

Polyelectrolyte multilayers are easily constructed by alternately exposing a charged surface to positively and negatively charged polymers. The aim of this study was to create a biocompatible surface for use in implant technology. The charged poly-amino-acids PGA (Poly (L)Glutamic Acid) and PLL (Poly (L)Lysine) were coated on an initial layer of PEI (Polyethylimin) on both silica and titanium surfaces. Multilayer build-up was monitored in-situ using both ellipsometry and QCM-D. The polyelectrolytes adsorbed firmly, with insignificant desorption upon rinsing, on both substrates used. In the ellipsometer up to 12 layer pairs were easily built while monitored in-situ. Comparing adsorbed amounts obtained from the ellipsometer, with those calculated from QCM-D measurements, one can see that these polymer-multilayer-films are highly hydrated (app. 70% water content). In the QCM-D measurements, an almost linear mass increase/layer are obtained from the second layer pair and up, whereas linear mass increase/layer is not achieved until the eighth layer pair in the ellipsometer. The observations indicate that the polymer film become denser with each added layer. This is also reflected in the increasing refractive index, which eventually level out at 1.457 after about 10 layer pairs. The large fluctuations in refractive index and thickness found initially suggests that the polyelectrolytes in the two first layer pairs are unevenly adsorbed with gaps and holes where water may get trapped. One possible explanation for the variations in film density would be that the gaps and holes will eventually fill up resulting in constant film density and linear mass growth. This work is a part of the SIMI project (Surface

Improvement of Metal Implants GRD1-2000-26823) funded by the European Commission.

4:00pm **BI-WeA7 Nanoscale Surface Properties of Microbial Cells**, ***Y.F. Dufrene***, Universita Catholique de Louvain, Belgium **INVITED**

Biological events such as microbial adhesion, microbial aggregation and molecular recognition play a pivotal role in the natural environment, in medicine and in biotechnological processes. Understanding the molecular bases of these phenomena requires knowledge of the structural and physical properties of microbial cell surfaces. With atomic force microscopy (AFM), it is now possible to explore the surface of single cells with nanometer lateral resolution and under physiological conditions. AFM can be used for visualizing surface ultrastructure (crystalline arrays, appendages), for following physiological changes (germination, growth) and for monitoring the effect of external agents (antibiotics, metals). These studies open the door to new applications in biotechnology and biomedicine, such as the rapid detection of microorganisms and the rationale design of drugs. AFM is actually much more than a microscope in that it also enables physical properties to be probed quantitatively: (i) surface hydrophobicity and electrical properties can be mapped using probes functionalized with defined functional groups (CH3, OH, COOH); (ii) surface softness can be measured by pressing the probe onto the cell surface; (iii) the elasticity of surface macromolecules, such as polysaccharides, can be addressed by means of force spectroscopy. These measurements have a great potential for elucidating the structure-function relationships of microbial surfaces (molecular recognition, conformational changes, surface interactions). In this contribution, I will discuss recent data obtained on fungal spores, yeasts and bacteria to highlight these unique capabilities.

5:00pm **BI-WeA10 Development of a Fluorescent Based Assay for Quantifying Ligand Surface Density on IPN-Modified PS for High Throughput Applications**, ***G.M. Harbers***, Northwestern University, *T.A. Barber,* University of California, Berkeley and University of California, San Francisco, *K.E. Healy,* University of California, Berkeley, *S.L. Golledge, D.G. Castner*, University of Washington

Biomimetic surface engineering exploits the power of specific ligand-receptor engagement to control cell-biomaterial interactions independent of bulk material characteristics. Accurate characterization of ligand surface density (Γ) is crucial for interpreting cellular response to these engineered surfaces. Currently, low throughput techniques including ellipsometry, SPR, and radiolabeling are employed to make these measurements. Lack of high throughput alternatives provided the motivation for the development of a fluorescence microplate reader based assay to measure Γ on a modular biomimetic surface developed to rapidly screen the adhesive potential of bioactive peptides. Poly(acrylamide-co-ethylene glycol/acrylic acid) interpenetrating polymer networks [p(AAm-co-EG-/AAc) IPNs] were grafted on to 96-well polystyrene (PS) plates. Fluorescently labeled peptides were subsequently coupled to the IPN using different input concentrations (0.01-100 μM) to modulate Γ. Surface characterization (contact angle goniometry and XPS) and cell-surface interactions were consistent with the results on previously developed IPN modified metal oxide surfaces. Reproducible control of Γ was observed over four orders of magnitude (~ 0.1-100 pmol/cm^2). Furthermore, competitive binding experiments using labeled and unlabeled peptides facilitated the determination of the equilibrium dissociation constants (K_d) of the various peptides. Although this technique may not be as sensitive as the others mentioned above, it allows for the characterization and rapid development of well defined biomimetic surfaces for high throughput applications.

Electronic Materials and Devices
Room: C-107 - Session EL+SS+SC-WeA

Semiconductor Film Growth and Oxidation
Moderator: R.K. Ahrenkiel, National Renewable Energy Laboratory

2:00pm **EL+SS+SC-WeA1 Scanning Tunneling Microscopy and Spectroscopy of Gallium Oxide and Indium Oxide Deposition on GaAs(001)-(2x4)**, ***M.J. Hale***, *J.Z. Sexton,* University of California, San Diego, *S.I. Yi,* Applied Materials, *D.L. Winn, A.C. Kummel*, University of California, San Diego

The surface structures formed upon deposition of Ga_2O and In_2O onto the technologically important As-rich GaAs(001)-(2x4) surface have been studied using scanning tunneling microscopy (STM) and spectroscopy (STS), low energy electron diffraction (LEED), and density functional theory (DFT) calculations. At submonolayer coverage, the initial bonding sites are different for Ga_2O and In_2O adsorptions due to the different activation barriers for the two oxides to chemisorb at various sites onto the surface. In_2O initially bonds in the trough between the arsenic dimer rows, whereas Ga_2O first inserts into the top layer arsenic dimer rows. Conversely, at elevated surface temperatures, both Ga_2O and In_2O form a crystalline monolayer. Both oxides form crystalline (2x1) surface reconstructions that are electronically unpinned: there are no states within the band gap. Although both oxides form a (2x1) surface reconstruction, the surface structures differ. At monolayer coverage the Ga_2O/GaAs surface has a much larger step density while the In_2O/GaAs surface shows a broad distribution of row oxide spacing. The DFT calculations confirm the observed surface structures and show that both oxides form unpinned surfaces because the bonding to these oxides restore the charge on the first and second layer As and Ga atoms to near bulk values.

2:20pm **EL+SS+SC-WeA2 Structure-Sensitive Oxidation of the Indium Phosphide (001) Surface**, ***G. Chen***, University of California, Los Angeles, *S.B. Visbeck*, Siemens & Shell Solar Gmbh, Germany, *D.C. Law*, University of California, Los Angeles, *R.F. Hicks*, University of California, Los Angeles; AVS fellow

Abstract The properties of oxide/semiconductor interfaces significantly affect the performance of indium phosphide-based electronic and photonic devices. In this study, indium phosphide films were grown on InP (001) substrates by metalorganic chemical vapor deposition (MOCVD). Then the samples were transferred to an ultrahigh vacuum system, and annealed at 623 and 723 K to produce the (2x1) and delta(2x4) reconstructions with phosphorus coverages of 1.0 and 0.125 ML, respectively. These structures were exposed to unexcited molecular oxygen, and the reaction characterized by X-ray photoelectron spectroscopy (XPS), reflectance difference spectroscopy (RDS) and low energy electron diffraction (LEED). At 298 K and above, the In-rich InP (001) surface rapidly oxidizes upon exposure to O2. The oxygen dissociatively chemisorbs onto the delta (2x4), inserting into the In-P back bonds and the In-In dimer bonds. By contrast, the P-rich (2x1) reconstruction does not absorb O2 up to 500,000 L at 298 K. Above 453 K, the (2x1) becomes reactive with oxygen inserting into both the In-P back bonds and the phosphorus dimer bonds. Based on these results, we conclude that the oxidation of indium phosphide (001) is highly structure sensitive. This means that the oxide/semiconductor interface formed on InP devices can vary widely depending on the process history.

2:40pm **EL+SS+SC-WeA3 The Addition of Sb and Bi 'Surfactants' during GaN Growth by Metal Organic Vapor Phase Epitaxy**, ***T.F. Kuech***, *L. Zhang, H.F. Tang, J. Schieke, M. Mavrikakis,* University of Wisconsin - Madison **INVITED**

The addition of certain impurities has been shown to modify the growth behavior of several lattice-mismatched epitaxial semiconductor systems, most notably SiGe-Si. Of the many impurities studied, antimony and bismuth have been shown to act as 'surfactants' during SiGe epitaxy altering the critical thickness and surface morphology. Such impurities have not been studied in detail in other systems, such as GaN and related materials. We present data on the role and effect of isoelectronic centers, Sb and Bi, on the structure and properties of GaN epilayers during metal organic vapor phase epitaxy. The Sb addition slightly improved the optical and structural properties of GaN epilayer at a low level of Sb incorporation. The addition of Sb resulted in changes in the GaN surface morphology, which was further explored by the lateral overgrowth epitaxy technique through the changes in the growth rates and the facet formation. The presence of Sb in the gas phase greatly enhanced the lateral overgrowth rate and altered the formation of the dominant facets. While Sb altered the growth facet present during LEO, only a small amount of Sb was incorporated into the GaN, suggesting that Sb may be acting as a 'surfactant' during the GaN MOVPE growth. Sb addition produces surface conditions characteristic of a Ga-rich surface stoichiometry indicating both a possible change in the reactivity of NH_3 and/or enhanced surface diffusion of Ga adatom species. Other changes in the surface chemistry and transport were studied by the use of state-of-the-art periodic self-consistent DFT calculations. Bismuth has also been studied as a surfactant to alter the surface chemistry and defect structure during the GaN growth. Bi addition resulted in a decrease in surface roughness as measured by atomic force microscopy while no significant Bi was incorporated over a broad range of gas phase concentrations.

3:20pm **EL+SS+SC-WeA5 Surface Reaction Study of Tungsten Nitride Precursors Decomposition on Si(100)-(2 x 1)**, ***Y.-W. Yang***, Synchrotron Radiation Research Center, Taiwan, *J.-B. Wu, Y.-F. Lin, H.-T. Chiu,* National Chiao-Tung University, Taiwan

Reaching an atomic-scale understanding of the surface reaction pathways followed by precursors during MOCVD thin-film growth is a daunting task. We have been studying the transition metal nitride growth on both Cu and

Si surfaces. Here, we report a thermal decomposition study of WN precursor on Si(100)-(2 x 1) using TDS and synchrotron-based XPS techniques. The studied precursors are (t-BuN)$_2$W(NHBu-t)$_2$ and (t-BuN)$_2$W(NEt$_2$)$_2$ and their structural characteristics consist of the presence of both W-N and W=N bonds and either the presence or the absence of β-H that influences the thermolysis of the precursors. XPS data show that the metallic tungsten already forms for a submonolayer dose of the precursors at room temperature, suggesting the complete abstraction of the amine ligands by the dangling bonds on Si(100) surface. The evolution of hydrocarbon and amine species during the pyrolysis are followed by the TDS and the results suggests the similarity to the amine adsorption on Si(100). High temperature annealing produces silicon carbides and silicon nitrides. In stark contrast, no metallic tungsten is ever formed during the pyrolysis of the same precursors on Cu(111) and the formation of tungsten nitride is secured through the gradual loss of excessive amine ligands. Based on these results, possible surface reaction mechanism and the structural effect of the precursor are to be discussed.

3:40pm **EL+SS+SC-WeA6 Thermal Decomposition and Desorption Study of Tetrakis(diethylamido)zirconium(TDEAZr) on Si(100) for MOCVD and ALD of ZrO$_2$**, ***K. Yong**, J. Jeong, S. Lim*, Pohang University of Science and Technology, Korea

Tetrakis(diethylamido)zirconium (TDEAZr) is used as a zirconium-precursor to deposit zirconium oxide by metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD). Surface reaction study of precursors can aid in describing the kinetics of MOCVD and ALD. Surface reaction and desorption of TDEAZr (Zr(N(C$_2$H$_5$)$_2$)$_4$) on Si(100) were studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). During TPD, ethylethyleneimine, diethylamine, acetonitrile, ethylene and hydrogen desorbed as main decomposition products of diethylamido, which was chemisorbed on Si(100) through the scission of zirconium-diethylamido bond in TDEAZr. The formation of silicon-carbide and silicon-nitride was observed on the surface after TPD runs. These results indicated that a complete decomposition of diethylamido also proceeded. A reaction pathway model of TDEAZr/Si(100) was proposed. Also, the coadsorption of TDEAZr with water on Si(100) was studied.

4:00pm **EL+SS+SC-WeA7 Reactions of Organosulfur Compounds with Si(100) for Chemically Controlled Epitaxy of II-VI Semiconductors on Si(100)**, *Z. Zhu, A. Srivastava, **R.M. Osgood Jr.***, Columbia University

The growth of silicon-based quantum devices requires precise control of ultrathin Si/wide-bandgap-semiconductor/Si heterostructures. We have investigated the initial stages of chemistry-based low-temperature epitaxy using organosulfur precursors. The approach uses the chemical insight gained from organic functionalization of Si.[1] Thus we have studied the reaction of (CH$_3$S)$_2$, CH$_3$SH, (CH$_3$)$_2$S with Si(100) at room temperature, under UHV conditions for atomic layer growth of functional-group-terminated sulfur on Si(100). This reaction is the first step in the layer by layer self-limiting epitaxy of ZnS, for example, on Si(100). AES studies indicate that each of these organosulfur compounds have different reaction kinetics with the Si(100) surface and reach different levels of sulfur saturation coverage. The differences observed for (CH$_3$S)$_2$ and (CH$_3$)$_2$S reactions have been shown to be explained by the relative bond strengths and the number of sulfur atoms present in the adsorbate molecule. Our TPD studies from 25-825°C show no sulfur-related desorption. Instead AES studies confirm that sulfur atoms remain on surface until ~ 525°C and then diffuse into the Si(100) substrate upon further annealing. TPD studies also indicate evolution of H$_2$ at temperatures similar to those obtained for H$_2$ desorption from saturated atomic H on Si(100). In our studies methyl desorption also occur at T > 650° C, temperatures higher than that of H$_2$ desorption. The amount of m/e = 15,16 fragments is dependent on the organosulfur compound examined. Chemical strategies are now being explored to grow layers of Zn on methyl-terminated sulfur layer as shown in the epitaxy using sequential H$_2$S/dimethyl cadmium dosing on ZnSe.[2]

[1] Bent SF, J Phys Chem B, 106(11): 2830-2842, 2002.

[2] Luo Y, Han M, Slater DA, Osgood RM, J Vac Sci Tecnol A 18(2): 438-449, 2000.

4:20pm **EL+SS+SC-WeA8 Kinetics and Mechanism of Adsorption and Ultrathin Oxide Growth by Ozone on Si(100)2x1 and Si(111)7x7**, ***K. Nakamura**, A. Kurokawa, H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Ozone is one of the promising oxidants to synthesize an ultrathin oxide film on silicon surfaces for the near-future MOSFET because of rapid oxidation rate at low substrate temperature, negligible thickness of structural transition layers in the oxide film, etc.[1] However, to control the thickness of an oxide film precisely and accurately,[2] kinetics and mechanism of initial oxide growth must be clarified. Thus, in this paper, we discuss chemistry of adsorption and ultrathin oxide growth by ozone on silicon surfaces. Si(100)2x1 and Si(111)7x7 were exposed to highly concentrated (>80%) ozone gas and monitored by x-ray photoelectron spectroscopy (XPS) and second harmonic generation (SHG). Kinetic analysis has suggested that initial dissociative adsorption of ozone on Si(100)2x1 and Si(111)7x7 proceed with the mechanism of leaving only one oxygen atom on the surface and of desorbing the other two, possibly, as a molecular oxygen. This adsorption, in contrast to that of oxygen, was featured with structure-insensitive kinetics, no activation barrier for the dissociation, and high sticking probability close to unity. After the adsorption was completed, first three oxide layers were synthesized by random adsorption of oxidant species on each layer in the consecutive manner. The formation of three layers led to the further growth of an oxide film with ozone with linear growth kinetics, but not with molecular oxygen. Each of these initial ozone-oxide layers has distinctively different activation energy for its growth: they were estimated 0 eV, 0.34 eV, 0.68 eV, and 0 eV for first, second, third, and above fourth layers on Si(100), respectively, enabling accurate control of the thickness of an oxide film.

[1] K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275.

[2] K. Nakamura, A. Kurokawa, and S. Ichimura, Jpn. J. Appl. Phys. 39 (2000) L357.

4:40pm **EL+SS+SC-WeA9 Stress-induced Dissociative Chemisorption of Oxygen on Si(001)**, ***M. Yata**, Y. Uesugi-Saitow*, National Institute for Materials Science, Japan

We have investigated the role of surface stress in dissociative adsorption process of O$_2$ on Si(001)-2x1by supersonic molecular beam technique. The tensile stress was externally applied on the surface along[110] direction. The Si(001)-2x1surface reconstructs by dimerization of atoms in adjacent rows. In areas of the surface separated by an odd number of monoatomic steps the orientation of the dimer bonds is rotated by 90° giving 2x1 and 1x2 orientational domains. Their domain populations are changed to relax the stress at the surface and the kinetics of the change depend on the surface temperature.[1] Below room temperature, the domain populations were almost equal during the molecular beam experiments. Two co-existing dissociation channels are seen, a trapping-dissociation channel at low translational energy of incident O$_2$ and a direct activated channel at high translational energy.[2] In case of the trapping-dissociation, O$_2$ molecule is trapped to a precursor state and undergoes a kinetic competition between desorption and dissociation. We have estimated a difference in activation barrier heights between desorption and dissociation at 30 meV. The initial dissociative sticking probability for low translational energy of incidence increases as the tensile stress increases. This indicates that trapping-mediated dissociation is enhanced by the stress. We have found that the difference in the activation barrier heights between desorption and dissociation decreases as the stress increases. We will discuss the change of dissociation dynamics with the tensile stress in detail.

[1] F. K. Men, W.E. Packard and M. B. Webb, Phys. Rev. Lett. 61(1988) 2469.

[2] B. A. Ferguson, C. T. Reeves and C. B. Mullins, J. Chem. Phys.110(1999)11574.

5:00pm **EL+SS+SC-WeA10 Direct Detection of D$_2$O and D$_2$ on D/Si(111) Surfaces under O Atom Exposures**, ***F. Rahman**, F. Khanom, A. Aoki, S. Inanaga, A. Namiki*, Kyushu Institute of Technology, Japan

Initial oxidation stage of D/Si(111) surfaces by atomic oxygen (O) have been studied from the absorption point of view. O/D/Si(111) co-adsorbed surfaces were prepared by various O exposure on 1.25ML D/Si(111). TPD measurement shows nearly 50% reduction of D adatoms from the surface for 2 min O exposure indicating the D adatoms abstraction by incident O atoms. Measurement of desorbing species have been done with a QMS during O exposures on the 1ML D/Si(111) surface for various surface temperatures (T$_S$). D$_2$O as well as D$_2$ molecules were observed. Rate curves of both species show an initial rate jump and then a gradual increase having a peak, which is followed by a nearly exponential decay with exposure time. Both D$_2$O and D$_2$ rates vs. T$_S$ curves show similar line shape to the similar plot of D$_2$ rates vs. T$_S$ curve obtained for the reaction system of H + D/Si(111) --> D$_2$. In a previous work, the later reaction was understood as due to the so-called β$_2$ TPD desorption arising from a dideuteride phase. Therefore, we consider that the O induced D$_2$ formation proceeds along the same mechanism as for the β$_2$-channel TPD. Regarding D$_2$O formation, it is significant and interesting since the reaction takes place as a result of picking up two D adatoms by single O atom upon collision. We will propose a possible mechanism to explain the O-induced D$_2$O formation on the D/Si(111) surfaces.

Homeland Security
Room: C-209 - Session HS+SS+BI-WeA

Chemical and Biological Detection
Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **HS+SS+BI-WeA1 Photonic Crystals Derived from Nanocrystalline Porous Si: Applications in Detection of Chemical Warfare Agents, Explosives, Pollutants, and Biochemicals**, ***M.J. Sailor***, University of California, San Diego **INVITED**

The optical properties of nanostructured porous silicon films are exploited for a variety of sensor applications. With appropriate modification of the electrochemical preparation conditions, multilayered structures can be generated that behave as photonic crystals. These structures can be encoded and used as remote sensors for chemicals. For example, small particles of nanoencoded microporous Si are used to detect chemicals by measurement of the intensity of reflected light from a remote laser probe. The particles contain a periodic porous nanostructure that defines the code. The periodic structure forms a Rugate reflector which displays sharp maxima in the optical reflectivity spectrum at wavelengths that are controlled by the etch parameters. The intensity and wavelength of reflected light is determined in part by the refractive index of the porous nanostructure, which can be modified by adsorption of vapors within the porous matrix. Using a 10 mW laser as an optical probe and telescope collection optics, detection of ethanol, acetone and toluene vapors has been achieved at a distance of 20 m. Control experiments using water vapor at comparable partial pressures show very little response, demonstrating selectivity towards the hydrocarbon analytes. Examples of irreversible detection and reversible sensing modes for explosives, nerve warfare agents, and various biochemicals will also be discussed. A catalyst can be incorporated into the nanomaterials to provide specificity for nerve warfare agents. For example, rapid detection of a fluorophosphonate is achieved by catalytic decomposition of the agent to HF and subsequent detection of the HF in the porous silicon interferometer. The catalyst system can be integrated on the silicon chip and consists of a TMEDA[Cu(II)] catalyst (TMEDA = tetramethylethylenediamine) encapsulated in cetyltrimethylammonium bromide (CTABr) micelles. An operational battery-powered unit has been constructed and tested on the live nerve warfare agent Sarin. These devices are all compatible with conventional Si microfabrication technologies.

2:40pm **HS+SS+BI-WeA3 Magnetic Labeling and Microarray Detection of Biomolecules**, ***L.J. Whitman***, Naval Research Laboratory **INVITED**

NRL is developing two novel biosensor systems using magnetic microbeads to probe for target biomolecules specifically bound to receptor-patterned surfaces, with an initial focus on detecting biological warfare agents. [1,2] The microbeads serve both as reporter labels and as force transducers to allow "force discrimination" - a technique developed at NRL that greatly reduces the background signal-enabling the identification of single biomolecular ligand-receptor interactions with high sensitivity and specificity. Assays using magnetic labeling and force discrimination have been developed for a variety of bacteria, viruses, and protein toxins (immuno-sandwich assays), and for oligonucleotide microarrays (hybridization assays). How the assays are incorporated into a practical sensor system depends on how the specifically bound beads are detected. We are currently perfecting two detection approaches, an optical system that images beads captured on a patterned nanoporous membrane, and a chip-based sensor system that directly detects beads using an array of giant magnetoresistive (GMR) magnetic field microsensors. The optical system has achieved sensitivities of 10 pg/ml for proteins, $10^{2.5}$ cfu/ml for bacteria, and 10^{3} pfu/ml for viruses. Using a single GMR sensor, we have successfully detected 1 fM of DNA in a 30 µL sample with only 15 min of hybridization. I will discuss how the interplay between surface chemistry, sensor design, and microfluidics determines the overall performance of our biosensor systems. Supported by ONR, the DoD JSTPCBD, and DARPA.

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[2] M. M. Miller et al., J. Mag. and Mag. Mat. 225, 138 (2001).

3:20pm **HS+SS+BI-WeA5 Optical Microarrays for Chemical and Biological Detection**, ***D.R. Walt***, Tufts University **INVITED**

We have used coherent imaging fibers to make fiber-optic chemical sensors. Sensors can be made with spatially-discrete sensing sites for multianalyte determinations. We are investigating the limits of our ability to create high-density sensing arrays containing thousands of microsensors and nanosensors. Micrometer- and nanometer-sized sensors have been fabricated by etching the cores of the optical imaging fiber to create wells and loading them with micro and nanospheres. Such arrays can be employed for making genosensors for bio-agent detection. We have also created optical sensors based on principles derived from the olfactory system. A cross-reactive array of sensors is created such that specificity is distributed across the array's entire reactivity pattern rather than contained in a single recognition element. The ability to use such information-rich assemblies for broad-based chemical sensing will be discussed.

4:20pm **HS+SS+BI-WeA8 Real-time Detection of TNT Using Microcantilevers with Microcyclic Cavitand Coatings**[1], ***N.V. Lavrik***, *T. Thundat, G. Muralidharan, P.G. Datskos*, Oak Ridge National Laboratory

Real-time detection of nitroaromatic aromatic explosive compounds in various environments is a highly significant task in forensics, anti-terrorist activities and global de-mining projects. In particular, ability to detect trace levels of trinitrotoluene (TNT) in air and soil could greatly reduce continued fatalities from land mines among civilians and be a measure in tracking and locating explosive materials. In our work, we address this challenge of detecting TNT vapors in gaseous environment by using an innovative, highly sensitive microcantilever transducer combined with a chemically sensitive molecular coating based on the macrocyclic cavitand of a calixarene family. We measured responses to vapors of TNT and its analogs, 0-mononitrotoluene and 2,4-dinitrotoluene vapors in the range of temperatures of 298 K to 318 K. Our results were used in order to estimate the limits of detection (LODs) for these compounds and optimize the temperature regime of the designed detection system. In the case of TNT, the steady state responses were large, however, the response kinetics was significantly elongated, which is consistent with an analyte depletion model. As compared to more traditional surface acoustic wave sensors with a proven potential for detection of TNT, our approaches offer a simpler, low-cost alternative without sacrificing the performance. The reported results together with these advantages of microcantilever based gas detectors clearly indicate a viable technological approach to mass produced detectors of explosive materials.

[1] This work was supported by the U.S. Department of Energy and Micro Sensor Technologies, Inc. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by UT-Battelle under contract DE-AC05-96OR22464.

4:40pm **HS+SS+BI-WeA9 A New Nanoscale Platform for Gas Sensor Applications**, *A. Kolmakov, Y. Zhang, G. Cheng*, ***M. Moskovits***, University of California Santa Barbara

The application of metal and semiconductor nanowires as solid state gas sensors has been an area of tremendous promise currently limited by challenges related to nanowire growth and device fabrication. We present an approach for fabricating individual and arrays of nanowires of a variety of metals and metal oxides with tunable, uniform diameters and length in the range of 10-100 nm and 5-200 micrometers, respectively, configured for gas sensing application. The materials successfully employed include Pd, Ag, Cu, Pb, PbO, CuO and SnO_2. Arrays of nanowires were fabricated in hexagonal close-packed nanochannel alumina templates. Electrodes deposited on the surfaces of these nanostructures provides electrical contacts which with the incorporated heaters determines the device architecture. Based on this method we explored the electronic and structural properties of Pd and SnO_2 nanowires using HRTEM, XPS and Auger spectroscopy. Chemical reactivity and gas sensitivity toward hydrogen and carbon monoxide of individual and assemblies of ca 10^{9} Pd and SnO_2 nanowires were assessed using conductivity measurements and TPD analysis. This approach constitutes a novel platform for micro- and nanosensor application.

5:00pm **HS+SS+BI-WeA10 Metal Phthalocyanine Thin Films as Gas Sensors**, ***L. Lozzi***, *S. Santucci*, INFM and University of L'Aquila, Italy, *C. Cantalini*, University of L'Aquila, Italy

Metal Phthalocyanine (MPc) thin films have shown interesting properties as gas sensor, in particular for NO2. The wide variety of different available molecules, changing both the central atom and/or the chemical structure of the outer benzene rings, allows a fine modulation of the film sensing properties. In this work we will present our result on the interaction between oxidating gases (O2 and NO2) and different MPc films. We have deposited thin films (about 50 nm thick) of Copper Phthalocyanine (CuPc) and Exadecafluoro-copper-phthalocyanine (F16CuPc) onto Si3N4 substrates, for the spectroscopic characterizations, and onto Pt interdigital circuits, for the gas sensing tests. These films have been analysed both as deposited and after different thermal annealing. The electrical sensing analyses have shown a sizeable decrease of the film resistivity during the film exposure to NO2, even at very low concentration (up to 100 ppb). We have studied the electronic structure by means of the X-ray and ultraviolet photoemission spectroscopies (XPS-UPS) after the exposure to NO2 and O2 both at room and at higher temperature, in order to investigate the surface reactivity of these samples and in particular the preferential adsorption sites.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI-WeA

Magnetization Dynamics
Moderator: S.E. Russek, NIST, Boulder

2:00pm **MI-WeA1 Investigation of Magnon Generation by a dc Current through a Point Contact/Magnetic Multilayer Junction**, ***W.H. Rippard***, *M.R. Pufall, T.J. Silva*, National Institute of Standards and Technology

We have studied the spin-momentum transfer (SMT) effect with mechanical point contacts and several types of magnetic multilayers, exhibiting both ferromagnetic (FM) and antiferromagnetic (AF) exchange-coupling. Electron spins flowing though a magnetic multilayer transfer angular momentum between the individual layers. At sufficiently high current densities, the resultant spin torque is large enough to induce magnetization dynamics.[1-5] Previous work using point contacts has shown that there is an abrupt step in the dc resistance, and corresponding peak in dV/dI, when the current reaches a critical value Ic. The linear dependence of Ic on applied magnetic field suggests a correlation with magnon generation. Earlier data were obtained from AF coupled films, with fields applied perpendicular to the film. In our measurements, we have explored a variety of parameters. We found that spin-momentum transfer is a robust effect, occurring for a wide range of experimental conditions. SMT-related phenomena are observed for both in-plane and out-of-plane fields, for AF exchange-coupled multilayers grown at both the 1st and 2nd GMR maxima, and for FM-coupled multilayers. Also, the dependence of Ic on field can vary substantially from contact to contact. Peaks in dV/dI can persist (albeit with reduced magnitude) down to zero applied field for AF-coupled samples. Multiple peaks can also occur, implying multiple excitation modes. For FM-coupled multilayers the SMT effects have large ~0.5 W steps in the dc resistance at the critical current, implying the onset of surprisingly large excitations. The persistence of SMT down to zero applied field suggests application of SMT as a novel high-frequency oscillator.

[1] M. Tsoi et al., Phys. Rev. Lett. 80, 4281 (1998)

[2] L. Berger, Phys. Rev. B 54, 9353 (1996)

[3] J. C. Slonczewski, J. Magn. Magn. Mater. 159, L1 (1996)

[4] J. A. Katine, et al., Phys. Rev. Lett. 84, 3149 (2000)

[5] E. B. Myers, et al., Science 285, 867 (1999).

2:20pm **MI-WeA2 Mechanical Detection of Ferromagnetic Resonance in Micron-size YIG Disk**, ***V. Charbois***, *O. Klein*, C.E.A. Saclay, France, *V.V. Naletov*, Kazan State University, Russia

We present room temperature measurements by Magnetic Resonance Force Microscopy (MRFM) of the ferromagnetic resonance (FMR) spectra on a normally magnetized YIG disk (with thickness 4.75µm and radius 80µm). The analysis of the influence of the tip for different probe-sample separation h led us to distinguish two cases. In the weak coupling regime, when the bias field generated by the tip is smaller than a few hundred Gauss, the prominent change is a shift of the entire spectrum to lower applied fields as h decreased. The result can be quantitativelly understood within the framework of the Damon and Eshbach model. In the strong coupling regime, the additional inhomogenous field produced by the tip can be used to localize new magnetostatic modes underneath the probe[2] (this allows local spectroscopy to be performed). However, in the case of YIG, the spatial extension of these modes is limited to 4µm. Simultaneous measurements of FMR both by standard susceptibility and mechanical detection demonstrate the higher sensitivity of MRFM[1] and its ability to measure smaller sample (in this case the spectroscopic response of the entire sample is obtained). Imaging of the magnetostatic modes can be performed by taking advantage of the localized probe. Ideally one should work at small h (to achieve high spatial resolution) with a tip producing a weak stray field (e.g. a tip coated with a thin film of ferromagnetic material). The last advantage of this technique is that it is sensitive to the longitudinal magnetization and thus it provides information complementary to conventional microwave susceptibility measurements.

[1] V.Charbois, V.V.Naletov, J.Ben Youssef and O.Klein, J.Appl.Phys 91, 7337 (2002).

[2] V.Charbois, V.V.Naletov, J.Ben Youssef and O.Klein, to be published in Appl.Phys.Lett. (June 24th issue)

2:40pm **MI-WeA3 Spin Wave Dynamics in Structured Magnetic Media**, ***S.O. Demokritov***, University Kaiserslautern, Germany **INVITED**

Spin waves are the fundamental dynamic eigen-modes of a magnetic system. The knowledge of the spin-wave properties in the small-amplitude limit is mandatory to understand the dynamic properties of a magnetic system in general. This presentation covers the recent results obtained on spin wave excitations in arrays of magnetic elements using Brillouin light scattering spectroscopy (BLS). Confinement of spin waves in magnetic elements leads to dramatic changes of the spin wave dispersion and density of states. The observed lateral quantization of spin wave modes in an element is one consequence of the confinement. The quantization conditions are determined by the stripe width, and by the boundary conditions at the lateral edges of the stripe. It is shown, that these conditions result in an effective "pinning" of a purely dipolar nature due to the inhomogeneity of the dynamic internal field near the stripe edges. An additional analysis of the BLS-intensity as a function of the transferred wavevector provides information on the mode profiles. According to the scattering theory from confined modes, the BLS-intensity of a given mode is determined by the Fourier-components of the mode profile. Thus, light scattering can be used as a "Fourier-microscope" and can provide information on the distribution of the dynamic magnetization in the elements with the resolution better than 200 nm. Another striking effect of magnetic confinement is a strongly inhomogeneous static internal magnetic field in the element. This inhomogeneity creates potential wells for spin waves near the edges of the elements. The size of the wells is much smaller than the lateral size of the element. The dynamic magnetic susceptibility in the well shows a strong maximum, causing a localization of low frequency spin wave modes in the well, which is experimentally confirmed using BLS-Fourier-microscope.

3:20pm **MI-WeA5 Spin Wave Excitations by Low Energy Electrons in Fe**, ***M.R. Vernoy***, *H. Hopster, D.L. Mills*, University of California, Irvine

A new spectrometer for spin polarized electron energy loss spectroscopy (SPEELS) has been constructed. The spectrometer is based on 127° cylindrical sectors as monochromator and analyzer, with the analyzer being rotatable for angle dependent measurements. A standard GaAs negative-electron-affinity photoemitter source is coupled to the monochromator and provides spin polarized electrons with polarization values around 25 %. SPEELS measurements were performed on thick (several 100 Å) epitaxial Fe films grown in situ on GaAs(100) substrates. The Fe films were remanently magnetized by a magnetic field pulse and SPEELS spectra were taken with the incoming beam polarization parallel or antiparallel to the magnetization. The primary energy used was 20 eV and an energy resolution of 25 meV (FWHM) was achieved. Strong spin asymmetries are detected in the energy loss spectrum. In addition to the well known Stoner excitation spectrum at high energies there is a distinct loss structure at small energies (100-300 meV) due to spin wave excitations. This spin wave energy loss structure has a highly asymmetric shape with a sharp onset around 100 meV, a maximum around 165 meV and a tail extending out to 350 meV. This peak shape can be explained by excitation of a continuum of bulk spin waves due to the non-conservation of q-perpendicular in the excitation process. We shall present comparison between the measured spectra and model calculations which employ a very simple description of the excitation process, and a Heisenberg model to describe spin waves at the crystal surface.

3:40pm **MI-WeA6 Dynamical Investigation of Transient Magnetic Anisotropy in $Ni_{80}Fe_{20}$**, ***R. Lopusnik****, *J.P. Nibarger, T.J. Silva, Z. Celinski*, National Institute of Standards and Technology

The values of static and dynamic uniaxial anisotropy in thin permalloy films are anomalously different by a factor of 2. The dynamic response of different thickness films are measured with a pulse inductive microwave magnetometer. The time-resolved precessional response was measured as a function of the applied bias field varying from 0 to 8 kA/m. The frequency range varies from 700 MHz to 3 GHz. Spectroscopic analysis of the data yields quantitative information about the intrinsic gyromagnetic properties of the films. The observed dependence can be fitted to high precision with the Kittel formula for ferromagnetic resonance to extract anisotropy field H_k, the spectroscopic factor g etc. The static anisotropy field value was obtained by a quasi-static measurement of a hysteresis loop along the magnetic hard axis. In this case, the saturation field corresponds to the anisotropy field of the sample. To understand this effect, variable angle measurements were performed for several different orientations of the uniaxial anisotropy with respect to the applied bias field. For each angle the value of the dynamical anisotropy was obtained. The angular dependence of the anisotropy can be fitted to a cosine function, but with an additional angle-independent offset field of ~400 A/m. The modulation amplitude of the fitted cosine function is equal to the static anisotropy field value of ~320 A/m. Both the cosine amplitude and angle-independent offset are found to be independent of film thickness below 100 nm. We interpret the constant offset field as a transient component of the magnetic anisotropy that only affects dynamical response at time scales below 10 ns. Similar behavior has been observed using magneto-optical methods.[1] In these recently reported studies, an initial fast response of the magnetization was followed by very

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***** Falicov Student Award Finalist

slow increase over a much longer time scale. We will discuss possible explanations, including non-linear dynamics and eddy currents.

[1] M. Bauer, R. Lopusnik, J. Fassbender, B. Hillebrands, J. Bangert, and J. Wecker, J. Appl. Phys. 91, 543 (2002); M. Pufall and T. Silva, IEEE Trans. Mag. 38, 129 (2002)

4:00pm **MI-WeA7 A New Equation for Magnetization Dynamics Based Upon Transverse Relaxation Processes**, ***T.J. Silva***, *R. Lopusnik, J.P. Nibarger,* National Institute for Standards and Technology, *T. Gerrits,* University of Nijmegen, The Netherlands

We present a new equation for magnetodynamic response, derived from the Bloch-Bloembergen formulation for spin relaxation phenomena. The new equation is vectorial and adapted for all possible field geometries. The longitudinal and transverse relaxation rates are constrained to insure conservation of the magnetization. As such, the new equation is amenable to finite-element micromagnetic simulations. Subject to the constraint of constant magnetization, the longitudinal relaxation rate cannot be constant during free induction decay in unbiased ferromagnetic films. However, if the transverse relaxation rate is held constant, the resulting equation is of the Landau-Lifshitz form but with an additional dependence of the damping term on longitudinal field. The field dependence strongly renormalizes the relaxation times for thin films in small bias fields such that MHz transverse relaxation rates for undressed excitations can result in nanosecond damping times in a thin film geometry. Such strong renormalization allows for a significant contribution by weak spin-orbit effects to the overall damping of precessional excitations in thin film structures. Inverse field dependence for the damping parameter in thin films is predicted by the new equation, in agreement with recent data obtained by inductive and optical methods.[1] In addition, highly viscous response is predicted when the magnetization is subject to large magnetic field pulses along the hard axis of uniaxial anisotropy films, also in agreement with recent observations of metastable states in homogeneous Permalloy films.[2] Implications for device performance and data storage applications will be discussed.

[1] T. J. Silva, T. M. Crawford, IEEE Trans. Magn. 35, 671 (1999).

[2] P. Kabos, S. Kaka, S. E. Russek, T. J. Silva, IEEE Trans. Magn. 36, 3050 (2001).

Nanometer Structures
Room: C-207 - Session NS+EL-WeA

Nanolithography & Self Assembly
Moderator: P.S. Weiss, The Pennsylvania State University

2:00pm **NS+EL-WeA1 Recent Development in Nanoimprinting Lithography**, ***L.J. Guo***, University of Michigan **INVITED**

Nanoimprinting lithography is an emerging technology that promises ultra-high resolution, high throughput and low cost. Unlike soft contact printing that uses an elastomer stamp, nanoimprinting uses a hard mold to create nanoscale features by directly imprinting into the polymer film at a temperature higher than its glass transition temperature (T_g). Sub-10 nm resolution and large area patterning have already been demonstrated in the past. This talk will present some recent development in nanoimprinting lithography, including imprinting at reduced temperature by using low T_g polymer materials; a reversed imprinting technique that enables "inking" of polymer materials onto a substrate, and patterning on non-flat surfaces without planarization, as well as the creation of simple 3D structures. This reversal nanoimprinting method also offers a unique advantage by allowing imprinting onto a flexible substrate that is otherwise difficult to spin-coat with polymer film, and we have demonstrated this by imprinting on a 50 mm thick flexible polyimide film. Nanoimprinting not only has the ability to pattern nanoscale features, but also it is compatible with polymer material processing. Based on these characteristics, we have applied it to two new applications. The first one is polymer micro-ring resonator photonic device fabricated by nanoimprinting, which is in the form of a micro-ring closely coupled to a waveguide, and offers unique properties such as narrow bandwidth filtering, high quality factor, compactness, and could find important applications in integrated photonic circuits. The second application is in organic polymer light emitting diodes (OP-LEDs), where we have developed a simple method based on nanoimprinting to define the OP-LEDs with pixel size ranging from nano- to micron-scale. The demonstration of those small size OP-LEDs indicates the possibility of fabricating ultra-high resolution OP-LEDs for applications such as micro-displays.

3:00pm **NS+EL-WeA4 Fabrication of Molecular Nanostructures by Scanning Near-Field Optical Lithography**, ***K.S.L. Chong***, *S. Sun, G.J. Leggett*, University of Sheffield, UK

Nanoscale patterns of self-assembled monolayers (SAMs) on gold and silver can be fabricated by a new technique called scanning near-field photolithography (SNP).[1] In SNP, a 244 nm laser coupled to a scanning near-field optical microscope is used to carry out nanometre scale photopatterning of SAMs. The photooxidised SAMs can be dipped into a solution of a different thiol, which displaces the oxidised material and adsorbs at the surface. Chemical patterns with linewidths of 40 nm were routinely obtained though patterns as small as 25 nm have been observed by friction force microscopy. The oxidised pattern can also be transferred to the underlying substrate by wet etching where linewidths of 80 nm have been obtained on gold substrates. Because of the ease by which SAMs can be patterned by this method, SNP can be routinely used to create nanoscale molecular patterns. Nanoscale patterns in SAMs can be used as templates for the attachment of biomolecules offering another approach to the miniaturisation of biological devices. Preliminary data have shown that proteins may be successfully immobilised to micron-scale patterned monolayers created using similar photochemistry. These methods are currently being combined with SNP in order to create biological nanostructures.

[1] Shuqing Sun, Karen S.L. Chong and Graham J.Leggett, J.Am.Chem.Soc, 2002, 124, 2414.

3:20pm **NS+EL-WeA5 Photoinduced Anisotropy of Second-Harmonic Generation from Azobenzene-Modified Alkylsiloxane Monolayers**, *Y.W. Yi,* ***T.E. Furtak***, Colorado School of Mines, *M.J. Farrow, D.M. Walba*, University of Colorado

Non-contact alignment of substrates in liquid crystal displays offers the advantage of reduced contamination and minimal surface charging. This approach also provides a means of reversible alignment after a device has been assembled. With this objective we have synthesized self-assembled monolayers based on dimethylaminoazobenzene units covalently attached to a glass surface by means of a short alkylsiloxane anchor (azo-SAM). The resulting architecture favors an orientation in which the axis of the azobenzene group should be nearly parallel to the surface with an isotropic azimuthal distribution. Under illumination with polarized UV light the trans-cis isomerization and subsequent relaxation serves to wiggle the molecule into an orientation perpendicular to the UV optical field. We have tested this scenario using optical second harmonic generation. We are able to identify a surface order parameter that characterizes the photoalignment of the azobenzene group. These data correlate with the recently reported behavior of nematic liquid crystal cells containing one substrate treated with the same azo-SAM.[1] This work is supported by NSF MRSEC grant DMR-9809555.

[1] "Liquid Crystal Alignment by Photo-Buffing Azo-SAMs", G. Fang, N. A. Clark, J. E. Mcclennan, M. Farrow, D. Walba, March Meeting of the American Physical Society, Indianapolis (3/20/20002).

3:40pm **NS+EL-WeA6 Nanostructuring of Hydrogenated Silicon Surfaces by Electron Beam Irradiation of Self-assembled Hydroxybiphenyl Monolayers**, *A. Küller, W. Geyer, V. Stadler,* Universität Heidelberg, Germany, *T. Weimann,* Physikalisch Technische Bundesanstalt, Germany, *W. Eck,* ***A. Gölzhäuser***, Universität Heidelberg, Germany

A new species of aromatic self assembled monolayers, hydroxy biphenyl, are formed on hydrogen terminated silicon and used as a negative tone electron beam resist. The formation of the monolayer and the electron induced modifications are observed by X-ray photoelectron spectroscopy. Nanometer patterns in the molecular layer were defined by low energy electron proximity printing as well as via conventional e-beam lithography. The patterns are transferred into silicon by a wet chemical etching process in KOH. The fabrication of patterns with lateral dimensions below 20 nm is demonstrated.

4:00pm **NS+EL-WeA7 Electrode Modification by Electron-induced Patterning of Self-assembled Monolayers**, ***B. Völkel***, *G. Kaltenpoth, T. Felgenhauer, W. Geyer, H.T. Rong,* Universität Heidelberg, Germany, *M. Buck,* University of St Andrews, UK, *A. Gölzhäuser*, Universität Heidelberg, Germany

Nanopatterns on electrode surfaces control the electrochemical deposition. An example is the formation of nanoscale dots or wires via the preferred nucleation at defects and step edges.[1] We present a method to artificially fabricate such electrochemical templates via coating of electrodes with self-assembled monolayers (SAMs) and subsequent patterning by electron beams. SAMs provide a flexible route to modify electrode surface properties via their molecular structure, ranging from inert alkane chains, which exhibit a blocking behavior, to redox active moieties. The e-beam patterning offers perspectives to generate arrays of microelectrodes with specific functionality. We coated gold electrodes with SAMs of w-(4'-

methyl-biphenyl-4-yl)-dodecylthiol (BP12) and hexadecanethiol (HDT) and patterned them by electron beam lithography. The subsequent copper deposition in an electrochemical cell revealed that the e-beam patterned alkanethiol behaves opposite than e-beam patterned biphenyl. Similar to the behavior of these materials as resists,[2] HDT acts as a "positive template" leading to copper deposition only on the irradiated parts. BP12 acts as a "negative template", where the irradiated biphenyl layer is cross linked and exhibits a blocking behavior,[3] hence copper is only deposited on the non-irradiated parts. By using these effects well defined Cu nanostructures could be generated.

[1] M. P. Zach, K.H. Ng, R.G.Penner, Science 290, 2120 (2000).

[2] A. Gölzhäuser, W. Geyer, V. Stadler, W. Eck, M. Grunze, K. Edinger, T. Weimann, P. Hinze, J. Vac. Sci. Technol B 18, 3414 (2000).

[3] T. Felgenhauer, C. Yan, H.T. Rong, A. Gölzhäuser, M. Buck, Appl. Phys. Lett. 79, 3323 (2001).

4:20pm **NS+EL-WeA8 Electrochemically Controlled Film Formation of Self-assembled Monolayers of Biphenyl-based Thiols**, *I. Thom, B.J. Livesay*, StAndrews University, UK, ***P. Cyganik***, Jagiellonian University, Poland, *M. Buck*, StAndrews University, UK

Usually self-assembled monolayers (SAMs) of thiols are prepared by mere immersion of the substrate in a solution containing the respective thiol. Whereas a number of preparation parameters such as the thiol concentration, temperature, immersion time, or solvent type have been investigated in some detail, no systematic studies have been performed on how the substrate potential affects the kinetics of film formation and the resulting SAM structure. Since the potential controls the bonding of a thiol to the substrate, i.e. its stability, the rate of adsorption/desorption and the mobility of the thiols are affected and, consequently, a pronounced influence of the potential can be expected. Using thiols which are characterized by a biphenyl unit and an alkane spacer chain between the aromatic moiety and the SH group we have studied the kinetics of film formation using nonlinear optical spectroscopies and scanning tunneling microscopy. Both the kinetics of film formation and the final film structure undergo significant changes ranging the potential from values near the reductive desorption of thiols to values around zero volts.

4:40pm **NS+EL-WeA9 Modification of Self-assembled Monolayers by Free Radical-dominant Plasma: The Effect of the Chain Length and the Substrate**, *M. Zharnikov, S. Frey,* ***M. Grunze,*** Universität Heidelberg, Germany, *M.-C. Wang, J.-D. Liao, C.-C. Weng,* Chung Yuan Christian University, Taiwan (ROC), *R. Klauser*, Synchrotron Radiation Research Center, Taiwan (ROC)

Synchrotron-based high-resolution photoelectron spectroscopy was applied to study the modification of aliphatic and aromatic thiol-derived self-assembled monolayers (SAMs) on (111) gold and silver substrates by a nitrogen-oxygen downstream microwave plasma. It was found that the plasma treatment does not result in a "soft" modification of SAMs, but in their massive damage and disordering. Contrary to the electron beam treatment, both the aliphatic and aromatic films became modified and damaged in a similar way, with the extent of the changes depending on the length of the molecular chains and, above all, on the substrate. For SAMs on Au a profound desorption of the entire SAM constituents and a complete fragmentation of the residual hydrocarbons is observed. For the SAMs on Ag only partial desorption and oxidation took place and, for short treatment times, the films remained practically intact. The desorption of molecular species was preceded by the oxidation of the pristine thiolates to weakly-bonded sulfones, which occurred after the penetration of chemically active oxygen species into the S/substrate interface via defect sites. Such a mechanism clearly explains the observed dependence of damage extent on the SAM thickness and emphasizes the importance of the strength of the thiolate-substrate bond. Thus, a stronger thiolate-substrate bond can be suggested for Ag as compared to the Au substrate. In addition, considering the similarity of the plasma-induced processes and UV-photooxidation, one can extend the major conclusions obtained for the plasma treatment to UV-photooxidation.

Organic Films and Devices
Room: C-102 - Session OF+EL+SC-WeA

Molecular and Organic Films and Devices
Moderator: N. Koch, Princeton University

2:00pm **OF+EL+SC-WeA1 Recent Developments in Organic Optoelectronics**, ***S.R. Forrest***, Princeton University **INVITED**

The interest in organic materials for optoelectronic device applications has undergone explosive growth in the last several years. This growth has been propelled by advances in organic thin films for displays, and for low cost electronic circuits. With a few successful product introductions employing active electronic organic devices, it is possible that the "age of organic optoelectronics" has finally arrived. This talk discusses some of the recent progress in organic device technology, with an eye to the future which may include making active electronic devices with a single molecule. In particular, we discuss extremely high external emission efficiency organic light emitting devices used for displays and lighting applications. Also, similar progress in high bandwidth, high efficiency of organic photodiodes, and efficient thin film photovoltaic cells are discussed. For example, multilayer organic nanostructure photodetectors are found to have very high frequency response with detection sensitivity in the visible spectral range. Finally, we present some new ideas on organic device fabrication enabling patterning of structures on the nanometer scale in both the vertical and horizontal directions.

3:00pm **OF+EL+SC-WeA4 Electron Transport in Platinum Complex Molecules: An Approach to Molecular Electronics**, *T.L. Schull, J.G. Kushmerick,* ***R. Shashidhar***, Naval Research Laboratory

Molecules that are highly conducting and which can be attached to metal on both sides via a functional chemical group form the basic elements of a molecular electronic device. Electron transport across different types of organic molecules are being actively investigated using different types of measuring test beds. In this paper, we present results of our electron conduction studies across a family of organo metallic molecules using a new cross-wire test bed developed recently.[1] We show that trans-platinum-bis-acetylides show good electron transport across their molecular length that are even better than the properties of the corresponding π-conjugated oligo(phenyleneethynylene) studied by several groups. The dependence of the metal ligands on the electron transport properties of materials is discussed. We have also used a simple extended Huckel Theory coupled with a Green Function approach to calculate the current voltage characteristics of these molecules. These theoretical calculations are compared with experiments.

1. J.G. Kushmerick, D.B. Holt, J.C. Yang, J. Naciri, M.H. Moore and R. Shashidhar, to be published.

3:20pm **OF+EL+SC-WeA5 Organic Light-Emitting Diodes and Solar Cells with Electrically Doped Transport Layers**, ***K. Leo***, TU Dresden, Germany **INVITED**

In classical semiconductor technology, controlled n- and p-type doping has always been a standard technique. In contrast, organic materials for devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form. We discuss results of a comprehensive study of controlled electrical doping of various thin-film molecular organic materials. The layers are prepared by co-evaporation of matrix materials with acceptor molecules and characterized by several electrical techniques. UPS and XPS measurements directly show the Fermi level shift and the reduction of space charge layer width due to increasing doping.[1] We further show that these electrical doping concepts can be successfully applied in devices. The concept of molecular doping is applicable for amorphous wide-gap hole transporting materials and allows for realizing devices with the lowest operating voltages reported so far for small-molecule devices.[2] The concept of controlled doping has also enabled us to prepare a semitransparent inverted OLED with outstanding performance. It features an inverted layer sequence with ITO efficiently injecting electrons into a highly n-doped layer, despite a very large energy barrier of around 1.8eV. The devices reaches display brightness of 100Cd/m2 at 3.4V, which is far below any other literature result. We will also present first results on doped phosphorescent OLEDs which show that the concept of electrical doping can be extended to high-efficiency emitters. Finally, we will discuss the application of doped transport layers in solar cells. (Work done in collaboration with M. Pfeiffer, J. Blochwitz-Nimoth, X. Zhou, J. Huang, D. Qin, B. Maennig, D. Gebeyehu, A. Werner, J. Drechsel.)

[1] J. Blochwitz et al., Organic Electronics, 2 , 97 (2001)

[2] J. Huang et al., Appl.Phys. Lett. 80, 139 (2002).

4:00pm **OF+EL+SC-WeA7 Understanding Charge Transport Across Metal-Molecule-Metal Junctions**, ***J.G. Kushmerick***, *R. Shashidhar*, Naval Research Laboratory

Charge transport across a metal-molecule-metal junction is regulated by three factors 1) the structure of the molecule 2) the nature of the metal-molecule contacts and 3) the choice of metal electrode. We use an experimentally simple crossed-wire tunnel junction to interrogate how each of these three factors influences the current-voltage characteristics of a molecular junction. Results on symmetric and asymmetric junctions 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. We will also show that the experimentally measured conductance of a molecular wire can be directly related to how well it's π-conjugated backbone mimics an ideal one-dimensional metal.

4:20pm **OF+EL+SC-WeA8 Zero-bias Anomaly in Molecular Monolayer Tunneling**, ***D.R. Stewart***, *D.A.A. Ohlberg, P.A. Beck, R.S. Williams,* Hewlett-Packard Laboratories

Electron tunneling is the dominant transport mechanism in nearly all proposed molecular electronic devices. Standard tunneling theory is normally used to predict device behavior, yet few experimental investigations of molecular tunneling exist due to the difficulty in constructing high quality molecular monolayer films. We describe detailed electronic transport characterization of several planar electrode / Langmuir-Blodgett (LB) molecular monolayer / electrode systems that show a large zero-bias anomaly and an anomalous exponential temperature dependence. Single-species LB monolayers of C_{22}, C_{20}, C_{18}, C_{16} and C_{14} carboxylic acid alkanes were sandwiched between upper and lower platinum electrodes, with active device areas of 7-200µm^2. Current and differential conductance were measured as a function of voltage ±1V and temperature 2-300K. Below 40K, device characteristics were constant. Surprisingly, from 40-300K device currents were exponential in temperature. A very wide ±150mV dip in conductance was also present and temperature activated. Both results contradict standard tunnel theory, indicating that the electronic transport is not yet understood even in this simplest symmetric alkane monolayer system.

4:40pm **OF+EL+SC-WeA9 Lateral Confinement of Interfacial Electrons by a Surface Dipole Lattice**, ***X.-Y. Zhu***, *G. Dutton*, University of Minnesota

Interface formation between molecules and a solid substrate often involves charge redistribution, the extent of which can influence a wide range of physical and chemical phenomena. In high mobility field effect transistors (FETs) based on organic single crystals, charge transport is believed to occur in one to two layers of molecules at the organic-dielectric interface. Such an interface may involve charge redistribution and dipole formation. The presence of surface dipoles may significantly alter lateral charge transport in the thin organic layer. When the interface is disordered, these surface dipoles are scattering centers for band transport. On the other hand, if the interface is ordered, there is essentially a two-dimensional lattice of dipoles. Such a surface dipole lattice should give rise to an electrostatic potential which provides periodic confinement of valence and conduction band electrons. We demonstrate this effect for image electrons on C60 thin film covered Cu(111) using angle resolved two-photon photoemission spectroscopy. Metal-to-molecule electron transfer within the first layer creates a (4x4) superlattice of surface dipoles. Such a surface dipole lattice provides lateral confinement of image electron wavefunction, effectively eliminating parallel dispersion for the n=1 image state on one monolayer C60 covered Cu(111). This is in contrast to the significant dispersion observed at higher coverages. The electrostatic potential from the surface dipole lattice is screened by additional layers of C60 molecules, thus, restoring the expected free electron behavior (parallel to the surface) for image states. Quantum mechanical simulation reproduces experimental findings and reveals the extent of wavefunction localization by the surface dipole lattice.

5:00pm **OF+EL+SC-WeA10 Measurement of the Site Specific PDOS of Organic Electronic Materials via Soft X-ray Emission Spectroscopy**[1], ***J.E. Downes***, *C. McGuinness, P. Sheridan, K.E. Smith,* Boston University, *J.A. Schlueter, U. Geiser,* Argonne National Laboratory, *G. Gard*, Portland State University

Recent advances in the technique of soft x-ray emission spectroscopy (XES) have produced a method to directly measure the bulk elementally and, in certain cases chemically, specific partial density of states of materials. While the detailed measurement of the valence band electronic structure of solids has traditionally been the realm of photoemission spectroscopies several problems have been encountered with the application of these techniques to organic materials. The principal issue is photon induced damage to the compound that modifies the electronic structure as it is being measured. Another is the fact that photoemission measurements probe the surface electronic structure of a material, which may or may not be representative of the bulk. We will show that the use of XES can avoid both of these problems and allows the detailed valence band electronic structure of recently developed organic electronic compounds to be measured. An overview of the technique of XES and its advantages for studying these organic compounds will be followed by specific results from several organic electronic compounds of current interest in the fields of molecular organic semiconductors, (TDATA, Alq_3, TPD, Cu-Pc etc.), and ET based conducting organic charge transfer salts, (β-$(ET)_2SF_5CH_2CF_2SO_3$).

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[1] Work supported in part by the DOE under DEFG0298ER45680; the SXE spectrometer was funded by the U.S. ARO under DAAH04950014. The experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.

Plasma Science
Room: C-103 - Session PS+BI-WeA

Plasma Processing for Biocompatible Surfaces
Moderator: H.J. Griesser, University of South Australia

2:00pm **PS+BI-WeA1 Application of Plasma in Tissue Engineering**, ***R.D. Short***, *D.B. Haddow, S. MacNeil, R.A. Dawson, D. Barton, S. Fraser*, University of Sheffield, UK **INVITED**

A novel device which comprises an acrylic acid plasma polymerized carrier substrate, which supports the attachment and release of human keratinocytes, has been used to successfully treat non-healing (chronic) skin wounds. In proof of concept studies, weekly delivery of keratinocytes, initially obtained from a small 2x1cm biopsy and expanded up many hundred fold, have promoted healing in diabetic foot ulcers and other indications. In this paper we explain the rationale behind this therapy and review the results (to date) from the treatment of the first seven patients. Although the "mode of action" of the device is still to be fully understood, the role the plasma polymer plays in promoting cell attachment and detachment is key to the success of the device. The physical and chemical nature of the plasma polymer has been explored in some detail, and to a first approximation, we are able to describe the features of the plasma polymer that promote cell attachment and speculate on why cells transfer to an in vitro human dermal wound bed model. By means of a multi-technique approach (mass spectrometry,quartz crystal microbalance, ion flux probe, x-ray photoelectron spectroscopy, secondary ion mass spectrometry) we have begun to unravel the processes by which the acrylic acid plasma polymer grows. A case is made for better understanding of plasma polymer growth mechanisms, rather than treating the plasma polymerization process as a "black box" that produces materials with desired properties.

2:40pm **PS+BI-WeA3 Can Plasma Polymerised Surfaces Promote the Co-culture of Human Dermal Fibroblasts and Human Epidermal Keratinocytes in the Tissue Engineering of Skin?**, ***M.C. Higham***, *S. MacNeil, R.D. Short,* University of Sheffield, UK

Within the field of tissue engineering there is a need to develop new approaches to achieve effective wound closure in patients with extensive skin loss or chronic ulcers. Plasma polymers are synthetic surfaces capable of influencing and controlling cell physiology either directly or through an adsorbed protein layer. This project exploits the well-known interdependency of epithelial keratinocytes and stromal fibroblasts in conjunction with plasma surface technology. The aim of my project is to produce a chemically defined surface, which with the aid of a feeder layer of lethally irradiated dermal fibroblasts will improve the performance of the keratinocyte cell. Unable to divide yet remain physiologically active, irradiated fibroblasts aid keratinocyte attachment and proliferation from which sub-confluent cells can be transferred to wound bed models. Plasma co-polymers of acrylic acid/octa-1,7-diene have been prepared and characterised using X-ray photon spectroscopy (XPS). The fibroblasts and keratinocytes were cultured on plasma polymer coated 24 well plates. Cell attachment and proliferation were assessed using MTT-ESTA and DNA assays. The performance of both cell types on the plasma polymer surfaces was compared to Tissue Culture Plastic (TCPS) and Collagen I, plus a negative control of a pure hydrocarbon layer. A pure acrylic acid surface, fabricated at a power of 10W and containing 9% carboxylate group was found to promote both fibroblast and keratinocyte attachment and proliferation and permit the co-culture of keratinocytes with irradiated fibroblasts. The performance of this surface was comparable to collagen I, a well-established substratum for the attachment of keratinocytes. Current work is examining the potential of plasma polymer surfaces within the field of tissue engineering for transfer of keratinocytes onto an in vitro wound bed model and thereafter clinical trials.

3:00pm **PS+BI-WeA4 The Role of Reactive Neutral and Ionic Species in the Deposition of Organic Thin Films from an Isopropyl Alcohol and Argon Plasma**, ***D.C. Guerin***, National Research Council, Canada, *V.A. Shamamian*, Naval Research Laboratory

We present the measurements of neutral species in an argon/isopropyl alcohol (iPrOH) plasma, using appearance potential mass spectrometry. IPrOH is a potential precursor for the cost-effective plasma deposition of non-fouling surfaces. This work complements previous research on the ionic character of the plasma. It had been discovered that tuning the plasma pressure and power caused large variations in the dominant ionic reactions. The resulting changes in the chemical nature of the ionic flux were reflected in the functional character of the deposited films. A significant flux of neutral radicals was detected at the deposition surface at low plasma pressure. However, at higher pressures the plasma region was more remote and the neutral radicals were completely attenuated. The attenuation mechanism was determined to be reaction with the precursor. For example, the methyl radical abstracts hydrogen from iPrOH. Thus, as the pressure increases, the methyl radical flux evolves into a flux of methane. Mean free path (MFP) calculations for hydrogen abstraction agree with the experimental results. At low pressures, the reactive MFP is larger than the chamber geometry. At higher pressures, the reactive MFP is much smaller than the distance between the plasma and deposition surface. The ability of the reactive ions to diffuse from the remote plasma to the deposition surface is explained as being due to charge exchange limitations. The radical species generated have lower ionization energies than iPrOH or argon. Thus, the radical ions are energetically unable to react with the main species in the plasma. In contrast, the flux of ions with ionization energy greater than that of iPrOH, such as argon and methane, is highly attenuated at higher pressures. These results provide some context to competing claims as to the importance of neutrals and ions in deposition from molecular plasmas.

3:20pm **PS+BI-WeA5 Plasma Micropatterning for the Spatially Controlled Adsorption of Proteins**, ***J.D. Whittle***, *R.D. Short, D. Barton, A.G. Shard*, University of Sheffield, UK

Many biological interactions are surface mediated, for example protein adsorption and subsequent cell adhesion. In vitro it may be desirable in a number of applications to exert spatial control over these interactions. i.e. Limiting the attachment of cells to particular surface regions. We investigate the use of masks as a method of fabricating surfaces with patterned chemistry by plasma polymerisation, with feature sizes down to around 10µm. We utilise imaging secondary ion mass spectrometry (SIMS) and fluorescent light microscopy to visualise these chemical patterns. We also show how these chemical patterns affect the adsorption of proteins, not only in terms of the the amount of adsorbed protein, but also their conformation. A natural extension of depositing well-defined regions of chemistry (patterns) is to be able to fabricate regions of controlled chemical change (gradients), the properties of which vary continuously along the length of the deposited feature without any sharp transitions. We show how plasma polymerisation may be used to deposit chemical gradient surfaces with chosen endpoints (for example, a gradient running from a hydroxyl though to an amine dominated surfaces), and profile (for example, linear, sigmoidal etc.) by careful manipulation of the plasma composition and deposition surface during the treatment. These gradient surfaces can be used to examine the affect of changing a particular surface parameter (for example, the surface concentration of amine functionalities) on protein adsorption.

3:40pm **PS+BI-WeA6 Chemical Surface Micropatterning by Plasma and VUV Photochemical Modification of Polymers for Controlled Cell Culture.**, ***N.A. Bullett***, *F.E. Truica-Marasescu, M.R. Wertheimer*, Ecole Polytechnique, Canada

The three dimensional nature of the biomolecular environment in contact with cells has an important influence on the initiation and control of cell processes such as adhesion, migration, growth, protein secretion and gene expression. Traditionally, cell culture uses homogeneous substrates with no control over the biochemical and topological features in the immediate vicinity of the cells. The shape of mammalian cells is determined by the interaction of cell contact receptors with other cells or extracellular matrix proteins. Regulation of the shape of cells may enhance the function and differentiation of the cells. Surface modification of polymeric materials by low-pressure plasma and VUV photochemical treatment provides a convenient route to the fabrication of well defined chemically functionalised surfaces. A variety of functional groups may be introduced into the polymer surface, including amine and hydroxyl. Using these techniques it is possible to engineer surfaces that have a wide variety of applications in biomaterials technology, such as cell and protein adhesive surfaces or non-fouling surfaces. Complex micropatterns of chemically different regions have been produced by the selective functionalisation of the polymer using photolithographically defined masks. By this method, chemically distinct regions are produced at the micrometer scale, with a third dimension being provided by nanoscale topographical features. This three dimensional environment, on the nano- or micrometer scale, provides a complex but controllable surface for the culture of many different cell types. Characterisation of the micropatterned surfaces has been performed by XPS, FTIR, imaging TOF-SIMS and fluorescence microscopy. The surfaces have subsequently been used to study the attachment and growth of various cell types, for example bone-derived cells with orthopaedic applications.

4:00pm **PS+BI-WeA7 Study of Adhesion Mechanism of Protein-based Hydrogel to Plasma Treated Polymer Surface**, ***O. Zabeida***, Ecole Polytechnique of Montreal, Canada, *M.-P. Faure*, Bioartificial Gel Technologies, Canada, *J.E. Klemberg-Sapieha, L. Martinu*, Ecole Polytechnique of Montreal, Canada

Biodegradable protein-based hydrogels (solid water solutions, SWS^{TM}) are a new class of biomaterials with great potential for use in numerous pharmaceutical and medical applications. Since they may contain up to 96% of water, some SWS are rather fragile and difficult to handle and manipulate. This problem can be solved by applying appropriate polymer backings; the latter one has to be surface treated in order to enhance the hydrogel's adhesion. We found that plasma modification of polymer backings can lead to a 20-fold increase of the adhesion force between the SWS and the polymer surface. In the present work we have applied a multitechnique surface analytical approach, including infrared spectroscopic ellipsometry, XPS, AFM, and TOF-SIMS, to investigate the adhesion mechanism of hydrogels to low pressure plasma-treated polymers (polypropylene, polyethylene terephthalate, and others). The surface chemical structure and morphology are correlated with the adhesion force of the SWS. The results suggest that introduction of amine groups plays a major role in the adhesion improvement, while the surface roughening, polymer chain scission and surface electric charge should also be considered.

4:20pm **PS+BI-WeA8 Permanent Hydrophilic Modification of Porous Membranes Using Low-Temperature Plasmas**, ***D.S. Wavhal***, *E.R. Fisher*, Colorado State University

We have explored the use of low-temperature plasmas to modify porous polymeric membranes with the goal of creating hydrophilic surface throughout the membrane structure. One motivation for this work is to decrease membrane fouling and to eliminate the need for wetting agents in a variety of applications. Porous polyethersulfone (PES) membranes were modified by CO$_2$ plasma treatment and Ar-plasma treatment followed by grafting of hydrophilic monomers (acrylic acid and acrylamide), in the vapor phase. Plasma treatment and plasma induced grafting rendered a complete hydrophilicity to the entire PES membrane cross section. The hydrophilicity of the membranes treated with only the Ar-plasma is not, however, permanent. In contrast, the PES membranes treated with CO$_2$ plasma and the grafted membranes are found to be permanently hydrophilic (for a minimum of six months). Chemical changes to the modified PES membranes were determined with FTIR and XPS measurements. Furthermore, water bubble point measurements and electron microscopy results reveal that pore sizes of the modified membranes are slightly affected. The pore sizes of the grafted membranes at higher grafting yield are slightly decreased. Due to incorporation of polar functionalities, the glass transition temperature (T_g) of modified membranes also increases. A moderate change in tensile strength of the modified membranes was observed. Most importantly, the surface of the modified membrane are less susceptible to absorbtion by bovine serum albumin (BSA) proteins and give greater flux recoveries. This suggests that the protein fouling layer is reversible because of hydrophilic nature of the modified membranes.

4:40pm **PS+BI-WeA9 Acrylic Acid Films Deposition by RF PACVD: Relation between Monomer Fragmentation and Surface Properties**, *P. Rossini, G. Ceccone*, European Commission, Joint Research Centre, Italy, *K. Jandt*, University Jena, Italy, ***F. Rossi***, European Commission, Joint Research Centre, Italy

The present study deals with the deposition of acrylic acid thin films by radio frequency plasma assisted chemical vapour deposition. The experiments have been carried out in a cylindrical capacitively coupled plasma reactor at different electrical powers (5-60 Watt), in order to optimise the precursors fragmentation and to tune selectivity and stability of the deposited polymers. In situ diagnostics (Mass Spectrometry and Optical Emission Spectroscopy) have been used in order to control the deposition processes and analyse the fragmentation steps. The films have been characterised with X-Ray Photoemission Spectroscopy (XPS) and Fourier Transformed Infrared Spectroscopy (FTIR). Surface energy of the coatings has been determined by contact angle measurement. The protein adsorption kinetics has been evaluated with the Quartz Crystal Microbalance (QCM-D) with HSA. The results demonstrate a strong link between monomer fragmentation in the plasma and functional groups retention in the films. By increasing the RF power, the COOH concentration in the films (XPS and FTIR) as well as hydrophylicity, hydrogen bondings and acid-base character decrease while the CO concentration in the plasma phase (MS and OES) increases. At the same time, the dispersive and the polar components of the surface free energy increase. These surface properties have a strong influence on the protein attachment kinetics, as determined by QCM measurements.

Plasma Science
Room: C-105 - Session PS+MM-WeA

Feature Profile Evolution /Plasma Processing for MEMS
Moderator: A. Kornblit, Bell Labs, Lucent Technologies

2:00pm **PS+MM-WeA1 Plasma Molding Over Trenches and Resulting Ion/Fast-neutral Distribution Functions**, ***D. Economou***, *D. Kim**, University of Houston

Plasma molding over surface topography finds applications in MEMS microfabrication, neutral beam sources, plasma extraction through grids, and plasma contact with internal reactor parts (e.g., wafer chuck edge). The flux, energy and angular distributions of ions incident on the substrate are of primary importance in these applications. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface topography. When the sheath thickness is comparable to or smaller than the feature size, the sheath tends to "mold" over the surface topography. A two-dimensional fluid/Monte Carlo simulation model was developed to study plasma "molding" over surface topography. 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 the walls of a trench will be reported. Emphasis will be placed on high aspect ratio features of interest to MEMS and neutral beam sources. Simulation results will be compared with experimental data, taken at Sandia National Labs, on ion flux and ion energy and angular distributions at the bottom of trenches. Work supported by the National Science Foundation and Sandia National Laboratories.

2:20pm **PS+MM-WeA2 Physically Based Modelling of High-Density-Plasma-CVD on the Feature Scale**, ***G. Schulze-Icking***, *A. Kersch*, Infineon Technologies AG, Germany, *A. Knorr*, Infineon Technologies, *A. Hausmann*, *J. Radecker*, Infineon Technologies Dresden GmbH & Co. OHG

Due to its low thermal budget and its highly directional deposition HDP-CVD of SiO2 has become an important process in IC fabrication. In order to study (and ultimately improve) the HDP-CVD process we have developed a physically based model for feature scale simulations. This model has been implemented into our custom Topography Simulator "Topsi" and extensive studies of the HDP-CVD process have been performed. In this presentation we give a survey of our simulation results and compare them to experiments. The model we propose retains the characteristics of a complex reactor scale model published by Meeks et al.[1] and extends it to the feature scale. A key aspect of both models is a "structural passivation" of the surface due to the chemisorption of gas phase precursors. In contrast to conventional CVD (at much higher temperatures) in HDP-CVD this passivation is removed by cations striking the surface. Accordingly ions not only sputter surface material but also are responsible for its directional deposition. The final topography therefore is the result of simultaneous neutral deposition/passivation, ion induced activation, and sputtering. It is well known[2] that the sputtering yield crucially depends on the ion energy and the angle of incidence. This probably also applies to ion induced surface activation, but very little is known about its energy and angular dependence. We therefore have performed deposition experiments and compared the final topography to simulations performed using our new model. With the derived set of parameters we are now able to predict the surface evolution as a function of process conditions. This is a major improvement over a more empirical model proposed by Conti et al.[3]

[1] E.Meeks et al.; J.Vac.Sci.Techn. A, 16, pp 544 (1998)

[2] C.Abrams et al.; J.Vac.Sci.Techn. A, 16, pp 3006 (1998)

[3] R.Conti et al.; DUMIC Conference (1999).

2:40pm **PS+MM-WeA3 Micro- and Nano-Fabrication Technology for High Aspect Ratio Micro-Electromechanical Systems (MEMS)**, ***S.W. Pang***, The University of Michigan **INVITED**

For many applications in micro-electromechanical systems (MEMS), having high aspect ratio sensors or actuators can improve performance, increase sensitivity, and lower power consumption. Micro- and nano-fabrication technology can be used to generate these high aspect ratio MEMS. Etch rate, profile, selectivity, and uniformity could vary as aspect ratio becomes higher since plasma etching characteristics depend on aspect ratio of microstructures. These variations could affect MEMS performance. In this talk, key issues to provide precise control in MEMS fabrication by plasma processing will be discussed. High aspect ratio MEMS including micromirrors for optical switching arrays, submicrometer resonators for accelerometers, sharp tips for emitters or scanning probes, and microheaters for micro-gas chromatography systems will be reviewed.

3:20pm **PS+MM-WeA5 Critical Tasks in the High Aspect Ratio Silicon Dry Etching for MEMS**, ***I.W. Rangelow***, University of Kassel, Germany **INVITED**

Microscopically uniform anisotropic etching of semiconductor layers is a critical step in ME(O)MS and ULSI circuit fabrication. The non-ideal etched feature limits density, yield and reliability of these devices. Artefacts such as RIE-lag, notching, sidewall bowing, micro-trenching, and mask facetting are typically accompaniment effects occurring during the etching high aspect ratio features in silicon. Because etch rates and the shape of etched features depend on circuit layouts-design, considerable effort have to be spent in the near feature to understood all common single and simultaneous phenomena during the high aspect ratio dry etching. The development of effective manufacturing processes requires a fundamental understanding of the factors, which determine etched feature shape. Gas reactivity, pressure (affecting ion bowing in the sheath due to scattering with neutrals), ion, electrons and reactant transport to the surface, and product transport away from the surface, have been identified as the key factors that control the microscopic etching uniformity in high aspect ratio etching. The choice of these can cause numerous secondary aspect ratio-dependent effects. The modelling of the most significant effects as RIE-lag, notching, bowing, facetting, micro-trenching, profile shape dependence etc. will be discussed.

4:00pm **PS+MM-WeA7 Deep Silicon Etch Profile Control for Micro-Sensor Applications**, ***R.J. Shul***, *M.G. Blain*, *S.G. Rich*, *S.A. Zmuda*, *C.G. Willison*, *R.P. Manginell*, Sandia National Laboratories

The ability to etch deep, high-aspect ratio, anisotropic, Si features has opened up new areas of application for microelectromechanical systems (MEMS) devices, as well as revolutionized the conception and implementation of "mixed technology" integration. For example, a fully integrated microsystem could include sensors, actuators, electronics, fluidics, and optics in a variety of material systems on a single chip or in a single package. Fabrication of such structures often requires profile control, multi-level etched features, and the ability to form freestanding membrane structures. For example, Si deep reactive ion etch (DRIE) has been used to fabricate a gas chromatographic (GC) separator as part of a micro-chemical analysis system (µChemLab™) used for the detection of trace concentrations of gas phase analytes. Maintaining uniform, controlled flow dynamics to optimize device performance requires well-controlled etch profiles and smooth etch morphologies. We will report on the use of the DRIE platform to fabricate anisotropic GC columns 100 µm wide, 400 µm deep with 25 µm walls. To improve the separation sensitivity of the GC columns, a new GC design that incorporates 50 µm diameter posts on 80 µm pitch located within 500 µm deep GC columns has recently been fabricated. A new DRIE process was developed to etch these features using parameter ramping, varying reactive gas flow, pressure, and ion energy. The profiles were very anisotropic with smooth features. The use of parameter ramping as well as multi-level masking processes to meet the challenges of advanced micro-sensor designs will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.
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4:20pm **PS+MM-WeA8 Profile Control as a Function of Process Parameters in Deep Anisotropic Etching of Silicon**, ***M.L. Steen***, *T.J. Dalton*, IBM T.J. Watson Research Center

Deep etching of silicon is integral to the fabrication of microcomponents for microelectromechanical systems (MEMs). New commercially-available etching tools from several manufacturers are capable of deep silicon etching beyond 300 µmm. These systems offer the time multiplexed deep etching (TMDE) technique developed and licensed by Robert Bosch Gmbh, which uses alternating etching and deposition cycles for anisotropic etching of deep silicon structures. During the deposition step, sidewalls are passivated by a polymer deposited from a C_4F_8 discharge. During the subsequent etching cycle flowing only SF_6, both the polymer and silicon are preferentially etched from the base of the trench by ion bombardment. Accurate control of the depth and anisotropy of etched structures is achieved by a fine balance between deposition and subsequent removal of the passivating layer. Processes are well controlled and many types of MEMS devices, such as pressure sensors and accelerometers, are produced using this technology. We are interested in expanding the number and scope of applications using deep silicon etching. Many of these applications have additional demands on surface morphology including minimization of the

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* PSTD Coburn-Winters Student Award Finalist

scalloping observed on vertical sidewalls during TMDE and the roughness of surfaces exposed to the discharge. Moreover, mask undercut and bowing of the etch profiles must be reduced to tailor the slope of etch profiles. Our goal is to understand the evolution of these traits as a function of operating conditions. Toward this goal, a number of process variables were explored using a commercial inductively-coupled plasma etcher. We report a significant increase in the silicon etching rate, minimization of mask undercut, and substantial reduction in bowing. These improvements demonstrate enhanced process performance and flexibility to meet a broad range of needs in deep silicon etching.

4:40pm **PS+MM-WeA9 Mechanisms Involved in the Silicon Cryogenic Etching Process**, ***M. Boufnichel***, GREMI / ST Microelectronics, France, *P. Lefaucheux, R. Dussart*, GREMI, France, *P. Ranson*, GREMI-Universite d'Orleans-CNRS, France

In this study, we investigated the etching and passivation mechanisms involved in the deep cryogenic etching of silicon trenches. More precisely, we studied the dependence of sticking coefficient of oxygen and fluorine as regards to wafer temperature. We showed that fluorine radicals sticking coefficient does not strongly depend on wafer temperature at the contrary to oxygen radicals. XPS measurements allowed us to obtain further informations concerning the nature and behaviour of the passivation layer deposited on trench sides during the cryogenic silicon etching with a SF6/O2 mixture. XPS measurements pointed at the fact that the passivation layer formed during the cryogenic etching of silicon is not mainly composed of SiO2 species. Furthermore, a new method has been employed to determine the effective angular dispersion of ions (EIAD) involved in the etching of silicon and its impact on trench etching evolution. A comparison of the performances of RF and LF bias generators has also been performed so as to highlight the impact of bias-frequency on profile characteristics. A complete study of the etching mechanisms would not have been possible without parallel measurements of physical plasma parameters using Langmuir probe and actinometry with Optical Emission Spectroscopy (OES). The parallel between the etching experiments and diagnostics measurements shows for example that local bowing seems to depend on ion local surface bombardment and passivating mechanisms. Finally, we are able to etch deep anisotropic trenches (100 microns deep and 2 microns in aperture) at a high etch rate, high selectivity (SiO2 mask) and high anisotropy. We performed to reduce or eliminate defects such as local bowing, undercut and notching for different application: etching of HARTs (High Aspect Ratio Trenches), LARTs (Low Aspect Ratio Trenches), vias, SOI (Silicon On Insulator) layers.

5:00pm **PS+MM-WeA10 3-Dimensional Feature Profile Evolution Using Level Set Methods**, ***H. Hwang***, *T.R. Govindan, M. Meyyappan*, NASA Ames Research Center

Modeling feature profile evolution due to etching of semiconductor materials is typically done in two dimensions. However, these 2-D simulations make assumptions about geometries, such as semi-infinite trenches, that are unrealistic. Since a semi-infinite trench will "collect" higher amounts of fluxes than a finite one, the calculated ion and neutral fluxes to the surfaces in 2-D will not account for the shadowing of the opening due to the finite size. These larger fluxes will then lead to a larger overall etch rate, compared with calculations done in 3-D. Furthermore, any asymmetries (due to ion angular distribution functions, for example) can only be captured in 2-D. Inherently 3-D situations, such as striation patterns of the trenches, cannot be studied without the third spatial dimension. We will present results using an etching 3-D simulation which uses level set methods to advance the moving front. This code is an extension of SPELS, the Simulation of Profile Evolution using Level Sets, to calculate etch rates of silicon in chlorine discharges. We will show animations of the evolving trench for different geometries as well as for different process conditions. We will make comparisons of cross sections of the 3D profiles to calculations from 2-D simulations and demonstrate the effects of a finite trench versus a semi-infinite trench on etch rates.

Surface Science
Room: C-108 - Session SS1-WeA

Gas-Surface Dynamics
Moderator: J.J. Boland, University of North Carolina at Chapel Hill

2:00pm **SS1-WeA1 Interaction of Gas-phase H Atom with Metal Surfaces : Cu(111) vs Pt(111)**, ***S.J. Lee***, *J. Kim, J. Lee*, Seoul National University, Korea

The gas-phase H atoms of thermal energy impinging upon metal surface undergo reflection, adsorption, or abstraction of a surface H atom. The probability of each process strongly depends on the inelastic nature of the H-metal surface collision. Inelastic energy loss via phonon excitation is expected to be quite inefficient because of the light mass of H atom. Recently, Nienhaus et al. (1) have experimentally shown that H atom collision with metal surfaces induces e-h pair excitation. Then, one can raise the following interesting questions; 1) Is e-h pair excitation a dominant inelastic loss mechanism in H-metal surface collision? 2) If it were the case, what would be the effect of electronic band structure of metal in its interaction with H atom? In order to gain further insight into these questions, we have measured and compared the initial sticking probability(S_0), saturation coverage(θ_s), and abstraction cross section(s_{abs}) for hydrogen atom at Cu(111) and Pt(111) at 90K. We measure S_0=0.72, θ_s=0.95ML, and s_{abs}=1.30Å for Pt(111) and S_0=0.45, θ_s=0.32ML, and s_{abs}=5.5Å for Cu(111). We interpret the results in terms of e-h pair excitation whose efficiency is determined by the electron density of state at the Fermi level.

2:20pm **SS1-WeA2 Anomalous Reactive Scattering: Hyperthermal Energy Collisions of State-selected Bromine Ions on Pt(111)**, *P.L. Maazouz*, ***M. Maazouz***, *D.C. Jacobs*, University of Notre Dame

The dynamics of scattering state-selected atomic and molecular bromine ions on Pt(111) are investigated across the hyperthermal energy regime (5 - 100 eV). Scattered ionic products are measured with mass-, angular-, and velocity-resolution. Scattered Br_2^-/Br^- product distributions are measured as a function of the incident Br_2^+/Br^+ collision energy, vibrational energy, and surface temperature. The yield for both atomic and molecular projectiles reveals an unusual behavior where negative ion conversion is most efficient for incident velocities near 7.6 km/sec. This sharp peak in the yield shifts to lower velocities with increasing surface temperature. A detailed analysis of the products' velocity distributions suggests an important interplay between charge transfer and energy transfer in this system.

2:40pm **SS1-WeA3 Hyperthermal Ejection of Atomic Cl from the Reaction of Cl_2 on the Al(111) Surface: Evidence of a Nonadiabatic Electron Harpooning Mechanism**, ***G.C. Poon***, *T.J. Grassman, 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_2 on the low work function Al(111) surface proceeds via a prompt nonadiabatic electron harpooning process. As Cl_2 approaches the Al(111) surface, an electron harpoons from the surface, suddenly converting Cl_2 to Cl_2^-. This places the molecule high on the repulsive portion of the Cl_2^- potential curve leading to rapid dissociation into Cl^- and Cl fragments. The Cl^- proceeds toward the surface and sticks while Cl is ejected into the gas phase. An experimentally observable signature of this harpooning process would be a hyperthermal translational energy of the ejected fragment, whose energy is determined by the vertical transition between Cl_2 and Cl_2^- and should be nearly independent of incident translational energy. Three beams of Cl_2 were prepared by seeding with translation energies ranging from 0.989 eV to 0.105 eV. Each of the three Cl_2 beams was directed at the surface at three incident angles: 0°, 20°, and 40°. The translational energy of the ejected Cl was shown to be a weak function of the incident translational energy. For 0.989 eV normal incidence Cl_2 the ejected Cl had a translational energy of 0.147 eV, while 0.105 eV normal incidence Cl_2 produced ejected Cl of 0.100 eV. Therefore, for incident Cl_2 with a velocity of 535 m/sec, the ejected Cl atoms were accelerated to a velocity of 740 m/sec. This acceleration of ejected Cl compared to incident Cl_2 is consistent with a nonadiabatic process that converts electronic to kinetic energy.

3:00pm **SS1-WeA4 Degradation of Alkanethiol Self Assembled Monolayers under Hyperthermal O^+ Bombardment**, ***T. Tzvetkov***, *X. Qin, D.C. Jacobs*, University of Notre Dame

We present experimental results on the reaction of 5-20eV O^+ with alkanethiol self-assembled monolayers (SAMs). Decanethiol or 1H, 1H, 2H, 2H-perfluorodecanethiol are used to form well-ordered SAMs on a clean gold surface. Scattered ionic products, formed as a result of hyperthermal O^+ ion bombardment, are collected with angle-, energy-, and mass-resolution. Chemical modifications in the SAM layer are monitored by X-ray photoelectron spectroscopy (XPS). Efficient removal of H from alkanethiol SAMs is observed at all incident energies. With increasing collision energy, C-C bond cleavage becomes important, as various scattered species of C_nH_m or C_nF_m radicals are observed, and the stoichiometry of the irradiated SAM is altered. The experimental results help us to understand the mechanisms of polymer degradation under O^+ bombardment at hyperthermal incident energies.

3:20pm **SS1-WeA5 Charge Transfer in Low Energy Li Ion Scattering from Halogen-covered Metal Surfaces**, ***Y. Yang***, *J.A. Yarmoff*, University of California, Riverside

Resonant charge transfer (RCT) for 400-3000 eV Li ions scattered from iodine- and bromine-covered Fe(110) and Ni(100) surfaces is probed with time-of-flight spectroscopy. RCT with alkali ions has traditionally been considered to reflect the overlap between the local surface potential and the ionization level of the exiting ion. In this work, it is shown that the local charge density can also influence the RCT process. For example, iodine would be expected to adsorb with some net negative charge, thereby producing a dipole directed into the surface that would raise the work function. In contrast, iodine decreases the work function, and the neutralization probabilities for Li singly scattered from the I sites are always higher than for scattering from metal sites. Thus, there is a local effect involved in RCT for this system. Bromine adsorption does not change the work function significantly, but still the neutralization probabilities for scattering from Br sites are larger than from the substrate. These results suggest that the local charge density does plays a significant role in determining the RCT probability.

3:40pm **SS1-WeA6 Adsorption and Radiation Induced Decomposition of SF_6 on Ru(0001)**, ***N.S. Faradzhev***, *D.O. Kusmierek, B.V. Yakshinskiy, T.E. Madey*, Rutgers, The State University of New Jersey

Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) techniques have been employed to study the adsorption and radiation-induced decomposition of fractional monolayers of octahedrally-coordinated SF_6 physisorbed on Ru(0001) at 25K. TPD reveals predominantly molecular adsorption of SF_6, which desorbs from 3 weakly-bound states below 100K. ESDIAD of both F^+ and F^- ions at 25K demonstrate "halo-like" patterns, and heating the substrate to ~90K results in formation of hexagonal angular distributions for both ions. ESD of F^+ and F^- occurs via different mechanisms but from the same chemical states of molecular SF_6, which appears to be adsorbed via three F atoms, with the other three pointed away from the surface. At low temperatures, the F atoms have a random azimuthal orientation, while upon annealing, lateral ordering occurs in two complementary domains. Prolonged electron beam exposure leads to dissociation of SF_6, and formation of SF_x (x=0 to 5) fragments. F^- ions escape only from undissociated molecular SF_6, while F^+ ions also originate from dissociation fragments; both normal beams and off-normal beams are seen in hexagonal F^+ ESDIAD patterns, and intensities vary with electron exposure. Electron exposures $>10^{16}$ e/cm^2 result in complete decomposition of SF_6, as verified by TPD and ESDIAD.

4:00pm **SS1-WeA7 Dynamical Behaviors of GaCl on GaAs Surfaces by Pulsed Molecular Beam Scattering**, ***M. Ohashi***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *M. Ozeki*, Miyazaki University, Japan

Gallium chloride (GaCl) is an important precursor in the growth of compounds containing Ga and plays an important role in halide vapor-phase epitaxy (VPE) and hydride VPE. The GaAs layer grown on a GaAs(001) substrate is completely mirror-like without surface defects, but the layer grown on a GaAs(110) substrate is slightly hazy. The cause of these results is unclear. As the initial process in GaAs epitaxial growth is defined that GaCl molecule trapped into a precursor state in GaCl/GaAs surface system, this precursor plays an important role in growth. The reason that a high quality layer can be grown on a GaAs(001) substrate but not a GaAs(110) substrate has not clarified because the dynamical behaviors in the precursor states of GaCl on these surfces, such as activation energy and desorption rate have not been clarified. We investigated the adsorption mechanism of GaCl on the GaAs(001) and GaAs(110) surfaces based on angular distribution and the temperature dependence of GaCl time of flight spectra reflected from these surfaces. These well-defined surfaces are prepared by molecular beam epitaxy system connected with molecular beam scattering apparatus. The angular distribution of reflected GaCl consists of two parts; inelastic direct scattering contribution and thermal desorption of trapped molecules on the GaAs(001) and GaAs(110) surfaces. We divided the time of flight spectra of thermally desorbed GaCl into the component with activation energies of 92 kJ/mol corresponding to GaCl trapping well on GaAs(001) 2x4 surface and the components with 54 kJ/mol on GaAs(110) 1x1 surface Trapped GaCl desorbed rabidly from the GaAs(110) 1x1 surface compared to GaAs(001) 2x4 surface. These results suggest that the interaction between GaCl molecules and GaAs surface deeply influences the quality to large grown on GaAs substrates. Most of above this work was supported by New Energy and Industrial Technology Development Organization (NEDO).

4:20pm **SS1-WeA8 A New Mechanism for Ion-Stimulated Surface Processes at Low Energies**, *Z. Wang*, ***E.G. Seebauer***, University of Illinois

Ion surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. Overall process behavior in these applications often reflects a delicate balance among several competing kinetic effects. 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 molecular dynamics simulations of low-energy noble gas atoms impacting Si and Ge surfaces, and describe a new phenomenon that lies at neither pole. The simulations, backed by experiments on surface diffusion, exhibit a surprising new form of tradeoff between the ion energy threshold for point defect formation and substrate temperature. Because of the vast difference in scales between ion energies and thermal energies, the tradeoff resembles an elephant being balanced by a mouse on a seesaw. The effect originates from instantaneous nonuniformities in net surface potential induced by thermal vibrations, which dramatically affect the locality of momentum transfer to the surface and greatly amplify the effect of temperature. This amplification may offer a new means for selecting specific elementary rate processes during plasma processing or ion beam assisted deposition by judicious tuning of temperature and ion energy.

4:40pm **SS1-WeA9 Photochemistry of Caged Molecules: CD_3Cl in Ice**, ***M. Asscher***, *Y. Lilach*, Hebrew University of Jerusalem, Israel

The interaction of two similar coadsorbed dipolar molecules, H_2O and CD_3Cl, has been studied over Ru(001) under UHV conditions. The complementary techniques of δP-TPD and work function change in a δφ-TPD mode were employed. Post-adsorption of water leads initially to compression, reorientation and then to the formation of CD_3Cl layers that are encapsulated between amorphous solid water layers. These caged molecules are explosively desorb at 165K. Unique photochemical reactivity is displayed by the trapped methyl chloride molecules upon irradiation by 6.4 eV photons from an ArF excimer laser. Radical chemistry based on hot, photochemically generated methyl fragments, lead to the formation of longer chain hydrocarbons as well as oxygenated products. The relevance of these observations to the origin of interstellar hydrocarbons is discussed.

Surface Science
Room: C-110 - Session SS2-WeA

Structure and Chemistry at Metal Surfaces
Moderator: B.J. Hinch, Rutgers University

2:00pm **SS2-WeA1 Real Time Monitoring of the Structure and Morphology of Growing Nanoparticles by Grazing Incidence Small and Wide Angle X-ray Scattering, in situ, in UHV**, ***G. Renaud***, CEA-Grenoble, France **INVITED**

Islands of nanometer size grown on substrates display a set of fascinating properties, which are of interest for both basic and applied research. They include model catalysts made of supported metallic particles whose reactivity and selectivity can be adapted to given needs, single-domain magnetic particles which show original spin-dependent transport properties and coherently strained semiconductor aggregates, the so-called "quantum dots", which exhibit remarkable opto-electronic properties. A strong promise of novel device applications merges up provided that nanoparticles could be purposely tailored to specific uses. The properties of these particles depend to a great extent on their internal atomic structure, their strain, their shape, size, size distribution and ordering, which in turn rely on the growth mechanisms. In this context, a challenging issue is to control the growth of large collections of particles by monitoring the relevant parameters in situ and in real time. A unique technique to probe collections of very small objects is Grazing Incidence Small Angle X-ray Scattering (GISAXS). However, to date, due to technical limitations, GISAXS has never been used during growth. In this report, we demonstrate this possibility using two prototypical cases. The first is the growth of metals (Ag, Pd, Pt) on MgO(001) at different temperatures, which are models of Volmer-Weber 3D growth of metal on oxide surfaces, and is thoroughly studied to investigate the elementary processes of heterogeneous catalysis. The second is the growth of cobalt on the herringbone reconstructed Au(111) surface, which is a model of self-organized cluster growth. We show that a complete description of the islands can be obtained by supplementing GISAXS measurements by grazing incidence wide angle x-ray scattering measurements performed in situ during growth, at the same time.

2:40pm **SS2-WeA3 Structural Analysis of Quasicrystalline Al-Pd-Mn using Angle-Resolved Low Energy Ion Scattering**, ***C.J. Jenks***, *P.A. Thiel, A.R. Ross, T.A. Lograsso,* Iowa State University, Ames Laboratory, *J.A. Whaley, B. Bastasz,* Sandia National Laboratories

We have used angle-resolved low-energy ion scattering to examine the clean surface structure and composition under ultra-high vacuum conditions of a single grain of icosahedral $Al_{71}Pd_{20}Mn_9$ oriented with a five-fold axis perpendicular to the surface. Our results are consistent with the surface maintaining five-fold symmetry after sputtering followed by annealing at 800 K. We find that the topmost surface layer is > 85 atomic % aluminum. A predominant neighbor atom distance of 7.6 Â± 0.5 Å and a nearest neighbor distance of 3.0 Â± 0.1 Å is calculated from our results. Our results are consistent with previous low energy electron diffraction intensity versus voltage (LEED-IV) calculations, recently published scanning tunneling microscopy results and a bulk model of Al-Pd-Mn quasicrystals.

3:00pm **SS2-WeA4 Structural Studies of Ti/Pt(111) Surfaces**, ***S. Hsieh***, *T. Matsumoto, J. Kim, B.E. Koel,* University of Southern California

Alloys of platinum and a second metal component are of increasing interest for a number of applications. Structural studies have been carried out for bimetallic surfaces with Pt alloyed with many transition metals and main group metals. In this work, we have used He$^+$-ion scattering (He$^+$-ISS), X-ray photoelectron spectroscopy (XPS), and low energy diffraction (LEED) to determine the structure of ordered Ti/Pt(111) surface alloys formed by depositing ultrathin Ti films on Pt(111) and annealing to different temperatures up to 1100 K. The Ti film coverage was determined by He$^+$-ISS. No LEED pattern was observed at room temperature immediately after Ti deposition. At 800 K, Ti started to alloy with Pt and formed a (6x √43) structure in LEED that grew sharper as the temperature was increased to 1000 K. A weak (2 x 2) pattern was observed for Ti coverages larger than 1 monolayer, but this structure was less stable and disappeared at high temperature leaving only the (6x √43) pattern. XPS showed that the Ti core level spectra shifted by 2.0 eV upon alloying compared to that from a thick Ti film. Observation and further characterization of the new Ti/Pt(111)-(6x √43) surface structure should aid in understanding and tailoring chemical properties of practical catalysts.

3:20pm **SS2-WeA5 Thermal Stability of Thin Ti Films on Al Single Crystal Surfaces**[1], ***C.V. Ramana***, *R.J. Smith,* Montana State University, *B.S. Choi,* Jeonju University, Korea, *B.S. Park, A. Saleh,* Charles Evans & Associates, *D. Jeon*, Myongji University, Korea

Chemical roughness and alloy formation at metallic interfaces can significantly degrade the performance of multilayer thin film magnetic device structures. We have investigated the use of metal interlayers, one or two atoms thick, to stabilize the interface for ordered growth of metal films with minimal intermixing. Specifically, thin Ti interlayers have been used to stabilize the Fe-Al(100) interface, a system characterized by considerable interdiffusion at room temperature. The benefits of the interlayer concept are strongly coupled to the stability of the interlayer at elevated temperatures. In this investigation we have characterized the structure of thin Ti layers on Al single crystal surfaces as a function of temperature using Rutherford backscattering and channeling (RBS/c) and low-energy ion scattering (LEIS). The Ti layers are shown to be stable up to temperatures of about 400Â° C, at which point diffusion of Ti into the Al lattice occurs. LEIS measurements, combined with RBS show clearly that the Ti atoms move into the surface at these temperatures. Channeling measurements show that the Ti atoms sit on Al lattice sites as a substitutional impurity. The stability of the Ti film appears to increase with the packing density of the Al surface, being slightly more stable for the close-packed Al(111) surface, and diffusing into the more open Al(110) surface at a lower temperature.

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[1] Work supported by NSF Grant DMR-0077534.

3:40pm **SS2-WeA6 Nucleation and Growth of Ag Films on a Quasicrystalline AlPdMn Surface**, *V. Fournée, T. Cai, A.R. Ross, T.A. Lograsso, J.W. Evans,* ***P.A. Thiel***, Iowa State University

Nucleation and growth of thin films of Ag on the 5-fold surface of an Al72Pd19.5Mn8.5 icosahedral quasicrystal is studied with STM. For low coverages, flux-independent island nucleation is observed, likely involving adatom capture at "traps". With increasing coverage, islands start growing vertically, but then spread, and ultimately form hexagonal nanocrystals. These have fcc symmetry and pyramid-like multilayer stacking along the <111> direction. The constituent hexagonal islands have five different orientations, rotated by 2p/5, thus remembering the symmetry of the substrate. These results are discussed in the context of strategies most likely to yield pseudomorphic growth.

4:00pm **SS2-WeA7 Helium Atom Scattering Studies of Si-Cu (001) and Sn-Cu (001) Surface Alloys**, ***L.V. Goncharova***, *D.V. Potapenko, B.J. Hinch,* Rutgers University, *X. Zhang, D.R. Strongin,* Temple University, *L. Wood*, Dow Corning Corporation

Copper acts catalytically in the commercial "Direct Synthesis" of dimethyldichlorosilane; the later being a key component in the manufacturing of silicone materials. While Cu-Si systems have been studied intensively, the roles of other components, such as Sn, Zn and Al, which act as promoters in the "Direct Synthesis", are not well understood. We report on the growth and dynamics of silicon and thin tin films on Cu (001), as studied with high-resolution helium atom scattering (HAS), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). We have shown that the incommensurate "5x3" structure is formed when silicon is deposited on Cu (001) via saturation exposure to silane at 420K.[1] With Sn deposition temperatures above 200K a series of ordered reconstructions are observed on Cu (001) in the submonolayer regime.[2] Coadsorption of tin and silicon on Cu (001) is of a key importance as it enables a new low temperature desorption mechanism of methylsilanes. The relationships between structures in coadsorbed tin and silicon on the Cu (001) surface, and yields of different methylsilane products will be presented.

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[1] A.P.Graham, B.J. Hinch, G.P.Kochanski, E.M. McCash, and W. Allison, Phys.Rev.B 50 (1994) 15304.

[2] E.McLoughlin, A.A. Cafolla, E. AlShamaileh, C.J. Barnes, Surf.Sci. 482-485 (2001) 1431.

4:20pm **SS2-WeA8 Growth and O_2 Reactivity of the Cu/Si(5 5 12) System**, *P.H. Woodworth, J.C. Moore,* ***A.A. Baski***, Virginia Commonwealth University

Our group has extensively studied the growth behavior of Group IB metals such as Ag and Au on the row-like template provided by the clean Si(5 5 12) surface.[1] Here, this work is extended to the remaining IB metal of Cu. Our scanning tunneling microscopy studies show that Cu forms two distinct phases on Si(5 5 12): a lower temperature phase (< 600 °C) where Cu decorates the underlying (5 5 12) surface, and a higher temperature phase (> 600 °C) where it induces faceting to the nearby (113) plane. Similar to the Ag and Au systems, the lower temperature phase results in the formation of Cu "nanowires" with a spacing equal to the 5.4 nm periodicity of the (5 5 12) surface. When the annealing temperature is increased, however, the (5 5 12) orientation is no longer stable to (113) faceting. At lower Cu coverages (< 0.5 ML), (113) planes appear to coexist with (5 5 12), but at higher coverages (> 0.5 ML) these planes form sawtooths with opposing (111) faces. The occurrence of (113) planes has also been seen for the higher temperature growth of Au on Si(5 5 12), indicating the inherent stability of this plane. We have also studied the O_2 reactivity of the Cu-induced (113)/(111) sawtooths at exposures of 50 to 200 Langmuirs and temperatures of 600 to 800 °C. As expected, an amorphous oxide appears to grow on the surface at lower temperatures (<650 °C), and etching occurs at higher temperatures (>650 °C). For the case of etching, the sawtooths are gradually removed to produce trapezoidal (113)/(111) islands. The density of these islands decreases with increasing temperature, providing a possible route for the controlled fabrication of such nanostructures on the surface.[1] A.A. Baski, K.M. Saoud, K.M. Jones, Appl. Surf. Sci. 182, 216 (2001).

4:40pm **SS2-WeA9 NIXSW Analysis of the Disorder Transition of Chlorine on Cu(111)**, ***A.G. Shard***, University of Sheffield, UK, *C. Ton-That,* University of Cambridge, UK, *P.A. Campbell*, University of Dundee, UK

Chlorine adsorbs on Cu(111) primarily in threefold hollow sites, with a slight preference for the 'fcc' site (above a third layer copper atom) as opposed to the 'hcp' site. We have monitored the relative population of the two sites at a variety of coverages and temperatures using Normal Incidence X-ray Standing Waves (NIXSW). Disordered surfaces at low coverages or high temperatures have approximately equal populations of the two hollow sites, providing a measure of confirmation for the small energy difference recently calculated between them.[1] Adsorption of chlorine to a Cu(111) crystal at 180K results in an ordered root 3 surface, with equal populations of 'fcc' and 'hcp' sites, implying the prolonged existence of metastable 'hcp' domains at this temperature. The room temperature root 3 structure has a large 'fcc' population, which decreases close to the disorder transition at 350K. These data are discussed and compared with Monte Carlo simulations.

[1] K. Doll and N. M. Harrison, Chem. Phys. Lett., 317, 282 (2000).

5:00pm **SS2-WeA10 Vibrations of Water Adsorbed on Ru(0001)**[1], ***P.J. Feibelman***, Sandia National Laboratories

To see whether vibration spectroscopy confirms or contradicts the idea that the wetting layer of D_2O/Ru(0001) is half-dissociated,[2] vibration spectra have been computed from first principles for comparison to experiment. The calculations show that dissociation of the non-hydrogen-bonding O-D bonds of a heavy-water bilayer eliminates the highest-energy O-D stretch feature, and replaces it with a lower frequency mode. This behavior agrees with recent Sum Frequency Generation observations,[3] lending credence to the argument that a half dissociated D_2O layer is needed both to explain why water wets Ru(0001) at all, and to account for the inference drawn from Low Energy Electron Diffraction data, that the O atoms of √3x√3-D_2O/Ru(0001) are nearly coplanar. Beyond helping to clarify the nature of the wetting layer, the computed vibration spectra also permit an estimate of its zero-point energy relative to that of competing adsorption structures. Zero-point energy is found to favor half-dissociated adlayers because, of every four oxygen-hydrogen bonds in an intact-water-molecule structure, one is replaced by a softer metal-hydrogen bond in a half-dissociated arrangement. For √3x√3-D_2O/Ru(0001), this zero-point stabilization amounts to about 30 meV per D_2O. In the case of H_2O adsorption, it would be ~50 meV/ad-molecule.

[1] Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. DOE.

[2] P. J. Feibelman, Science 295, 99(2002).

[3] D. N. Denzler, unpublished.

Thin Films
Room: C-101 - Session TF-WeA

Atomic Layer Deposition - Applications of ALD

Moderator: R.J. Carter, IMEC, Belgium

2:00pm **TF-WeA1 Influence of Film Roughness on the Electrical Properties of W / Al_2O_3 Films Grown on Si(100) by Atomic Layer Deposition**, ***F.H. Fabreguette***, *M.D. Groner, Z.A. Sechrist, S.M. George*, University of Colorado

The SiO_2 interfacial layer seriously impacts the electrical behavior of alumina high k dielectrics on silicon substrate, and produces a reduction of the overall dielectric constant with decreasing thickness of the high k dielectrics. To avoid the SiO_2 interfacial layer and probe the electrical properties of ultrathin dielectrics, Al_2O_3 layers were grown on tungsten on Si(100) using Atomic layer Deposition (ALD) technique. Si/W/Al_2O_3 structures are expected to exhibit a dielectric constant independent of the Al_2O_3 film thickness, because the tungsten layer should act as an equipotential electrode. These Si/W/Al_2O_3 structures were grown in a viscous flow ALD reactor using $Al(CH_3)_3$ and H_2O for the Al_2O_3 ALD, and WF_6 and Si_2H_6 for W ALD. The W thickness was kept constant while the Al_2O_3 thickness was varied. Ellipsometry was used to measure the Al_2O_3 ALD film thickness. Surface roughness was measured using Atomic Force Microscopy. The dielectric constant calculated from C-V curves was apparently reduced for the smaller Al_2O_3 thicknesses, even though impedance spectroscopy did not exhibit any interfacial oxide. By comparing this apparent dielectric constant reduction and the film roughness, the apparent reduction was discovered to be linked with the film roughness. The film roughness was then minimized using a Hadamard matrix optimization approach to adjust the various ALD parameters. With the surface roughness minimized, Si/W/Al_2O_3 structures were fabricated where the Al_2O_3 dielectric constant was almost independent of the Al_2O_3 layer thickness.

2:20pm **TF-WeA2 Growth and Structure of Al_2O_3/W Nanolaminates Fabricated Using Atomic Layer Deposition Techniques**, ***Z.A. Sechrist***, *F.H. Fabreguette,* University of Colorado, *O. Heintz,* Universite de Bourgogne, *S.M. George*, University of Colorado

Nanolaminates are expected to have unique thermal, mechanical, electrical and optical properties. Atomic layer deposition (ALD) methods have been used to grow Al_2O_3/W nanolaminates. Al_2O_3 ALD is based on the binary reaction: $2Al(CH_3)_3 + 3H_2O \text{ --> } Al_2O_3 + 6CH_4$. W ALD is based on the binary reaction: $WF_6 + Si_2H_6 \text{ --> } W + 2SiF_3H + 2H_2$. To optimize Al_2O_3/W nanolaminate growth, W ALD has been examined using in situ quartz crystal microbalance (QCM) investigations. The QCM measurements reveal extremely linear W growth versus the number of binary reaction cycles. The W deposition rates are dependent on substrate temperature and Si_2H_6 exposures. The W ALD deposition rates vary from ~4 Å per AB cycle at 177°C and ~10^5 L Si_2H_6 exposures to ~7 Å per AB cycle at 325°C and ~10^7 L Si_2H_6 exposures. QCM studies of Al_2O_3/W nanolaminate growth reveal that the nucleation of W ALD on Al_2O_3 surfaces is a critical variable. Atomic force microscope studies indicate that the shortest nucleation times yield the lowest surface roughnesses for the Al_2O_3/W nanolaminates. W ALD nucleation times were shortened by increasing Si_2H_6 exposures. Al_2O_3 nucleation times were shortened by finishing the W growth with a WF_6 exposure. The structural analysis of these nanolaminates using transmission electron microscopy (TEM) yields very well-resolved superlattice structures. X-ray reflectivity (XRR) measurements confirmed very conformal Al_2O_3 and W deposition with low interfacial roughness. Secondary ion mass spectrometry (SIMS) gave chemical confirmation of alternating oxide/metal nanolayers with regularly repeating AlO^+ and W^+ ion signals as the ion beam milled through the nanolaminate.

2:40pm **TF-WeA3 Examination of New ALD Processes for Microelectronics**, ***M. Ritala***, *K. Kukli, T. Aaltonen, P. Alen, M. Vehkamäki, T. Hänninen, T. Hatanpää, R. Matero, A. Niskanen, A. Rahtu, V. Pore, M. Leskelä*, University of Helsinki, Finland

During the past years the atomic layer deposition (ALD) method has gained a lot of interest among semiconductor industry as a potential future manufacturing technology. Though the method has been widely examined by several groups, the studies have mainly focused to only a few processes: $Al(CH_3)_3$ - H_2O, $ZrCl_4$ - H_2O, $HfCl_4$ - H_2O and $TiCl_4$ - NH_3. While the $Al(CH_3)_3$ - H_2O process can be considered as a nearly ideal ALD process, the others have some limitations and drawbacks, thereby leaving room for improvement and calling for new chemical approaches for a deposition of the corresponding materials. In addition, there is a whole range of other materials, like metals and ferroelectrics, for which efficient ALD processes should be developed. In this presentation, our recent results on developing new ALD processes for microelectronic applications will be presented.

3:00pm **TF-WeA4 Temperature Effects during Quartz-crystal Microbalance Measurements of Thin Film Growth during Atomic Layer Deposition**, ***M.N. Rocklein***, *S.M. George*, University of Colorado, Boulder

The quartz-crystal microbalance (QCM) has become a very useful, in situ tool for monitoring atomic layer deposition (ALD) in viscous flow reactors. Mass changes can be measured for individual reactant pulses and for the entire ALD reaction cycle. These mass changes reveal information about the ALD reaction stoichiometry and the ALD film growth rate. Unfortunately, serious error in the QCM mass measurement can occur because of temperature effects. We will show that instantaneous apparent mass changes may be caused by differences in temperature between the reactant gas pulse and the QCM and that slow apparent mass drift may be caused by the integrated effect of many individual reactant gas pulses. These effects are clearly demonstrated by modifying the temperature profile along the length of the reactor tube and by using an exposure sequence of inert gases. These temperature effects are also illustrated using Al_2O_3 ALD as a model system. The primary factors influencing the magnitude and sign of the temperature-induced apparent mass change are determined to be the QCM temperature, the temperature profile of the reactor before the QCM, the type of gas, the gas flux, the ALD timing sequence and adiabatic cooling of the reactant gas. The results of this study also suggest methods to minimize these temperature-induced apparent mass changes for reliable QCM measurements of ALD in a viscous flow reactor.

3:20pm **TF-WeA5 Atomic Layer Deposition of Tribological Coatings for MEMS Devices**, ***T.M. Mayer***, *P.G. Kotula, R.S. Goeke,* Sandia National Laboratories, *J.W. Elam, S.M. George*, University of Colorado

Friction and wear are major concerns in the performance and reliability of micromechanical (MEMS) devices. However, the severe geometric constraints of many micromechanical systems (high aspect ratios, shadowed surfaces) make most deposition methods for friction and wear-resistance coatings impossible. We have produced highly conformal coatings of Al_2O_3 and ZnO, deposited by atomic layer deposition (ALD), for use on surface micromachined (SMM) and LIGA structures. We demonstrate extremely uniform deposition of 10 nm films of amorphous Al_2O_3 on micromachine structures with aspect ratio up to 50 (feature depth vs. width). Friction coefficient of the Al_2O_3 on flat surfaces is measured to be approx. 0.3, while wear resistance of the films is improved over that of the SiO_2/Si substrate. ZnO is a potentially lubricious film, whose tribological properties depend on the crystallite structure in the film. Thin, nm-thick films are shown to be nanocrystalline with low friction coefficient, while thicker films with larger grain size exhibit high friction coefficient. We can control crystallite size through thickness and temperature control in the deposition process, or by laminating the ZnO film with nm-thick layers of Al_2O_3 in the ALD process. We will report the tribological properties of ZnO films and nanolaminates as a function of crystallite size and preparation methods.

3:40pm **TF-WeA6 Conformal Coating of Ultrahigh Aspect Ratio Anodic Alumina Membranes by Atomic Layer Deposition**, ***J.W. Elam***, University of Colorado, *D. Routkevitch, P.P. Mardilovich,* Nanomaterials Research Corporation, *S.M. George,* University of Colorado

Anodic alumina (AA) membranes are unique nanostructures that are permeated by highly uniform, nanometer-scale pores arranged in a hexagonal close packed array. The application of AA membranes to gas sensors requires that the nanopores with ultrahigh aspect ratios of L/d~1000 be coated by uniform films of chemoresistive materials such as ZnO. In this study, AA membranes were coated with Al_2O_3 and ZnO atomic layer deposition (ALD) films in a viscous flow ALD reactor. The coated membranes were analyzed using cross-sectional scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). SEM analysis of individual nanopores revealed that the AA membranes with nanopore dimensions of d=65 nm and L=50 µm could be coated conformally by Al_2O_3 ALD using sufficient reactant exposure times. EPMA measurements with a spatial resolution of 3-5 µm were performed following ZnO ALD on the d=65 nm, L=50 µm AA membranes. The EPMA Zn concentration profiles showed the progressive infiltration of the ZnO ALD into the nanopores with increasing exposure times. Monte Carlo simulations of these experiments assuming Knudsen diffusion accurately reproduced the experimental ZnO EPMA concentration profiles. Furthermore, this modeling predicted that the diffusion-limited coating process would become reaction-limited given a sufficiently low ALD reaction probability. To test this idea, Fourier transform infrared absorption measurements were performed during the coating of the AA membranes by Al_2O_3 and SiO_2 ALD. In agreement with the predictions, diffusion-limited behavior with a $t^{1/2}$ time dependence was observed for Al_2O_3 ALD during the AlOH* + $Al(CH_3)_3$ -> $AlOAl(CH_3)_2$* + CH_4 reaction. In contrast, reaction-limited behavior with a t^1 time dependence was observed for SiO_2 ALD during the SiOH* + $SiCl_4$ -> $SiOSiCl_3$* + HCl reaction.

4:00pm **TF-WeA7 Low Temperature Al_2O_3 Atomic Layer Deposition**, ***M.D. Groner***, *F.H. Faberguette, J.W. Elam, S.M. George*, University of Colorado at Boulder

Although Al_2O_3 is one of the most common dielectric materials grown by atomic layer deposition (ALD), very little is known about Al_2O_3 ALD at the low temperatures. Deposition at temperatures < 150°C is required for many important coating applications such as deposition of gas diffusion barrier layers on thermally sensitive polymers. Thin Al_2O_3 films were deposited by ALD at low temperatures in a viscous flow reactor using alternating exposures of trimethylaluminum and water. Deposition temperatures ranged from ~ 30°C to 125°C. The properties of Al_2O_3 ALD films grown on Si(100) substrates were studied versus growth temperature. Al_2O_3 film thicknesses, growth rates, densities, and optical properties were determined using surface profilometry, atomic force microscopy, quartz crystal microbalance, and ellipsometry measurements. In addition, current-voltage (IV) and capacitance-voltage (CV) measurements were employed to evaluate the electrical properties of the low temperature Al_2O_3 ALD films. The film densities and dielectric constants were reduced at the lower deposition temperatures. However, deposition at lower temperatures still achieved conformal Al_2O_3 growth. Low temperature Al_2O_3 ALD was also demonstrated on polymeric substrates. Preliminary measurements have characterized the effects of these Al_2O_3 ALD films on gas permeabilities.

4:20pm **TF-WeA8 Theoretical and Experimental Investigation of Atomic Layer Deposition of Copper(I) Oxide**, ***T. Törndahl***, *M. Ottosson, K.M.E. Larsson, J.-O. Carlsson*, Uppsala University, Sweden

Atomic Layer Deposition (ALD) of copper(I) oxide from copper(I) chloride and water has been investigated both theoretically and experimentally. The theoretical modeling was conducted on the reconstructed non-polar (111) surface of copper(I) oxide, using gradient corrected density functional calculations. Among the studied process steps related to the film growth were copper(I) chloride adsorption on different copper(I) oxide (111) surface sites and reactivity against water. The experimental studies have been carried out from 350 °C, were the films start to grow, up to 700 °C, where the deposition rate starts to decrease. The texture of the films was controlled to a large extent by the substrates. On fused silica no texture was observed while on aluminium oxide, (102) oriented, films with strong (110) texture were obtained. The experimental results will be discussed in connection to the theoretical modeling of the deposition process.

Vacuum Technology
Room: C-104 - Session VT-WeA

Vacuum Measurements, Components, and Control
Moderator: P.C. Arnold, Helix Technology, Inc.

2:00pm **VT-WeA1 Eight Unconventional Gauges: A User's Impressions**, ***B.R.F. Kendall***, Elvac Laboratories **INVITED**

Conventional vacuum gauges are unlikely to fill emerging needs for accurate measurements below the mid 10E-10 Torr range. There is also an unmet need for rugged, accurate, inexpensive sensors operating in the low micron range. The solutions may lie in the development of modern versions of gauges now found mainly in the pages of the more arcane textbooks. Laboratory evaluations are given for a number of original and updated gauges likely to be useful in modern applications. For the UHV range these include the extractor, modulated Bayard-Alpert, and X-Ray-neutralized Bayard-Alpert gauges, plus several variants of the inverted magnetron and magnetron cold-cathode gauges. For the micron range, test results are given for thermistor, viscosity and molecular drag gauges. The need for fresh approaches to vacuum gauging is particularly important at this time, when the recent trend has been to restrict commercial production to a few of the most popular general-purpose types. Formation of a users' group to encourage continued production and development of reliable UHV gauges is suggested.

2:40pm **VT-WeA3 The Effect of Ambient Temperature on the Sensitivity of Hot-Cathode Ionization Gauges**, ***P. Abbott***, National Institute of Standards and Technology, *P. Mohan*, National Physical Laboratory, India

A recent comparison of the high vacuum standards of several National Metrology Institutes (NMIs) was performed over the range of 10^{-6} to 10^{-3} Pa using hot-cathode and spinning rotor gauges as transfer standards. Among the participants, their laboratory ambient temperatures varied by as much as five degrees Celsius. It is necessary to know how laboratory temperature affects the sensitivity of the hot-cathode transfer standards (spinning rotor gauges explicitly account for the gas temperature) so that individual laboratory results can be corrected accordingly. The results are presented for an experiment in which the sensitivities of several hot-cathode ionization gauges were measured for ambient laboratory temperatures between 23 and 31 degrees Celsius. It was found that all of the ionization gauges exhibited very similar behavior, and that the sensitivity dependence on temperature could be adequately modeled with a linear fit over the investigated temperature range.

3:00pm **VT-WeA4 The Method of Calibrating and Adjusting Sensitivity of Mass Spectrometer**, ***Y. Feng***, *D.T. Li, D.X. Zhang*, Lanzhou Institute of Physics, P.R. China

The mass spectrometer is used as a partial pressure gauge in many fields on vacuum, especially in monitoring and measurement of vacuum system. It is necessary to calibrate the parameters of the mass spectrometer in order to improve the accuracy during the pressure measurement. A vacuum system, Calibration apparatus of mass spectrometer for partial pressure analysis with dynamic flow method, has been established in our center, which can be used to calibrate some parameters of the mass spectrometer with one kind of gas or some kinds of mixed gases. In this paper, the principle of the system is introduced, and the method and results for calibrating the sensitivity of QMS422 which manufactured by BALZERS is given. In the process, we get the curve on the sensitivity change with the emit ion current, the cathode volts and the focus volts change. At last, the better method is recommended to make the mass spectrometer in the good measurement condition with the largest or the most stable sensitivity.

3:20pm **VT-WeA5 Using DeviceNet for Improved Vacuum Monitoring**, ***C.E. Karlsen***, Lawrence Livermore National Laboratory **INVITED**

DeviceNet is a new standard for an industrial, device-level network for connecting a wide variety of industrial instruments, actuators, and control computers. Over 300 manufacturers make products that are certified by ODVA to work with this standard. It reduces overall installation costs by minimizing wiring and improves measurement accuracies by eliminating transmitted analog signals. This talk will give an overview of the DeviceNet standard as applied to vacuum systems. It will cover typical costs, performance issues, design parameters, and some of the products available. It will include a study on the use of DeviceNet on the Spatial Filter Vacuum System in the National Ignition Facility (NIF) at the Lawrence Livermore National Laboratory (LLNL.).

4:00pm **VT-WeA7 Closed Loop Process Control for Reactive Sputter Deposition of Dielectric Films**, ***D. Carter***, *H. Walde, G. McDonough, G.A. Roche*, Advanced Energy Industries

Pulsed-dc reactive sputter deposition of dielectric films has be an active area of study over recent years. It has been demonstrated that transition region sputtering can produce quality dielectric films at high deposition rates making this approach attractive to the alternatives of high frequency sputtering from ceramic targets. As with all processes, time based control and repeatability are critical to the acceptance of such technology. While voltage reversal during pulsing has proven effective in stabilizing arc activity, additional controls are required to stabilize the reactive environment to ensure film composition and controlled sputtering target condition. Various techniques are available to monitor the sputtering environment including partial pressure, optical emission and sputter source impedance but all typically require the addition of costly, complex, intrusive and sometimes unreliable components if one is to be used in a feedback-control-loop system. This study looks at a non-intrusive, cost effective approach to the incorporation of a Closed-Loop-Control (CLC) system in a pulsed-dc reactive sputter deposition process for the production of Al2O3 and SiO2 thin films. This approach uses target voltage as the primary feedback parameter to directly control the setpoint to a high-speed sonic piezo-driven mass flow controller. Target transition region control is demonstrated in the aluminum-oxygen and silicon-oxygen systems and the approach is evaluated for film quality, long-term process stability, process repeatability, and susceptibility to arcs and other potential anomalies encountered in such difficult to control reactive processes.

4:20pm **VT-WeA8 Soft LaserBellows**, ***D.U. Chang***, LaserTech USA

New and innovative welding technology brought precision, high quality "soft" metal bellows to practical reality. Thin gage annular disks are laser welded automatically with the aid of computer-controlled precision guidance by a machine vision seam tracking system. The resistance to the axial motion of the bellows (spring rate) is reduced to 47% to 19% compared with conventional bellows of the same size. These "soft" bellows are especially suitable for hermetic sealing of vacuum valves and manipulators for ultra-high vacuum and semi-conductor applications. Higher positioning accuracy and low motor power are some of the benefits of these bellows. The "soft" bellows are 100% checked for weld integrity by automatic welding/inspection machines, followed by mass spectrometer leak check. Randomly selected samples go through life cycle testing. The bellows last more than 5 million cycles without failure. Finite element analysis (FEA) of the bellows was used extensively in the design of bellows. Comprehensive life cycle testing and leak testing verified the analytical prediction.

4:40pm **VT-WeA9 An Ultra-sensitive Leak Detection and Calibration System**, *Ping Chen, Xu Chen, Q. Jin,* ***Liangzhen Cha***, Tsinghua University, P.R. China

Although the minimum detectable leak rates can be as low as 10^{-12}Pa*m^3/s for most commercial dry leak detectors, but demands on lower and reliable detection limit are challenging for highly reliable vacuum devices. To meet these demands, an ultra-sensitive leak detection and calibration system is developed. In order to improve the dynamic leak detection limit, it is necessary to decrease the background noise of the vacuum system. An all-metal ultra high vacuum system consisted of a turbo-molecular pump, an ion pump, a dry roughing pump and an UHV comparative Quadrupole Mass Spectrometer is developed with a minimum working pressure of 10^{-7}Pa. The leak detection limit can still be improved if the undesirable background gas is pumped out by a getter pump during the accumulation process. By using a 10^{-7}Pa*m^3/s molecular flow platinum wire-glass reference leak[1] with an adjustable device to change the inlet trace gas pressure and (or) concentration, a range of leak rate more than 6 orders of magnitude can be directly calibrated without extrapolation. Experimental result shows that Helium leak rate lower than 10^{-14}Pa*m^3/s has been detected and calibrated reliably by this system.

[1] Liangzhen Cha, Theoretical and experimental studies of a platinum wire-glass standard leak, Vacuum,Vol 41,PP:1860-1862(1990).

5:00pm **VT-WeA10 A Compact Leak Rate Calibration System for Both Pressure and Vacuum Modes**, ***Xu Chen***, *Ping Chen, Q. Zhang, Q. Liu, Liangzhen Cha*, Tsinghua University, P.R. China

To meet the quality control of the industrial leak detection, especially the growing demand in sniffing application, a compact leak rate calibration system is developed to calibrate the leak rate from high pressure to atmosphere (pressure mode) and from atmosphere to vacuum (vacuum mode). A new method based on constant volume change in pressure for pressure leak rate calibration is utilized. A differential capacitance diaphragm gauge (CDG) is used to markedly decrease the temperature effect. It is found that $1*10^{-5}$ Pa*m^3/s pressure leak rate at room temperature can be calibrated with an accuracy of better than ±5% (with confidential level 95%) and leak rate as low as $3*10^{-6}$ Pa*m^3/s can be calibrated with an accuracy of better than ±15% with an environmental temperature change less than ±0.1°C. The total test period is about 30 minutes. This compact system is suitable for leak rate calibration in industrial environment for both pressure and vacuum modes.

Applied Surface Science
Room: C-106 - Session AS-ThM

Practical Surface Science I
Moderator: R. Hull, University of Virginia

9:00am **AS-ThM3 Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces**, ***T.L. Niederhauser***, *Y.-Y. Lua, G. Jiang, S.D. Davis, R. Matheson,* Brigham Young University, *D.A. Hess, I.A. Mowat,* Charles Evans & Associates, *M.R. Linford*, Brigham Young University

We have demonstrated a facile, chemomechanical method of simultaneously functionalizing and patterning silicon with single organic monolayers by scribing it while it is wet with 1-alkenes,[1] 1-alkynes,[1] and 1-haloalkanes.[2] This method can be used to create different monolayer coatings in distinct and precisely controlled regions on an individual surface. Like microcontact printing, this technique allows multiple, patterned, surface features to be prepared with ease. To create these arrays a Si surface is 1) wet with a reactive compound, 2) scribed in a specific region with a computer-controlled diamond-tipped rod, 3) rinsed with a solvent, and 4) dried. Without moving the Si surface from its original position, this process is then repeated to create monolayer coatings in regions distinct from the first. With this technique we have prepared arrays of functionalized, scribed regions on single Si surfaces of a) the homologous series of 1-alkenes from 1-pentene to 1-octadecene, b) a series of alcohols and, c) a series of mixed monolayers on scribed Si from two 1-alkenes or from a 1-alkene and an alcohol. The preparations were performed in the air without any special treatment or degassing of chemicals. The ability to create surfaces with different monolayer coatings in precisely controlled regions should prove technologically valuable, for example, in creating functionalized surfaces to perform multiple bioassays.

[1] T. L. Niederhauser, G. Jiang, Y.-Y. Lua, M. J. Dorff, A. T. Woolley, M. C. Asplund, D. A. Berges, M. R. Linford, Langmuir 2001, 19, 5889-5900.

[2] T. L. Niederhauser, Y.-Y. Lua, Y. Sun, G. Jiang, G. S. Strossman, P. Pianetta, M. R. Linford, Chem.Mater. 2002, 14, 27-29. .

9:20am **AS-ThM4 Surface Analytical Characterization of SiO_2 Gradient Membrane Coatings on Gas Sensor Microarrays**, ***M. Bruns,*** Forschungszentrum Karlsruhe GmbH, Germany, *H. Baumann,* Universität Frankfurt/Main, Germany, *M. Frietsch, E. Nold, V. Trouillet,* Forschungszentrum Karlsruhe GmbH, Germany, *R. White, A. Wright,* Thermo V.G. Scientific, England

The growing demand for inexpensive, space-saving and intelligent gas sensor systems led to the development of a gas sensor microarray at the Forschungszentrum Karlsruhe. The microarray currently comprises 38 sensor elements on an area of $4x8mm^2$ and is based on an 150 nm thick SnO_2 layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere. The basic structure of the microarray is manufactured by R.F. magnetron sputtering, applying a shadow masking technique. Parallel platinum strip electrodes for the conductivity measurement are sputtered on top of the metal oxide, thus subdividing the latter into the initially identical sensor elements. In order to modify the gas response of individual sensor segments, a gas-permeable SiO_2 membrane with a thickness variation of approximately 2 to 50 nm was deposited across microarray using ion beam assisted deposition.[1] Auger electron spectroscopy already has been proven to be a powerful tool in quality control of the fabrication of gas sensor microarrays[2] and, therefore, was used for rapid evaluation of the geometrical integrity of the electrode pattern. The chemical state determination of the layer constituents was carried out by X-ray photoelectron spectroscopy. Parallel ARXPS (angle resolved XPS) data collected with the Thermo VG Theta Probe can provide thickness information from the SiO_2 membrane in a non-destructive manner using a well-controlled analysis area (X-ray spot size 50 µm). In addition, ellipsometry, nuclear resonant reaction analysis, and non-Rutherford backscattering spectrometry were used to achieve a comprehensive characterization.

[1] M. Frietsch, L.T. Dimitrakopoulos T. Schneider, J. Goschnick, Surf. Coat. Technol., 120-121 (1999) 265

[2] R. Schlesinger, M. Bruns, Thin Solid Films, 366 (2000) 265.

9:40am **AS-ThM5 Surface Properties of Chemically Processed Niobium**, ***E.S. Gillman***, *A.M. Valente*, Jefferson Lab

Many high-performance accelerators, such as CEBAF at Jefferson Lab, rely on superconducting radio-frequency (SRF) technology. SRF technology at Jefferson Lab is based on the use of superconducting niobium accelerating cavities. The accelerating cavities are contained in cryomodules where liquid helium maintains the temperature at 2 K. To realize the highest energy and lowest heat loss from these accelerators means improving the performance of the accelerating cavities. We have studied the surface of chemically processed, heat-treated niobium used in these cavities with angle-resolved x-ray photoelectron spectroscopy (ARXPS) to ascertain the effect of process conditions on cavity performance. Our data indicates correlations between the passivation oxide layer thickness and stochiometry with processing conditions and that processing conditions can be directly correlated with cavity performance. This work was supported by U.S. DOE Contract No. DE-AC05-84-ER40150, the Commonwealth of Virginia and the Laser Processing Consortium.

10:00am **AS-ThM6 DC Field Emission Analysis of GaAs and Plasma-source Ion Implanted Stainless Steel**, ***C. Hernandez***, *T. Wang, T. Siggins, H.F. Dylla,* Jefferson Lab, *N.D. Theodore, D.M. Manos,* College of William and Mary, *C.E. Reece*, Jefferson Lab

Field emission studies have been performed on a GaAs wafer and a sample of its stainless steel (SS) support electrode that are part of the new photocathode gun for the 10 kW upgrade FEL at Jefferson Lab. The objective of the studies presented here is to characterize the effect of both, the cleanliness of the wafer and the plasma source ion implanted layer on the electrode to suppress field emission. Field emission is the limiting factor to achieve the required 6 MV/m at the surface of the wafer. Potential field emitters are first located on the surface of 1-inch diameter samples with a DC field emission scanning apparatus at 60 MV/m, then each emitter is characterized by SEM equipped with EDS. The GaAs wafer was hydrogen cleaned before the study. The results show three emitters caused by indium contamination during wafer handling. The GaAs wafer thus shows good high voltage characteristics and the need to maintain cleanliness during handling. The SS sample is hand polished with diamond paste to a 1-micron surface finish, then implanted with N_2/SiO_2 in a plasma source ion implantation chamber in preparation for the field emission studies.[1]

[1] This work is supported by the US Dept. of Energy and the Office of Naval Research.

10:20am **AS-ThM7 Study on Electron Emission from Some Metals and Carbon Materials and the Surface Characterization**, ***S. Kato***, KEK & The Graduate University for Advanced Studies, Japan, *M. Nishiwaki,* The Graduate University for Advanced Studies, Japan

We focus on secondary electron emission from metals and carbon materials in conjunction with potential and actual problems of photoelectron instability and electron multipactering in several particle accelerators in the world. Therefore it is quite important to explore promising materials which have secondary electron yields as low as possible. While a plenty of reports on investigation of secondary electron emission was made over years, the experimental conditions with poor vacuum have deteriorated the quality of the data and lack of surface characterization has made understanding the data and applying the data to surface engineering confusedly difficult. For this purpose, an UHV system was newly developed which consisted of a x-ray source, an ultraviolet photon source, an electron gun, an ion gun, residual gas analyzers, a hemispherical energy analyzer and a sample manipulator with cooling and heating capabilities. This system gives us useful basic informations about dependences of secondary electron yields and the energy distributions on primary electron energy, material, the material temperature and the surface state. In-situ surface characterization of the materials was also performed before and after conditionings such as heating, gas exposure and electron or ion bombardments. Prepared materials were oxygen free copper (single and poly-crystalline), pure titanium, stainless steel, isotropic graphite and carbon fiber reinforced carbon composite. Mechanical surface roughing on the materials was attempted to reduce electron emission in addition. The introduction of the system, the measured results and the discussion will be described in this paper.

10:40am **AS-ThM8 Investigation of the Interfacial Interactions Associated with the Application of a Polymer Coating onto Oxide-free Phosphate Films on Metals**, ***Y.Q. Wang***, *P.M.A. Sherwood*, Kansas State University

This paper will report the results of a continuing study focused on preparing novel surface chemistries with oxide-free phosphate films on metal surfaces. We have developed a new more easily applied process, based on our earlier studies and patent for oxide-free phosphate films. The new process is carried out under ambient conditions using aqueous phosphoric acid. The chemistry of the surface prepared by the new process and its effects on the coating of polymers on metalic aluminum and iron will be investigated by XPS to evaluate the potential of this film to serve as a corrosion inhibitor and other applications. It will also be seen that the valance band photoemission, interpreted by band structure and other calculations can be used to study the interfaces involved in, is a very effective tool for conclusively identifying the surface species present.

This materials was based upon work supported by the National Science Foundation under Grant No. CHE-0137502.

11:00am **AS-ThM9 Valence Band X-ray Photoelectron Spectroscopy Studies of Different Forms of Sodium Phosphate**, ***A.L. Asunskis***, *P.M.A. Sherwood*, Kansas State University

Valence band X-ray photoemission can be used to identify subtle differences in surface chemistry. There are a very large number of phosphate species, and it is often important to distinguish between these species. Our group has been examining phosphate surfaces on metals, and has shown[1] that it is possible to prepare oxide-free phosphate films on the surfaces of a variety of metals (e.g. iron, aluminum, copper, and titanium) by treatment of the oxide-free metal surface with orthophosphoric acid. Studies of core X-ray photoelectron spectroscopy (XPS) are of little value in distinguishing between different phosphate species. We have shown that it is possible to distinguish between orthophosphate and metaphosphate from differences in the valence band region which can be understood by comparison with spectra predicted by band structure calculations. In this presentation we report the extension of our earlier studies to include linear phosphates of different chain length and other phosphate species. The spectra show that valence band XPS can be used to distinguish between these species and that the spectral differences can be interpreted by spectra predicted by band structure calculations. This material was based upon work supported by the National Science Foundation under grant No. CHE-0137502.

[1] J.A. Rotole and P.M.A. Sherwood, Chem. Mater., 13, 3933-3942 (2001).

11:20am **AS-ThM10 The Study of Vanadium Phosphates by Valence Band X-ray Photoelectron Spectroscopy**, ***D.J. Asunskis***, *P.M.A. Sherwood*, Kansas State University

This paper presents a study of various vanadium phosphates synthesized by the reaction of vanadium with phosphoric acid in a variety of conditions, including choice of solvent and acid hydration. It is known that the differences in the nature of the vanadium phosphates can impact their role in catalysis, and we are interested in the nature of vanadium phosphate films on metals. In this study valence band X-ray photoelectron spectroscopy, in conjunction with core level X-ray photoelectron spectroscopy, is used for the identification of the synthesized compounds. The valence band spectra, which have been interpreted by band structure calculations, prove to be a conclusive way to identify the species present in each of these compounds. This material is based upon the work supported by the National Science Foundation under grant No. CHE-0137502.

11:40am **AS-ThM11 Sorbed Water, as the Source of the Dissolved H_2 and D_2 In Metals at Friction**, *E.A. Rodina*, ***E.A. Deulin***, Bauman Moscow State Technical University, Russia

Results shows, that concentration of the H_2 dissolved in the steel 304 after keeping in normal atmosphere (pressure of H_2 P_{H2} =5*10^{-2} Pa, pressure of D_2 P_{D2}=7*10^{-6} Pa) is C_{H2} = 2*1019 at/sm^3, instead of theoretically expected C_{H2} = 2*10^{19} at/sm^3, similarly, for D_2, dissolved at P_{D2} = 7*10^{-6} Pa, its concentration, instead of theoretically expected C^{theor}_{H2} = 8*10^{15} at/sm^3 is C_{D2} = 1*10^{18} at/sm^3. As for H_2 also as for D_2 it is possible to explain their increased concentration by the relay dissociation of sorbed water.[3] The results show that the residual atmosphere of H_2 or D_2 influences on ions exchange processes of D_2 and H_2 in layers of sorbed water. So, in the submitted results it is enough 0,002% dissociation of sorbed water to ensure the pointed mentioned concentration. Concentration of the dissolved gases (N=6000 cycles, Sigma= 1500 MPa, n = 600 cont/s) grows up to C^{max}_{D2} = 2*10^{21} at/sm^3 and C^{max}_{D2} = 3*10^{19} at/sm^3 as a result of mechanical action influence that corresponds to the 8,5% dissociation of H_2O, and corresponds to 0,1% dissociation of HDO (for used in a result of D_2 interaction from a surface).

[1] E.A. Deulin, A.A. Gatsenko, B.A. Loginov. Friction force of smooth surface of SiO2-Si02 as a function of residual pressure. Surface Science 433-435 (1999) 288-292.

[2] E. A. Deulin, R.A. Nevshupa. Deuterium penetration into the bulk of a steel ball of a ball bearing due to its rotation in vacuum. Applied Surface Science 144-145 (1999) 283-286.

[3] K.Akagi, M. Tsukada. Theoretical study of hydrogen relay dissociation of water molecules on Si(001) surfaces. Surface Science 438 (1999) 9-17.

Biomaterials
Room: C-201 - Session BI+HS+SS-ThM

Biosensors and Biodiagnostics
Moderator: J. Hickman, Clemson University

8:20am **BI+HS+SS-ThM1 Surface Functionalization for Self-Referencing and Multi-Channel Surface Plasmon Resonance (SPR) Biosensors**, ***J. Ladd***, *C. Boozer, Q. Yu, J. Homola, S. Yee, S. Jiang*, University of Washington

Recently, a novel SPR sensor with on-chip referencing has been realized. In this sensor, one half of the gold sensing surface is covered with a high refractive index overlayer of tantalum pentoxide (Ta2O5). When polychromatic beam illuminates the sensing surface, surface plasmon resonance in the areas with and without the overlayer occur at different wavelengths. Therefore, the reflected light exhibits two dips associated with SPRs in those two areas. When functionalized properly, one of the areas can be used as a specific sensing channel for detection of specific bio-interactions and the other can act as a reference channel for compensation for background refractive index fluctuations. In this work we present a new functionalization approach for these mixed architecture chips. The gold side of the chip is functionalized with a mixed self-assembled monolayer of polyethylene oxide (PEO) and biotin terminated thiols whereas the Ta2O5 side is coated with PEO terminated silanes. The PEO terminated thiols and silanes serve as a protein resistant background, while the biotin-terminated thiols are used to bind streptavidin, which in turn immobilizes biotinylated antibodies. Hence, the gold side of the chip is used for the binding and detection of target analytes and the Ta2O5 side functions as a reference channel that monitors bulk refractive index changes and temperature drift. We have applied this functionalization to an SPR based biosensor and have studied two model systems: mouse IgG and human hCG. In addition, we have quantified and compared the protein resistance of the PEO thiols versus the PEO silanes. This information will help us better compensate for non-specific effects and improve robustness of SPR measurements.

8:40am **BI+HS+SS-ThM2 Chemical Sensing Using Ultra-Fast Micro-Boiling**, ***O. Thomas***, *R.E. Cavicchi, M.J. Tarlov*, National Institute of Standards and Technology

We report a novel liquid sensing method that exploits micro-boiling phenomena on the surface of rapidly heated thin film heaters. The heaters are thin films of platinum and gold-plated platinum that are approximately tens of micrometers in width and hundreds in length. The micro-heaters are immersed in solutions where they are rapidly heated to high temperature with short, 5 - 40 microsecond, square voltage pulses. The temperature-time responses of the micro-heaters are obtained by measuring their resistance during the application of the heating pulse. The bubble nucleation event associated with boiling is signaled in the temperature-time transient by an inflection point that results from a change in heat transfer when a vapor film forms on the heater. Because of the extremely high heating rates, superheating is observed where nucleation temperatures approaching 300°C have been measured for aqueous solutions. The bubble nucleation temperature and average heater temperature during the micro-boiling process have been found to be highly dependent on the surface wettability of the heater, as well as the presence of surfactant molecules. We will report on the use of alkanethiol self-assembled monolayers to investigate the effect of surface wettability on micro-boiling. We will demonstrate that temperature-time transients of hydrophobic SAMs are distinct from those of hydrophilic SAMs and that information on SAM stability can be gleaned from transient data. We will also present preliminary results on using the micro-boiling phenomenon to detect surface binding events such as DNA hybridization and biotin-avidin coupling.

9:00am **BI+HS+SS-ThM3 Nanofluidic and Biomimetic Bioanalytical Systems**, ***G.P. Lopez***, University of New Mexico **INVITED**

This talk will present recent progress on the development of hybrid nano-materials containing synthetic and biosynthetic components for use in bioanalytical applications including separation and biosensing. Examples include the development of mesoporous silica microbeads that incorporate functional biomolecular components (e.g., transmembrane proteins in lipid bilayer systems) and stimuli-responsive polymers for the formation of "cell mimics" that preserve biological function in a robust, deterministic, nonliving system. Microscopic beads can be used in a variety of bioanalytical system formats including suspension assays in flow cytometry and microfluidic assays and separations in affinity microcolumns. Several aspects of these bioanalytical systems will be explored including optimization of ligand-receptor pairs for direct transduction of biomolecular recognition, microfluidic considerations, and fluorescence detection principles.

9:40am **BI+HS+SS-ThM5 A Gold Nanoparticle Sensor to Interrogate Biomolecular Interactions in Real-time on a Surface**, *N. Nath, **A. Chilkoti***, Duke University

We present a label-free optical technique to study biomolecular interactions in real time on a surface that is based on particle surface plasmon resonance (PSPR). We demonstrate that the absorbance spectrum of immobilized gold nanoparticles on glass exhibits a red shift as well as an increase in the absorbance at peak wavelength as a function of binding of biomolecules at the solid-water interface. The results obtained with the absorbance sensor were compared with those obtained using conventional SPR for fibrinogen adsorption onto a COOH-terminated surface and for the binding of streptavidin to a biotin-functionalized surface. We have also examined the sensitivity and dynamic range of the sensor as a function of nanoparticle size, and found a threefold improvement in sensitivity as the size of the nanoparticles is increased from 13 to 50 nm. This sensor is attractive because of its simplicity: gold nanoparticles are easily prepared with high reproducibility, they can be readily immobilized on glass, and their absorbance spectrum can be easily measured using widely available UV-vis spectrophotometers. Furthermore, this technique should be easily amenable to the design of chips in an array format for application in high-throughput immunoassays and proteomics.

10:00am **BI+HS+SS-ThM6 Evaluation of Methodologies for Arraying a Porous Inorganic Bioassay Support[1]**, ***C. Cole***, Nova Research, Inc., *D.B. Chrisey, R.J. Colton, H. Kim, B.R. Ringeisen,* Naval Research Laboratory, *C.R. Tamanaha,* Geo-Centers, Inc., *L.J. Whitman*, Naval Research Laboratory

A membrane-based immunosensor has been developed for the detection of eight biological agents with a response time of <15 minutes and a sensitivity ~3 orders of magnitude higher than conventional ELISAs. The Force Discrimination Biosensor[2] (FDB) uses generically functionalized 0.8 µm-diameter beads to label captured target; a magnetic field gradient removes nonspecifically bound beads, thus improving sensitivity by reducing both background and the incident of false positives. Already demonstrated for single analyte detection, methodologies to array the alumina ultrafiltration membrane for multiplexed detection have been evaluated. One of the biggest challenges is to array hydrophobic antibody conjugates onto porous hydrophilic PEG-biotin surfaces without losing pattern integrity due to lateral wicking. Patterning via a PDMS stamp or mask works reasonably well, but is too cumbersome for the patterning of the large number of membranes needed for practical applications. Instead, a pulsed laser transfer technique developed at NRL has been adapted to pattern antibody conjugates[3] onto PEGylated membranes. With an average element dimension of (100 µm)^2 and 200 µm spacing between elements, a 10 x 10 array can be written in 3 mm^2. Such arrays can be patterned to give a single diagnostic for a variety of bacterial, viral, or protein agents without requiring the use of an additional membrane for positive/negative controls. Multiplexed assays for bacterial spores and cells, viruses, and protein toxins have been performed with these filters; results will be presented to demonstrate the application of pulsed laser writing to biosensor patterning.

[1] Supported by the Joint Service Technical Panel for Chemical and Biological Defense.

[2] Lee et al., Anal. Biochem. 287, 261 (2000).

[3] Ringeisen et al., Biomaterials 23, 161 (2002).

10:20am **BI+HS+SS-ThM7 DIOS-MS for Reaction Monitoring and Chemical Analysis**, *Z. Shen,* 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 small molecules as well as biomolecules 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 demonstrate the application of DIOS-MS to small molecule quantitative analysis, high throughput screening, chemical reaction monitoring, enzyme-substrate reaction and inhibition characterization, drug metabolism studies, and protein identification. We will also discuss aspects of the desorption and ionization mechanisms of DIOS.

10:40am **BI+HS+SS-ThM8 ToF-SIMS Analysis of PNA/DNA Hybridization on Thiolated Biosensor Chips**, ***M. Schröder***, Westfälische Wilhelms-Universität Münster; Germany, *J.C. Feldner, S. Sohn, H.F. Arlinghaus*, Westfälische Wilhelms-Universität, Germany

We have investigated a diagnostic method that uses peptide nucleic acid (PNA) biosensor chips to detect hybridization of unlabeled DNA. Using two different approaches, different PNAs were immobilized onto Au-coated spots with an approximate diameter of 100µm. One method was to immobilize thiolated PNA in a single-step reaction to the Au-surface via an Au-S-bond. The other method was to crosslink the N-terminal end of the PNA to a preformed layer of 11-mercaptoundecanoic acid (MUA) in a reaction consisting of two steps forming an amide bond. These layers were hybridized with complementary and non-complementary unlabeled single-stranded DNAs (ssDNA). Since the backbone of DNA, in contrast to PNA, contains phosphorous, it is possible to identify DNA-PNA-hybrids with time-of-flight mass spectrometry (ToF-SIMS) via DNA-specific phosphate-related ions at the masses 63 amu (PO_2^-) and 79 amu (PO_3^-). In addition to these signals, the deprotonated bases M-H$^-$ were detected in both immobilization approaches. In the case of the two-step-immobilization, it was possible to independently control the different steps by measuring characteristic peaks of MUA-fragments. Due to the manifold control-possibilities, especially variation of surface-density of the immobilized PNA and saturation of the remaining active Au-binding-sites with different thioles, it is possible to optimize hybridization conditions and suppression of uncharacteristic bonding of the ssDNA to the Au-surface. From the obtained data it can be concluded that both PNA immobilization approaches are very promising for designing PNA biosensors and that ToF-SIMS is a useful tool for identifying DNA-PNA-hybrids on these biosensor chips with good discrimination.

11:00am **BI+HS+SS-ThM9 Covalent Attachment and Hybridization of DNA Oligomers at Polycrystalline Diamond Thin Films**, *T. Knickerbocker, W. Yang, W. Cai,* University of Wisconsin-Madison, *J.N. Russell, Jr., J. Butler,* Naval Research Laboratory, *D.M. Gruen, J.A. Carlisle,* Argonne National Laboratory, *L.M. Smith, D. Van der Weide, **R.J. Hamers***, University of Wisconsin-Madison

Diamond has a number of unique properties, including a very wide range of electrochemical stability and very good electrical and thermal properties. These properties may make diamond a particularly attractive material to use as a substrate for biological sensors. We have explored the covalent bonding of DNA to several different types of diamond thin films, including free-standing polycrystalline films, thin films of microcrystalline diamond on silicon substrates, and ultrananocrystalline diamond thin films. Starting with H-terminated diamond, we prepared a homogeneous amine-terminated surface using a photochemical attachment processes, optimized using core-level photoemission spectroscopy. These amine-terminated diamond surfaces are then used as a starting point for subsequent attachment of DNA oligomers. The efficiency and selectivity of hybridization have been determined using conventional fluorescence measurements after the surface-bound oligomers are hybridized with fluorescently-tagged complementary and non-complementary oligomers. Our studies show that DNA-modified diamond surfaces show good hybridization properties and good selectivity. More importantly, the DNA-modified diamond surfaces show extremely good stability with repeated hybridizations, and retain this selectivity even after being dried and later reconstituted. This talk will discuss the fabrication of DNA-modified diamond surfaces for biosensor applications, and the differences and similarities between the various forms of DNA-modified diamond thin films.

11:20am **BI+HS+SS-ThM10 Direct Electronic Detection of DNA Hybridization at Surfaces**, ***W. Cai***, *J. Peck, D. Van der Weide, R.J. Hamers*, University of Wisconsin-Madison

We have explored the use of electrical measurements to detect DNA hybridization in a label-free manner at surfaces. Our work has emphasized materials that are compatible with microelectronics, including DNA-modified surfaces of silicon, gold, and diamond. While most previous studies have focused on detection via low-frequency measurements, our work has focused on measurements at high frequencies, from ~10 kHz up to 10 GHz. The use of radio- and microwave-frequencies brings with it reduction in 1/f noise, the possibility of constructing electrically resonant devices for enhanced sensitivity, and the ability to perform single-ended measurements based on reflection instead of transmission. At these high frequencies, the electrical properties are controlled by the capacitance of the electrical double-layer, with some possible contributions from the space-charge region of semiconducting substrates. Using electrochemical impedance spectroscopy, we find a small, but reproducible change in capacitance at the interface when DNA oligomers are hybridized with the complements. By comparing the responses generated when the surface-bound oligos are exposed to matched and mismatched sequences in solution, we can separate the changes in dielectric properties arising from hybridization from other possible sources of systematic error. To enable measurements to be performed with high sensitivity on very small areas, we have constructed a novel heterodyne reflectometer that allows us to measure the dielectric properties of very small interfaces in a manner that is essentially zero-background. To do this, we take advantage of the fact that the electric double-layer is intrinsically nonlinear, and that hybrization and other biological binding processes modify the dielectric properties of the double-layer region. This talk will discuss different schemes for direct electronic detection of DNA hybridization, with particular emphasis on the use of RF and microwave methods.

11:40am **BI+HS+SS-ThM11 Engineered Biointerfaces for Protein Biochip Applications**, ***H.B. Lu***, *M. Mariano, S. Schweizer, H.M. Tran, L.A. Ruiz-Taylor, H. Hong, H.H.J. Persson, R.L. Cicero, P. Kernen, P. Wagner,* Zyomyx, Inc.

Protein biochip technology promises breakthroughs in large-scale protein analysis. Measuring and analyzing protein activities in a highly efficient, miniaturized and parallel fashion requires advanced surface chemistries for reproducible protein immobilization and minimized non-specific adsorption. Controlling the solid-liquid interface of a miniaturized biochip becomes a key step for maintaining protein activity and integrating highly sensitive detection techniques. We present several reactive surfaces engineered for protein biochip applications at Zyomyx. Systematic efforts on designing organic layers on different substrates have been carried out to improve packing density, orientation, and functionality of immobilized capture reagents, as well as to minimize non-specific biomolecule adsorption in complex biological samples. The latter is particularly important for improving detection limits and obtaining meaningful results in multiplex protein assays. To reduce non-specific adsorption and optimize chip performance, we incorporated oligo- and poly-ethylene glycol (EG) molecules in our organic layers that are well known to reduce non-specific protein adsorption. Effects of substrate type, surface coverage, and molecular structure of the assembled organic layers on specific and non-specific interaction of biomolecules with the surfaces are presented. Specificity, loading capacity and detection sensitivity of protein immunoassays using high-density protein arrays configured with these surfaces are demonstrated and discussed.

Dielectrics
Room: C-107 - Session DI+EL-ThM

Issues for Gate Dielectrics
Moderator: D.P. Norton, University of Florida

8:20am **DI+EL-ThM1 Epitaxial Oxides on Silicon for Alternative Gate Dielectrics and More**, ***D.G. Schlom***, Penn State University **INVITED**

The epitaxial growth of oxides on silicon presents opportunities to harness the full spectrum of electronic, optical, and magnetic behavior available in oxides, while simultaneously exploiting the properties of the underlying semiconductor. One key application for epitaxial oxides on silicon, which will be the focus of this talk, is to produce a viable gate dielectric alternative to SiO_2 for silicon MOSFETs with higher dielectric constant (K). As a first step in the identification of such an alternative gate dielectric, we used tabulated thermodynamic data to comprehensively assess the thermodynamic stability of binary oxides and nitrides in contact with silicon at temperatures from 300 to 1600 K. Sufficient data exist to conclude that the vast majority of binary oxides and nitrides are thermodynamically unstable in contact with silicon. The dielectrics that remain are candidate materials for alternative gate dielectrics. Of these remaining candidates, the oxides have significantly higher K than the nitrides. We then extended this thermodynamic approach to multicomponent oxides comprised of candidate binary oxides. The result is 13 silicon-compatible gate dielectric materials with $K > 20$, of which at least six have an optical bandgap ≥ 5 eV. Having identified promising candidate materials with high K, high optical bandgap, and the likelihood for thermodynamic stability in contact with silicon, we have been using MBE to epitaxially integrate the candidate materials having the best lattice match with silicon. High-resolution cross-sectional TEM analysis of the epitaxial interface between silicon and epitaxial oxides will be shown. Some of these interfaces were formed by growing silicon on the dielectric; others were formed by growing the dielectric on silicon. Achieving the former interface is easier as it involves the deposition of a single component material (Si) in a vacuum environment. In contrast, the latter involves multiple components, and as one of these components is oxygen, the possibility of oxidizing the silicon surface and not only losing the epitaxial template, but also forming an undesired SiO_2 layer. Over the last two decades, three strategies have been used to grow epitaxial oxides on silicon: (1) to grow with no excess oxidant, (2) to grow with excess oxidant at high substrate temperatures, and (3) to grow with excess oxidant at low substrate temperatures. The overarching goal of all three strategies is to avoid the formation of an amorphous SiO_2 layer that would result in the loss of the substrate's crystalline template before the oxide has a chance to nucleate on it. Most reports of the epitaxial growth of oxides on silicon fall into the high temperature / excess oxidant regime. Although successful for the nucleation of an epitaxial oxide layer, these growth conditions typically lead to the growth of an SiO_2 layer at the silicon interface. To avoid this layer, whose replacement is the purpose of the alternative gate dielectric, we have studied the last of the three regimes-the low temperature / excess oxidant regime. In this regime the oxidation of silicon by the oxidant is limited by kinetics. However, kinetic barriers to the oxidation of the constituents of the desired oxide at these low temperatures can also occur. We have performed in situ oxidation studies to assess the low temperature oxidation of various elements. Examples illustrating oxides that can be grown epitaxially on silicon in the low temperature / excess oxidant regime will be presented, as well as epitaxial oxide / silicon heterostructures that make use of the integration of the overlying epitaxial oxide layers and the underlying silicon.

9:00am **DI+EL-ThM3 Electrical and Material Properties of 10 nm Thick Hf-Doped Tantalum Oxide High k Dielectrics**, ***J. Lu***, *J.Y. Tweg, Y. Kuo,* Texas A&M University, *P.C. Liu,* AMD, *B.W. Schueler*, Physical Electronics

A high k gate dielectric material that replaces the nm thick SiO_2 is necessary for sub 100 nm ULSICs for many practical reasons.[1] Metal oxides such as Ta_2O_5, HfO_2, ZrO_2 and Al_2O_3, are promising candidates and have been intensively investigated. However, they suffer from problems such as the high leakage current and high interface states. It was reported that by adding a third element into the metal oxide, some of the dielectric properties could be improved.[2,3] In this paper, we studied the Hf-doped Ta_2O_5 thin films deposited by reactive magnetron sputtering. Electrical properties of the 10 nm thick films, such as the k value and leakage current, were measured. Compositions, microstructures, and interfacial properties of the film were probed with ESCA, TEM and SIMS. Compared with the undoped film, the doping process reduced the leakage current, improved the k value, and lowered the fixed charge density. Influences of the post-deposition annealing process parameters, such as temperature and time, to high k properties were also studied. We are going to present these experimental results and to compare them with literature reports. This project is supported by the Texas Higher Education Coordination Board ATP program (project # 0005120003-1999).

[1] International Technology Roadmap for Semiconductors, 1999 edition, SIA.

[2] Y. Kuo, J. Y. Tewg, J. P. Donnelly, and J. Lu, ECS Procs. Intl. Semi. Technol. Conf., 2001-17, 324, 2001.

[3] Y. Kuo, J. Y. Tewg, and J. P. Donnelly, ECS Meeting Abstract, 2001-1, No. 232, 2001.

9:20am **DI+EL-ThM4 The Effect of N_2 Annealing on $Al_xZr_yO_z$ Oxide**, ***J. Pétry***, *O. Richard, W. Vandervorst, T. Conard,* IMEC, Belgium, *J. Chen, V. Cosnier,* International Sematech c/o IMEC, Belgium

In the path to the introduction of high-k dielectric into IC components, a large number of challenges have to be solved. One of these concerns the stability of high-k oxides to high temperature annealing. Indeed annealing will most likely be necessary to improve the electrical characteristics of the high-k layer itself and the high-k stack will be submitted to annealing in further processing. In this study, we investigated the effect of annealing of ALCVD AlZrO layers in N_2 from 700 to 900C by XPS, TOFSIMS, TEM and FTIR. The effect of the Si surface preparation (HF-last, 0.5 nm RTO, Al_2O_3) on the modification of high-k oxide and interfacial layer upon annealing was also analyzed. We first studied the compositional changes of the mixed oxide upon annealing. For all temperature and surface preparation considered, we observed a segregation of the mixed oxide with the Al oxide at the surface. We also observed an increase of the Si concentration in the high-k film itself, with a diffusion profile towards the surface of the film. On the other hand, the modification of the interfacial layer is strongly dependent on the system considered. In the case of mixed oxide grown on 0.5 nm RTO, no changes are observed between the as-deposited layer and the layer annealed at 700C. At 800C, radical change appears: the initial RTO layer seems to be converted to a mixed layer composed of the initial SiO_2 and AlO coming from the mixed oxide, without forming an Al-silicate layer. This remains for annealing at 900C. When grown on 1.5 nm Al_2O_3 on 0.5 nm RTO, the only difference from the previous system is the observation of an Al-silicate fraction in the interfacial layer for the as-deposited and 700C annealed samples, which disappears at higher temperatures. Finally, when grown on HF-dipped Si, we observe a slight increase of the interfacial thickness after annealing at 700C and no further changes for higher annealing temperature.

9:40am **DI+EL-ThM5 Pulsed Plasma Enhanced MOCVD of High k Y_2O_3 Layers for Gate Dielectric Applications**, ***C. Durand***, *B. Pelissier, C. Vallee, M. Bonvalot, L. Vallier, O. Joubert,* CNRS/LTM, France, *C. Dubourdieu*, CNRS/LMGP, France

CMOS transistor scaling is rapidly reaching its limits with traditional SiO@sub2@ gate oxide due to increasing tunneling currents. Rare earth oxides, as high k materials to replace SiO@sub2@, have shown promising results. Here, we focus on the elaboration of Y@sub2@O@sub3@ thin films by an innovative technique, namely pulsed injection Plasma Enhanced Metal Organic Chemical Vapor Deposition (PE-MOCVD). In this technique, dissolved Y(thd)@sub3@ precursors are sequentially injected into an evaporator, which allows perfect reproducibility of the amount of precursors delivered to the plasma chamber and then onto the SiO@sub2@ (8 @Ao@)/Si substrate heated at 350@degree@C. An Ar/O@sub2@ plasma is applied to favor precursor decomposition and surface reactivity. Preliminary experiments have shown that no Y@sub2@O@sub3@ film is deposited on substrates heated at 350@degree@C by pulsed MOCVD only, whereas stoichiometric layers (typ. 5 nm thick) are obtained with the plasma. The plasma induces a lower deposition temperature compared to MOCVD. Based on X-rays Photoelectron Spectroscopy (XPS) and infrared spectroscopy studies of the initial stages of the thin film formation, it seems that metallic yttrium atoms react with SiO@sub2@ to form silicate compounds. The thickness of the initial SiO@sub2@ layer gradually changes leading to silicate layer formation. The SiO@sub2@ underlayer can be fully consumed. Y@sub2@Osub3@ thin films have been annealed at a temperature of 600@degree@C under several atmospheres. Subsequent XPS analyses indicate that carbon contamination can be reduced by half, independent of the annealing atmosphere Ar or O@sub2@, thereby suggesting densification of the layer. Further experiments are under way to determine optimum annealing conditions leading to fully oxidized Y@sub2@O@sub3@ layers without carbon atoms. Simultaneously, the behavior of the silicate interface during this annealing treatment will be carefully analyzed.

10:00am **DI+EL-ThM6 Plasma Enhanced MOCVD of Hafnium Oxide and Hafnium Silicate Thin Films**, *V. Rangarajan,* ***H. Bhandari***, *T.M. Klein*, University of Alabama

Hafnium oxide films were deposited by Metal Organic Chemical Vapor Deposition (MOCVD) on Si using hafnium t-butoxide as the metal organic precursor. X-ray diffraction data show a monoclinic crystal structure when films were deposited at 400°C. Films were subjected to ex-situ furnace anneal and compared with as deposited films using XPS that showed a significant interfacial silicon dioxide growth. Hafnium silicate films were deposited by both thermal and plasma enhanced MOCVD using SiH_4 as the Si precursor. Plasma excitation improved Si incorporation resulting as much as 21.5 at.% Si. The films were subjected to furnace anneals up to 1100°C in oxygen and XPS analysis was done to confirm the silicate formation, composition and stability. Surface and bulk film morphology was studied using AFM and XRD respectively. Thermally grown Hf silicates had a measured 1.1 nm rms roughness, while plasma deposited films had 5.2 nm rms roughness. Both thermal and plasma deposited Hf silicates are amorphous as deposited, however thermal films exhibit crystallinity after a 30 min 1100°C furnace anneal in oxygen while plasma deposited films remained amorphous after the same treatment. Reflection FTIR measurements were performed and results show no evidence of bulk carbon incorporation. In-situ anneals in Ar ambient were done on thin films of HfO_2 and silicates and their change in chemical state was studied using XPS.

10:20am **DI+EL-ThM7 UHV-CVD of Al_2O_3 for Gate Dielectric Applications**, ***B.R. Rogers***, *Z. Song, R.D. Geil, V. Pawar, D.W. Crunkleton, R.A. Weller*, Vanderbilt University

Successful replacement of silicon dioxide-based MOSFET gate dielectrics by a high-permittivity (high-k) dielectric is a critical step in the continued drive to build the smaller, faster, lower-power, more-integrated circuits that society is demanding. Our goal toward this effort is to develop a thermodynamically and microstructurally stable, amorphous material system, having no interfacial silicon dioxide formation. In this presentation I will briefly discuss the need for an alternative gate dielectric and a "wish list" of characteristics for this material. I will then discuss our work on developing alumina/zirconia alloys as a potential gate dielectric. We have begun this effort by studying the deposition of alumina films in an ultra-high-vacuum chemical vapor deposition (UHV-CVD) system. I will present our findings to date in relation to the CVD process. In addition I will discuss the characterization of these films using spectroscopic ellipsometry and time-of-flight medium energy backscattering (ToF-MEBS), a characterization capability unique to Vanderbilt University.[1]

10:40am **DI+EL-ThM8 Hafnium Oxide As an Alternative Gate Dielectric in MOSCAP and MOSFET Application**, ***Y. Lin***, *R. Puthenkovilakam, J.P. Chang*, University of California, Los Angeles

HfO_2 is investigated in this study to replace SiO_2 as the gate dielectric material in metal-oxide-semiconductor devices. HfO_2 films were deposited on P-type Si (100) wafers by an atomic layer chemical vapor deposition (AL-CVD) process using hafnium (IV) t-butoxide $Hf(OC_4H_9)_4$ as the precursor and oxygen as the oxidant. The two chemistries were introduced sequentially into the reactor with purging and evacuation in between. The deposited films were stoichiometric and uniform based on X-ray photoemission spectroscopic and ellipsometry. The X-ray diffraction analysis indicated the deposited film was amorphous, however, it showed an interfacial layer formation at on the silicon substrate based on the chemical etching resistance experiment. This interfacial layer will be examined by the high-resolution transmission electron and medium energy ion scattering analysis. The step coverage will also be examined by depositing HfO_2 on 200 nm features with an aspect ratio of 4. The thermal stability of HfO_2 thin film on silicon was examined by Synchrotron radiation x-ray photoemission spectroscopy. The HfO_2 thin films were thermally stable up to 950° C in vacuum. In-situ Infrared analysis and ellipsometer measurement are underway to enhance our ability to understand the surface reactions. Isotope labeling of oxygen will be perform to study the effect of the oxidation/annealing processes on film composition. The dielectric constant of HfO_2 was 18 from the C-V measurement, which was slightly lower than the bulk HfO_2 . In the C-V measurement a small hysteresis and the interface state density was approximately 5.22×10^{11} cm^{-2} eV^{-1} are observed. The leakage current is 2~3 order magnitude lower than SiO_2 at the same equivalent oxide thickness. NMOS transistors will be fabricating to exam the applicability of HfO_2 for MOSFET application.

11:00am **DI+EL-ThM9 Hafnium Silicate and Nitrided Hafnium Silicate as Gate Dielectric Candidates for SiGe-based CMOS Technology**, ***S. Addepalli***, *P. Sivasubramani, H. Zhang, M. El-Bouanani, M.J. Kim, B.E. Gnade, R.M. Wallace*, University of North Texas

Strained epitaxial Si_xGe_{1-x} layers on Si have attracted considerable technological interest due to the enhancement in hole mobility, as well as ease of integration with existing Si CMOS technology. One of the major drawbacks, however, is the inability to produce a high-quality gate oxide in direct contact with Si_xGe_{1-x}, while maintaining the integrity of the oxide-Si_xGe_{1-x} interface. The introduction of a stable high-κ dielectric provides the prospect of simultaneously enhancing the capacitance of the gate stack and reducing leakage current for high performance SiGe devices. We have investigated hafnium silicate and nitrided hafnium silicate as viable candidates for SiGe-based CMOS technology. Hafnium silicide and nitrided hafnium silicide films were sputter deposited directly on Si_xGe_{1-x}. These films were subsequently converted to hafnium silicate and nitrided hafnium silicate respectively by employing a room temperature UV-ozone assisted oxidation approach in order to preserve the pseudomorphic nature of the Si_xGe_{1-x} layers. The bonding and composition of these films were characterized by X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and Rutherford Backscattering Spectrometry (RBS). The deposition and post-deposition processing parameters were optimized using XPS, High-resolution transmission electron microscopy (HRTEM), and FTIR. The electrical performance of the films was evaluated from capacitance-voltage (C-V) and current-voltage (I-V) measurements. The effects of various post-deposition annealing treatments on the electrical performance of the films were also studied. This work is supported by DARPA through SPAWAR Grant No. N66001-00-1-8928, and the Texas Advanced Technology Program.

11:20am **DI+EL-ThM10 XPS Study of Chemical Phase Separation in Amorphous Zr Silicate High-k Dielectrics**, ***G.B. Rayner***, *D.H. Kang, G. Lucovsky*, North Carolina State University

X-ray photoelectron spectroscopy (XPS) was used to investigate chemical phase separation in pseudo-binary Zr silicate alloys, $(ZrO_2)_x(SiO_2)_{1-x}$, deposited at 300C on Si substrates as a function of alloy composition, film thickness and subsequent annealing temperature. Based on previous infrared (IR) and x-ray diffraction (XRD) studies, it been shown that a chemical phase separation in (a) ZrO_2 and (b) SiO_2 with up to about 5 atomic percent ZrO_2 occurs in Zr silicate alloys when annealed at 900C in a non-oxidizing ambient such as Ar.. This separation is not accompanied by crystallization for silicate alloys with x~ 0.25, but crystallization of the ZrO_2 phase occurs for x> ~ 0.5. For Zr silicate films ~30 nm thick and x < ~0.6 the XPS O1s core level peak shapes are essentially unchanged for annealing temperatures to 500C. However, for annealing at 900C, the O1s core level peak splits into a distinct doublet with binding energies independent of alloy composition for 0.35 < x < 0.6. The peak at low binding energy, assigned to O^{2-} ions in the ZrO_2 phase, scales approximately linearly with composition. These results indicate a transition from silicate bonding, characterized by

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[1] This work is supported by the National Science Foundation grant # CTS-0092792.

Si-O-Zr alloy bonds, into bonding characteristic of the end-member oxide phases, SiO_2 and ZrO_2. The XPS results presented here provide additional insights into local bonding that are complementary to what has been revealed previously in IR studies, as well as confirming the chemical phase separation that occurs for annealing temperatures > 900C in inert ambients. Included also are the results of a parallel study on the effect of chemical phase separation on the electrical performance of metal oxide semiconductor capacitors.

11:40am **DI+EL-ThM11 Electrical Properties of SiO_2 Films Grown by Si(100) Reactions with Oxygen, Wet-oxygen and Wet-hydrogen**, ***Y. Liu***, *J. Hebb*, Axcelis Technologies, Inc.

The oxidation of Si(100) by oxygen (O_2), wet-oxygen (H_2O+O_2) and wet-hydrogen (H_2O+H_2) is of great importance for silicon oxide (SiO_2) dielectric film formation in the advanced CMOS devices. At the atmospheric pressure and high temperatures (>1100°C), 20 to 100 Å SiO_2 films have been grown on Si(100) wafers (dia.=200 mm) using a hot-wall rapid thermal processor (Summit 200, Axcelis) enhanced with a small volume (3-liter) quartz reactor for rapid gas switching. Wet-oxygen and wet-hydrogen with controlled compositions are produced using a hydrogen-rich and an oxygen-rich catalytic water vapor generator (WVG), respectively, and are monitored in real-time with a residual gas analyzer (RGA). Kinetic equations for Si(100) reactions with oxygen and water vapor are used to control oxidation temperature, oxidant fractional pressure and time to achieve desired oxide thickness. To grow a thermal oxide film, a Si(100) wafer is rapidly heated to a desired temperature in nitrogen or hydrogen. Rapid gas sequencing is carried out to expose the wafer to oxygen, wet-oxygen or wet-hydrogen for oxidation, and back to nitrogen or hydrogen for annealing and cooling. Critical electrical properties of the thermal oxide films grown under various conditions are measured and compared systematically using a powerful and non-contact Corona Oxide Characterization of Semiconductor (COCOS) tool (FAaST, SDI). These properties include equivalent oxide thickness (EOT), oxide capacitance, flat band voltage, effective oxide charge, interface trapped charge, interface trap density, and interface trap density spectrum. Gate oxide integrity (GOI) of these films is quantified by leakage current versus voltage (I-V) and stress-induced leakage current (SILC) measurements. Correlation between growth conditions and oxide qualities will be made.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+SS-ThM

Magnetic Spectroscopies
Moderator: D.A. Hite, NIST

8:20am **MI+SS-ThM1 Photoemission and X-Ray Absorption Measurements on the CMR Materials $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$**, ***N. Mannella***, University of California at Davis, *A. Rosenhahn*, Lawrence Berkeley National Laborarory, *S. Mun*, Intel Corporation, *S.-H. Yang*, IBM Almaden Research Center, *Y. Tomioka, Y. Tokura*, Joint Research Center for Atom Technology, Japan, *C.S. Fadley*, Lawrence Berkeley National Laboratory

We report core and valence photoemission results obtained with synchrotron radiation for a set of high quality single-crystal CMR samples, namely $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ with x ranging from 0 to 0.4. The measurements were performed after cleaving the crystals in situ in UHV, yielding very clean and stoichiometric surfaces. X-ray absorption spectroscopy (XAS) and high-resolution valence band measurements at temperatures above and below the Curie temperature will also be discussed. The Mn 3s core level spectra show the expected multiplet splitting in binding energy, an effect which can sensitively probe the spin state of magnetic atoms. Our data reveal a non-linear dependence of the multiplet splitting on the hole concentration x, contrary to what one would expect in the simplest picture according to which hole doping causes a corresponding number of Mn^{3+} ions to become Mn^{4+}. These results may indicate an inadequacy of the conventional model based on the nominal Mn^{3+} - Mn^{4+} valence states. We have also measured Mn 3s spectra as a function of temperature. Our data suggest a short-range-order magnetic transition above the bulk Curie temperature, yielding a quantitative estimate of temperatures higher than T_C at which the material shows magnetic order of local character. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098.

8:40am **MI+SS-ThM2 MOKE Studies of Magnetic Coupling in $Co/Cr_2O_3/CrO_2$**, ***R. Cheng***, *A.N. Caruso, L. Yuan, S.-H. Liou, P.A. Dowben*, University of Nebraska-Lincoln

CrO_2 is an attractive material for spin-polarized electron tunneling because of the high electron polarization and is among the predicted half metallic ferromagnets (metallic for one spin direction while insulating for the other spin direction, i.e. 100% spin polarization). Because the native surface layer of CrO_2 is Cr_2O_3, by evaporating Co thin films (5~20 nm) on top of epitaxial CrO_2 films on TiO_2 (100) substrates, a $Co/Cr_2O_3/CrO_2$ trilayer can be readily fabricated. >From in situ MOKE studies and ex situ SQUID measurements for the magnetic $Co/Cr_2O_3/CrO_2$ trilayers, the characteristic behavior of ferromagnetic-paramagnetic-ferromagnetic coupling above room temperature was observed. The thickness of Co and the temperature dependence of the magnetic hysteresis loops, obtained from MOKE, indicate different shapes, and the coercive fields show strong but not monotonic temperature dependence. These results indicate that there are changes in magnetic coupling and magnetization orientation particularly apparent as the temperature approaches the T_c of CrO_2.

9:00am **MI+SS-ThM3 Polarized X-Rays and Magnetic Interfaces**, ***H. Ohldag***, Stanford Synchrotron Radiation Laboratory, *A. Scholl, E. Arenholz*, Advanced Light Source, *F. Nolting*, Swiss Light Source, *Y. Acremann, J. Stohr*, Stanford Synchrotron Radiation Laboratory, *F.U. Hillebrecht*, Forschungszentrum Karlsruhe, Germany, *S. Maat, M.J. Carey*, IBM Almaden Research Center **INVITED**

While interfaces are supposed to dominate the behavior of magnetic multilayer their identification and characterization remains an experimental challenge. A prominent example is the loop shift (exchange bias) and the coercivity increase found if a ferromagnet (FM) is coupled to an antiferromagnet (AFM). Although exchange bias was discovered over 40 years ago our understanding of its origin is still poor. We use dichroism x-ray absorption spectromicroscopy in a photoemission electron microscope to study the magnetic coupling between AFM NiO(001) and FM Co. We observe large (1-20mm) AFM domains at the surface of bare NiO(001) single crystals. Upon in situ deposition of thin FM Co layers (1.5nm) a reorientation of the AFM axes takes place. The uniaxial anisotropy axes of the FM and the AFM are then aligned parallel domain by domain. Spectroscopy data show that the Co deposition causes a chemical reaction and formation of an interfacial CoNiOx layer. Microscopy images reveal its polarization to be aligned parallel to the Co layer. Upon annealing both, the uniaxial anisotropy and the amount of interfacial spins increases indicating the direct link between interfacial polarization and parallel exchange coupling. A small fraction of interfacial spins does not follow the external field. These so called pinned moments lead to an additional vertical shift in the hysteresis loop of the interfacial spins. The number of pinned spins can be diretly correlated to the size of the exchange bias field. Our findings clearly show that a proper description of magnetic coupling in Co/NiO as well as in other AFM/FM systems needs to consider the properties of a distinct interfacial layer that can deviate significantly from the bulk properties of each material.

[1] H. Ohldag, A. Scholl et al., PRL 86(13), pp. 2878, 2001.
[2] F. U. Hillebrecht, H. Ohldag et al., PRL 86(15), pp. 3419, 2001.
[3] H. Ohldag, A. Scholl et al., PRL 87 art. no 247201, 2001.

9:40am **MI+SS-ThM5 A Compact Angle Resolving Spin-Polarized Photoemission Spectrometer for "Double Polarization" X-ray Diffraction Spectroscopy of Magnetic Nanostructures**, ***S.A. Morton***, University of Missouri-Rolla, *J.G. Tobin*, Lawrence Livermore National Laboratory, *G.D. Waddill*, University of Missouri-Rolla

Recent studies of spin dependent x-ray photoelectron diffraction from magnetic nanostructures excited with circularly polarized photons have demonstrated that the technique can provide a powerful probe of element specific atomic scale magnetic structure; however, the asymmetries involved are low, typically 1-2%. Calculations suggest that combining excitation via circularly polarized photons with spin polarized photoelectron detection in a "double polarization" experiment should lead to a 5-10 fold increase in asymmetry. However combining high angular resolution XPD with spin resolving capability poses significant experimental challenges. The authors describe a unique new compact angle resolving spin spectrometer currently being developed at the Advanced Light Source, Lawrence Berkeley National Laboratory. This combines a large (11 inch) diameter fixed hemispherical analyzer with a novel rotatable input lens system allowing data with +-1 degree angular resolution to be acquired for any combination of incident and emission angles, including normal incidence/ normal emission: a geometry critical for certain magnetic measurements. The analyzer is equipped with both multichannel detection for spin integrated spectroscopies, such as magnetic linear or circular dichroism, and a Mott detector capable of resolving the photoelectron spin polarization along the two perpendicular axis of the rotational plane. Rapid switching between spin integrated and spin resolved modes is achieved by focusing the photoelectrons through a small hole in the detector of the hemispherical analyzer and into the compact mini-Mott detector situated immediately behind the channelplates. The spectrometer system also incorporates additional sample growth and characterization facilities such as co-evaporation from multiple deposition sources, LEED and Auger together with sample heating and cooling to provide a comprehensive system for the preparation and analysis of magnetic nanostructures.

10:00am **MI+SS-ThM6 In-plane Vector Magnetometry on Rectangular Co Dots using Polarized Neutron Reflectivity**, ***K. Temst***, *M.J. Van Bael, J. Swerts, D. Buntinx, C. Van Haesendonck, Y. Bruynseraede,* K.U. Leuven, Belgium, *H. Fritzsche,* Hahn-Meitner-Institut Berlin, Germany, *R. Jonckheere*, IMEC vzw, Belgium

We have measured the off-specular polarized neutron reflectivity of a periodic array of rectangular magnetic polycrystalline Co-dots, which were prepared by a combination of electron beam lithography and molecular beam deposition. The dots have a strong shape anisotropy, imposed by a length-to-width ratio of 4:1. The intensity of the off-specular satellite reflection was monitored as function of the magnetic field parallel to the rows of dots and in the plane of the film, allowing us to analyze the magnetization reversal process using the four spin-polarized cross-sections. Analysis of the neutron reflectivity provides in-plane vector magnetometry during magnetization reversal. The neutron reflectivity data are complemented by micromagnetic simulations.

10:20am **MI+SS-ThM7 Magnetism of Adatoms and Clusters**, ***P. Gambardella***, Ecole Polytechnique Fédérale de Lausanne, Switzerland **INVITED**

In the last ten years, x-ray magnetic circular dichroism (XMCD) has found widespread application as an element-specific magnetometry tool in the study of magnetic thin films. Here we show that x-ray absorption spectroscopy (XAS) and XMCD can be successfully employed to probe diluted transition-metal systems with surface impurity concentration as low as 3 x 10^{12} atoms cm^{-2}, thus leading to the direct characterization of the electronic and magnetic configuration of impurity systems as well as supported nanostructures. Combined XAS-XMCD provide simultaneous information about the the d-valence state and related spin and orbital moment of transition-metal atoms that is not accessible by traditional techniques such as, e.g., magnetic susceptibility, resistivity, and electron paramagnetic resonance measurements. A first fundamental issue is how the magnetic moment of surface adatoms depends on the interaction with the host conduction electrons. We show that Fe, Co, and Ni, owing to d-electron localization, display large spin and orbital moments on low electron density simple-metal substrates which are progressively quenched as the surface electron densitiy increases.[1] A second fundamental issue is how the interaction with the substrate and adjacent adatoms influnces the magnetic anisotropy of the system. We report giant magnetic anisotropy values up to 3.3 meV/atom for Co clusters and atomic wires on Pt surfaces. A clear correlation is established between the atomic coordination, the magnitude of the orbital moment and the anisotropy energy, with implications for magnetic ordering phenomena.[2]

[1] P. Gambardella et al., Phys. Rev. Lett. 88, 047202 (2002).

[2] P. Gambardella et al., Nature 416, 301 (2002).

11:00am **MI+SS-ThM9 Probing Buried Interfaces with Soft X-ray Standing Wave Spectroscopy: Application to the Fe/Cr Interface**, ***S.-H. Yang***, *B.S. Mun,* Lawrence Berkeley National Laboratory, *N. Mannella,* University of California, Davis, *S.K. Kim, J.B. Kortright, J. Underwood, F. Salmassi, E. Arenholz, A. Young, Z. Hussain, M.A. van Hove,* Lawrence Berkeley National Laboratory, *C.S. Fadley*, University of California, Davis

We will discuss a novel type of non-destructive method for spectroscopically studying buried nanometer-scale interfaces and other nanostructures with soft x-ray standing waves. Strong standing waves with a period of 4.0 nm and approximately 3:1 contrast ratios are created via Bragg reflection from a synthetic multilayer of form [B4C/W]40. By growing a wedge-shaped Fe/Cr bilayer on top of this multilayer, the mechanical translation of the sample exposed to a fixed and finely focussed synchrotron radiation beam is converted into a translation of the standing wave through the interface. Analyzing various core photoelectron intensities as a function of angle and beam position permits deriving layer thicknesses and interface mixing/roughness scales. Magnetic circular dichroism in photoemission from the 2p and 3p levels of Fe and Cr further permits deriving the positions and widths of regions with decreased (increased) ferromagnetic alignment for Fe (Cr), showing that normally antiferromagnetic Cr becomes ferromagnetic just below the center of the interface but with antiparallel alignment with respect to Fe, and that the equal-concentration region in the center of the interface strongly inhibits magnetic alignment for both species along the direction of net magnetizations that is probed. The magnetically-altered regions in both metals are only 1-2 atomic layers in thickness. 3s spectra from Fe and Cr further indicate that the local spin moments on both atoms do not change on crossing the interface. This standing wave-plus-wedge method should have a range of applications for the characterization of magnetic and non-magnetic nanostructures and their interfaces. Work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098.

Microelectromechanical Systems (MEMS)
Room: C-210 - Session MM+TF-ThM

Development and Characterization of MEMS Materials
Moderator: R. Ghodssi, University of Maryland

8:20am **MM+TF-ThM1 Tetrahedral Amorphous-carbon (ta-C) for MEMS Applications**, ***T.A. Friedmann***, *J.P. Sullivan, R.V. Ellis, T.M. Alam, M.P. de Boer, T.E. Buchheit*, Sandia National Laboratories **INVITED**

This presentation will focus on ta-C film properties (primarily stress relaxation) and MEMs and sensor devices fabricated from low stress ta-C material (not coatings of Si devices) with an emphasis on mechanical and adhesion property measurements enabled by device fabrication. Pulsed laser deposition (PLD) was used to grow the ta-C films. They can be fully stress relieved by simple thermal annealing without significantly altering the film mechanical properties. Two mechanisms for stress relief in these materials have been postulated, each involving strain-relieving transformations between sp^2 and sp^3 carbon. Recently, we have made fully ^{13}C enriched films by ablating from a ^{13}C (99%) target. NMR magic-angle spinning measurements of these enriched films have been made to quantify the changes in structure with annealing in an effort to validate the proposed models. Results of these measurements will be presented along with Raman, TEM, and cross-section EELS experiments. The low stresses that are achievable in ta-C enable interesting MEMS and sensor applications. We have demonstrated several one-level MEMS structures from this material (e.g. cantilever beams, microxylophone resonators, fatigue test, tensile test, and membrane based sensors) and used these structures for materials property measurements. Results of selected experiments will be presented. *This work was supported by the U.S. DOE under contract DE-AC04-94AL85000 through the Laboratory Directed Research and Development Program, Sandia National Laboratories.

9:00am **MM+TF-ThM3 Challenges of Compressible Microfluidics and MEMS Device Development**, ***C.B. Freidhoff***, Northrop Grumman ES, *E. Hong,* The Pennsylvania State University, *R.L. Smith,* University of Maryland-Baltimore County, *T.T. Braggins, S.V. Krishnaswamy,* Northrop Grumman ES, *S. Trolier-McKinstry,* The Pennsylvania State University **INVITED**

MEMS vacuum pump for a miniature mass spectrograph challenges current modeling techniques compared to other microfluidic devices that utilize incompressible fluids. The ability to estimate boundary layers accurately is needed to save resources in determining the optimum dimensions for geometries in the micrometer scale. This device development also adds in the need for dynamic analysis over a broad pressure range. Results for actuator and pump performance measurements as well as results on the expected reliability of the thin films used in the pump's mechanical operation will be presented. The paper will discuss the challenges and empirical results we have achieved to date.

9:40am **MM+TF-ThM5 Micro-Mechanical Characterization of Indium Phosphide (InP) for Active Optical MEMS Applications**, ***M.W. Pruessner***, University of Maryland, *T. King,* NASA Goddard Space Flight Center, *D. Kelly, R. Ghodssi*, University of Maryland

Monolithic integration of InP-based optoelectronics with MEMS actuators will enable wavelength division multiplexed (WDM) lossless switches, tunable lasers, and optical filters at the 1550 nm communications wavelength. Before InP-based MEMS can be realized, however, the mechanical properties of thin-film InP need to be determined. Three methods are presented. In nanoindentation, the applied load vs. displacement of thin films or bulk substrates is measured, and Youngs modulus (E) and film hardness (H) can be extracted. In the bending test, load-displacement data of microbeams is used to extract E. Finally, M-Test takes advantage of the pull-in instability of electrostatically actuated microbeams. Measurement of the pull-in voltage enables E and residual stress to be extracted. A surface micromachining fabrication process for InP-based MEMS actuators was developed. The devices consist of 1.7 µm thick InP beams oriented in the [011] direction with 1.7 µm In$_{0.53}$Ga$_{0.47}$As sacrificial layer on a (100) InP substrate. Fabrication utilizes methane-hydrogen-argon RIE of InP followed by sacrificial etching of the InGaAs layer and supercritical CO_2 drying. After release the longer cantilevers curved out of plane indicating a stress gradient. Furthermore, the longer fixed-fixed beams buckled indicating compressive stress. Both are likely the result of arsenic (As) contamination of the InP beam layer during MBE sample growth. An optimization of growth parameters should alleviate this effect. Bulk nanoindentation experiments resulted in E=103 GPa and H=6.3 GPa. Bending tests on short fixed-fixed beams resulted in E=80 GPa. InP beam-type electrostatic actuators were also demonstrated. However, M-Test could not be performed reliably on the existing samples due to out-of-plane curvature of the longer beams. Short beams were flat but required excessive actuation voltage. Device design and experimental results are presented.

10:00am **MM+TF-ThM6 Stiction/Friction Studies of MEMS Materials Using a Novel Microtriboapparatus**, *H. Liu*, ***B. Bhushan***, The Ohio State University

Microelectromechanical systems (MEMS) are the next logical step in "silicon revolution". Many studies have shown that stiction/friction impacts the efficiency, power output, and steady-state speed of microdevices. It is essential to study the stiction/friction of the compoents and materials that are commonly used in MEMS/NEMS devices. A microtriboapparatus is needed which can be used to perform stiction/friction studies using microcomponents relevant for applications. Such an apparatus has been developed and used in this study. In this apparatus, two components/specimens are mounted on two piezos, which can deliver the motion in X and Z directions, respectively. A total of four fiber optical sensors are used to measure the sample displacement in X and Z directions, adhesive force, friction force, and normal load. The microtribological properties of silicon, diamond like carbon films are investigated by this apparatus. Experiments have been also performed to study the effect of velocity, relative humidity and temperatures on these materials.

10:20am **MM+TF-ThM7 Free-standing Single-crystal Ni_2MnGa Thin Films: A New Functional Material for MEMS**, *J.W. Dong, J.Q. Xie, J. Lu, Q. Pan, J. Cui, S. McKernan, R.D. James*, ***C.J. Palmstrom***, University of Minnesota

Ferromagnetic shape memory (FSM) alloys are a new type of materials that experience thermodynamically reversible martensitic phase transformations and demonstrate ferromagnetic property. This ferromagnetic property provides unique handle on the configuration of the martensitic phases. Practically, moderate external magnetic/stress field can be applied to the FSM alloys in the twinned martensitic phase to adjust the volume fraction of the variants by the motion of twin boundaries, which will yield macroscopic shape change. In bulk single crystals of Ni_2MnGa, a typical FSM alloy, strain as large as 9.5% has been demonstrated.[1] This makes Ni_2MnGa a promising candidate for magnetic field driven actuator material. For micro-electro-mechanical-system (MEMS) actuators, several conceptual designs based on single crystal Ni_2MnGa films have been proposed.[2] The first single crystal growth of Ni_2MnGa thin film has been reported in ref. 3. The 300 Å-thick film grows pseudomorphically on a GaAs (001) substrate (a = b = 5.65 Å, c = 6.12 Å) and has a Curie temperature ~320 K. Furthermore, 900 Å-thick single-crystal Ni_2MnGa films have been processed into free-standing bridges and cantilevers.[4] The free-standing cantilevers show two-way shape memory effect under repeated thermo-cyclings. In this presentation, focus will be put on the shape memory effect and the magnetic field induced strain in the free-standing Ni_2MnGa films to elucidate the concept of using it as a new functional material in MEMS design.

[1] A. Sozinov, et al., Appl. Phys. Lett., 80, 1746 (2002).

[2] K. Bhattacharya, et al., Mat. Sci. Eng. A, 275, 685 (1999).

[3] J. W. Dong, et al., Appl. Phys. Lett., 75, 1443 (1999).

[4] Q. Pan, et al., to be published in J. Appl. Phys.

10:40am **MM+TF-ThM8 A New Approach to Electrical Characterization of Spin-on Dielectrics for Power MEMS Applications**, ***A. Modafe***, *R. Ghodssi*, University of Maryland

We have developed a new method and special-purpose test structures for electrical characterization of spin-on low-k dielectrics for Power Micro-Electro-Mechanical Systems (MEMS) that operate under high voltages. The spin-on low-k dielectrics in this study are ACCUGLASS T-12B, a methylsiloxane-based spin-on glass (SOG) from Honeywell and CYCLOTENE 3022-35, a polymer based on B-staged bisbenzocyclobutene (BCB) monomer from Dow Chemical. Due to their simple, low-temperature processes, these materials are suitable for the inter-level dielectric layer in a Power MEMS device, in this case a bottom-drive variable-capacitance micro-motor supported on micro-ball bearings. The existence of relatively high voltages makes the electrical components of the device, especially the inter-level dielectric more vulnerable to failure. Furthermore, the likelihood of failure increases with time due to absorption of moisture and dust. The proposed method performs capacitance and current vs. voltage measurements (C-V and I-V) on the inter-digit comb-type and spiral-type capacitor test structures to characterize the electrical properties of the dielectric film under test, i.e. dielectric constant, dielectric strength, leakage current, and their dependency on absorbed moisture and operation time. The measurement of the dielectric constant is based on a geometry-extractor method that compares the capacitance of the test structure before and after dielectric deposition. The dielectric constant is calculated by extracting a geometry factor representing the shape of the test structure from the C-V test. The dielectric constant measurement error is minimized using the extracted geometry factor, instead of measuring the geometrical features in separate experiments. The measurement of the dielectric strength and the leakage current is based on a ramped voltage-stress (RVS) method using the I-V test on the developed test structures. Preliminary results for electrical characterization are presented.

11:00am **MM+TF-ThM9 Physics of Metal Micro-contact Events in Micro-Electro-Mechanical (MEM) Relays**, ***J.W. Tringe***, *T.A. Uhlman*, Air Force Research Laboratory, *A.C. Oliver, J.E. Houston*, Sandia National Laboratories

Much research has been previously performed on the physics of electrical contacts, but this has mostly focused on larger contact areas, force and current levels than are relevant for typical MEM switches. Recent work using interface force microscopy (IFM) has experimentally approximated single-asperity gold-gold electrical contact events under conditions appropriate to MEM relay materials. The contact force and resistance were measured simultaneously under constant-current conditions as a function of relative probe-surface separation using parabolic gold probes a few microns in diameter on an electroplated gold surface, typical of the contact surface found in MEM relays. Results will be presented which demonstrate that a very small number of asperities define the electrical behavior of gold-gold MEM switches. Further, the existence of a non-metallic contamination layer on the gold surfaces, up to many tens of angstroms thick, will be shown to critically determine the force and current levels necessary for low contact resistance (on the order of a few ohms or lower). Contact resistance decreases precipitously upon break-down or thinning of the contamination layer, then more slowly and linearly as the probe-surface contact area increases. The contamination layer deforms plastically upon initial contact, then maintains physical and electrical contact with the tip to distances over 5 nm from the point of initial contact. Due to the topography of the electroplated gold surface and the mechanical, electrical and chemical nature of the contamination layer, contact events in gold-gold microsystem relays involve relative contact areas on the order of 0.1%.

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

11:20am **MM+TF-ThM10 Growth and Characterization of Doped 3C-SiC Films for Micro- and Nanoelectromechanical Systems**, *A.J. Fleischman*, ***C.A. Zorman***, *M. Mehregany*, Case Western Reserve University

An outstanding combination of mechanical, electrical, and chemical properties coupled with recent advances in micromachining make SiC a leading material for microelectromechanical systems requiring performance characteristics that cannot be achieved using Si. For these applications, 3C-SiC is particularly attractive since it is the only SiC polytype that can be grown as single and polycrystalline thin films on Si substrates, giving it a versatility unmatched by the other leading polytypes, specifically 4H- and 6H-SiC. Recently, 3C-SiC has found favor as a material for nanoelectromechanical systems (NEMS), due to the fact that it has a higher acoustic velocity than Si. For nanomechanical resonators, 3C-SiC is currently used solely for its mechanical and chemical properties, while electrically active components are constructed of other materials. Advanced 3C-SiC NEMS will likely capitalize on the electrical properties of 3C-SiC, requiring the use of doped material grown in a well-characterized and highly controllable fashion at the submicron level. In this study, 0.5 micron thick, doped 3C-SiC films were epitaxially grown on (100) Si wafers by APCVD, using silane and propane as precursor gases, hydrogen as a carrier gas, and phosphine and diborane as doping gases. To investigate the effects of dopant incorporation on microstructure, the films were grown as thin multilayers, with a doped layer sandwiched between two undoped layers. SIMS and XRD were used to characterize the multilayer samples. In general, phosphorus doping had no adverse affect on the microstructure of the single crystal films. In contrast, boron doping did influence the microstructure, with high diborane concentrations resulting in the formation of polycrystalline SiC layers. Details concerning the experimental procedure, the effects of outgassing reactor components on the composition of the films, and the implications for submicron 3C-SiC devices will be covered in this presentation.

11:40am **MM+TF-ThM11 Incorporating Chemically Functional Materials on MEMS Structures**, ***S. Semancik***, *R.E. Cavicchi, N.O. Savage, C.J. Taylor, D.C. Meier, C.B. Montgomery*, National Institute of Standards and Technology

Low power microsensors and microanalytical systems based on MEMS platforms are expected to profoundly impact the areas of chemical and biological sensing. Fabrication of such chemical microdevices, however, requires that chemically functional materials be integrated with a variety of MEMS structures, challenging researchers to develop processing methods that are reliable, as well as compatible with microelectronic materials and micromachining. In this presentation we describe a range of film deposition procedures for localized deposition of oxides, metals, polymers and other materials on surface-micromachined components. The procedures, which have been developed within our chemical microsensor program, are typically performed on target areas of ~ 100 µm x 100 µm. They include: self-lithographic, thermally-activated CVD on microhotplate structures; addressable electrodeposition; spinning on and selectively removing sol-gels and colloidal suspensions as well as thermally-evolved resists; the use of microheaters to process high area porous films (from silsesquioxanes); utilization of tiny (lithographically-defined) shadow masks with evaporation; and micro-pipetting. Locally-deposited materials are characterized by SEM, AFM, EDS and other spectroscopic methods, and by electrical probing when it is relevant. We provide examples of processing for nanostructured SnO$_2$ and TiO$_2$, high-area SiO$_2$, ultrathin Pt, Au, Ni and Pd, organosilanes and modified polymers. These materials have been employed on MEMS platforms, individually and in certain combinations, for sensing, preconcentration, separation and patterning. The role of multielement microarrays in efficiently optimizing deposition methods for some films will also be discussed.

Nanometer Structures
Room: C-207 - Session NS-ThM

Single Molecule Devices
Moderator: T. Michalske, Sandia National Laboratories

9:40am **NS-ThM5 Toward the DNA Electronics**, *T. Kawai*, ***H. Tabata***, Osaka University, Japan **INVITED**

DNA is one of the most promising molecules as the scaffold for molecular nanotechnology toward nanoelectronics. DNA has the special double helix structure with p-electron cores of well-stacking bases for one-dimensional charge transport. The investigations of DNA on the nanostructure, electrical conductivity and electronic states have significant implications for the application of DNA in electronic devices and in DNA-based electrochemical biosensors. It is worthily noted that divergent and controversial conclusions were reported in DNA-mediated charge transport. The direct measurements of the intrinsic electrical characteristics of polynucleotides using a conducting probe atomic force microscope have been performed using self-assembled two dimensional DNA networks. It has been revealed that DNA without carrier doping is a wide-gap semiconductor. Upon carrier doping, poly(dG)?poly(dC) show the p-type behaviors, presumably due to the shallow ionization potentials of DNA bases. The conductivity of these molecules has been successfully controlled by chemical doping, electric field doping and photo-doping. It is found that the poly(dG)?poly(dC) has the best conductivity and can act as a conducting nanowire. The conductive mechanism is discussed by the charge hopping model based on the SPM observation of DNA nanostructure. For the advanced construction of DNA based molecular memories and circuits, gold and cobalt particles have been assembled within the two-dimensional DNA networks. Gold particles are arranged artificially with DNA molecular template as an average separation distance of 260nm. The pattern of the complex is controlled by changing the concentration of the DNA solution, suggesting that this method is effective in achieving the positional control of nano-scale molecular memories and circuits.

T.Kawai et al; Appl.Phys.Lett.,77,3848(2000), Appl.Phys.Lett., 77,3105(2000), Surf.Sci.Lett,432,L611(1999), J.Vac.Sci.Technol.B17,1313(1999), Jpn.J.Appl.Phys. 39, 581(2000), 38,L606(1999), 38,L1211(1999)

10:20am **NS-ThM7 Lander Molecules Acting as Nanomolds on Cu(110)**, ***F. Rosei***, *Y. Naitoh, P. Thostrup, M. Schunack,* University of Aarhus, Denmark, *P. Jiang, A. Gourdon,* CEMES-CNRS, France, *E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark, *C. Joachim,* CEMES-CNRS, France, *F. Besenbacher,* University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110)surface.[1] Manipulation experiments on isolated Landers anchored at step edges at low temperatures, reveal a restructuring of the Cu steps. Surprisingly, when the molecule is removed from the step, a tooth-like structure appears (two atomic rows in width), corresponding to the distance between the spacer legs within the molecule. Scanning Tunneling Spectroscopy measurements are in progress to investigate the electronic states of the Lander on Cu(110). This is the first prototype of more complex molecular machines able to selffabricate nanostructures with the prospect of developing planar and atomically precise interconnections of molecular nanodevices. Furthermore, by nanopatterning the substrate via O$_2$ chemisorption and using this template for Lander adsorption, we show that it is possible to self-assemble long 1D molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

10:40am **NS-ThM8 Electronic Properties of Individual Defects in Molecular Circuit Elements**, ***S.V. Kalinin***, *M. Freitag, A.T. Johnson, D.A. Bonnell*, University of Pennsylvania

The local property variations of nanowires, nanotubes, and functional molecules dictate the behavior of nanoelectronic devices. Scanning Gate Microscopy (SGM) provides information regarding individual defects during dc transport. To determine local properties of defects during ac transport, we have developed Scanning Impedance Microscopy (SIM). In combination these measurements quantify the electronic structures of individual defects in nanocircuits. A circuit is configured with a molecule or nanotube on an oxidized Si wafer with metal contacts at each end and a back electrode. In the case of a semiconducting single walled carbon nanotube the defects become depleted at a gate voltage that is related to the local electronic structure of the defect. The depletion voltage for each individual defect can be accessed in several ways. In SGM the current through the circuit is measured and the scanning probe tip provides a local gate voltage. In SIM an ac signal is applied across the circuit while the tip measures the local potential amplitude. The gate voltage in this case can be applied both from the back electrode (back gate) and the tip (tip gate). In both SGM and SIM the defects are manifest as sharp discontinuities in the image when they are depleted. The gate voltage dependence of the image contrast is a direct measure of the difference in Fermi energies at these defects. A comparison of results from nanotube circuits and molecular circuits will be presented and implications to local electronic structure and transport mechanisms will be discussed.

11:00am **NS-ThM9 Single Molecular Switches**, ***P.S. Weiss***, The Pennsylvania State University **INVITED**

We use intermolecular interactions to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements on single or bundled molecules. We use and develop scanning probe microscopes to determine both local structures and the electronic and other local properties. We have applied these to isolate molecules with electronic function to determine the mechanisms of function, and the relationships between molecular structure, environment, connection, coupling, and function. We have been able to demonstrate that single molecules can function as multistate switches, and have determined important aspects of the mechanism, function, and persistence of switching. We will discuss the origins of switching and the relevant aspects of the molecular structure and environment required.

11:40am **NS-ThM11 High-bias Conductance in Single-atom Contacts of Au Alloys**, *J. Mizobata, A. Fujii, S. Kurokawa,* ***A. Sakai***, Kyoto University, Japan

Single-atom contacts of Au have a strong tendency to exhibit a conductance quite close to 1G0, one quantum unit of conductance, as long as a bias voltage is less than 1 V. They show a well-defined peak at 1G0 when their conductance data are plotted in a histogram. With increasing the bias, however, the 1G0 peak decreases in height and disappears at 1.9 V at room temperature. This result suggests that a single-atom 1G0 contact of Au becomes unstable under high biases, perhaps due to an extremely high current density in the contact, which may cause electromigration or current-induced bond weakening. In an effort to improve the stability of single-atom contacts of Au, we have recently carried out experiments on Au alloy contacts, containing Ag and Pt as solute atoms, and compared their high-bias conductance with that of pure Au. All measurements were performed at room temperature with varying the bias from 0.2 V to 2.0 V. In the case of an Au20wt%Ag alloy, we found that the 1G0 peak is systematically higher than that of pure Au for 0.2-1.2 V. The Ag alloying is thus effective for improving the stability of Au single-atom contacts against high contact current. However, the 1G0 peak height difference between AuAg and pure Au disappears for higher biases, and the positive effect of Ag alloying is somehow limited for biases lower than 1.4 V. On the other hand, an alloying with 20wt%Pt yields no enhancement in the 1G0 peak height, and the peak disappears at 1.0 V. Therefore the effect of alloying on the high-bias 1G0 conductance of Au depends on an alloying element.

Photonic Materials Topical Conference
Room: C-111 - Session PH-ThM

Photonic Nanostructures
Moderator: G. P. Nordin, University of Alabama at Huntsville

8:20am **PH-ThM1 Enhanced Optical Properties Utilizing Photonic Crystal Technology**, ***L.A. Kolodziejski***, *G.S. Petrich, J.D. Joannopoulos, E.P. Ippen,* Massachusetts Institute of Technology, *S. Fan*, Stanford University **INVITED**

The optical performance of a number of photonic devices can be greatly enhanced by incorporating photonic crystal (PC) technology into the device design. One-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) variations in the dielectric constant enable creation of photonic crystals; the operating wavelength is determined by the lattice constant with the size of the corresponding bandgap dictated by the contrast in dielectric constant and the structure's geometry. Due to the considerable difficulty in fabricating 3D semiconductor-based photonic crystals, 1D and 2D photonic crystal designs are being explored using GaAs-based high dielectric materials with large index contrast established by the use of oxidized AlAs (or Al_xO_y). As one example, the optical performance of a light-emitting diode (LED) is enhanced by utilizing a particular PC design. By etching a triangular array of holes into the top InGaP cladding layer of an InGaAs quantum well LED structure, the 980nm emission is resonantly extracted in the direction normal to the surface of the LED. Photoluminescence measurements indicate that a greater than 100-fold enhancement is obtained at the wavelengths corresponding to the resonant or leaky modes available for radiation; the data agree very well with three-dimensional simulations of the actual structure. Alternatively, by creating a PC with a greater volume ratio of air-to-dielectric, enhanced optical pumping can be achieved by improved coupling of the pump light into the high dielectric slab. As a second example,a 2D arrangement of dielectric rods offer opportunities for waveguiding and the creation of nanocavities. Unique differences exist in the case of guiding light within a 2D PC constructed of rods since the propagation of light now occurs in the lower effective dielectric constant material. Novel opportunities, as well as fabrication-related difficulties, will be discussed for photonic devices enhanced with PC technology.

9:00am **PH-ThM3 "Colloidal Self-Assembly, Multi-Beam Interference Lithography, and Photonic Crystals"**, ***P. Wiltzius***, University of Illinois at Urbana-Champaign **INVITED**

Photonic crystals are materials that allow us to manipulate light in new and unexpected ways. Semiconducting materials played a tremendous role in microelectronics and we expect photonic crystals to revolutionize the world of microphotonics in a similar way. Colloidal self-assembly and multi-beam interference lithography are great tools to build crystals with interesting optical properties. I will review some recent progress towards constructing photonic band-gap materials and switchable 3D Bragg gratings.

9:40am **PH-ThM5 The Fabrication and Properties of Silicon-based Three-dimensional Photonic Lattices**, ***J.G. Fleming***, *S.-Y. Lin*, Sandia National Laboratories **INVITED**

Three-dimensional photonic lattices are structurally complex elements with submicron minimum feature sizes when active in the infrared. While photonic lattices were proposed over 15 year ago and were demonstrated in the millimeter regime relatively quickly, progress towards infrared and lower wavelength structures has been slow due to fabrication challenges. However, such structures can now be readily fabricated using modifications of standard silicon processing techniques. The minimum feature sizes required to manipulate 1.5 micron radiation, 0.2 microns, are now well within the capabilities of current lithographic tools and planarity can be maintained using chemical mechanical polishing (CMP). This approach has numerous advantages, the required infrastructure is in place and is very well supported, there is a high level of control over individual feature sizes and positions and the final structures possess full three dimensional bandgaps. The ability to carefully control the position and size of structures is of critical importance to the creation of waveguides and cavities. The disadvantage of the approach is that, while the infrastructure is well established, the initial capital investment required is substantial. However, if a suitable "killer application" can be found it would be possible to quickly apply this infrastructure to the fabrication of such devices. In this presentation we will outline the range of structures that have been achieved, examples of process flows, and the properties of the structures obtained.

10:20am **PH-ThM7 Resonant Photoemission of the TiO_2/CuI Interface: Towards New Solid State Photovoltaic Cells**, *W.R. Flavell,* ***A.G. Thomas***, *A.R. Kumarasinghe, A.K. Mallick, D. Tsoutsou, G.C. Smith,* UMIST, UK, *R.L. Stockbauer,* Louisiana State University, *M. Grätzel, R. Hengerer,* Swiss Federal Institute of Technology

Currently, nanocrystalline metal oxide semiconductor films, notably anatase TiO_2, are the subject of intense discussion because of their potential application in a number of charge-separating devices such as dye sensitised liquid state and solid state solar photovoltaics, which are considered to be possible alternatives for Si based solar cells. In a recently proposed solid state device, p-type CuI is deposited onto n-type 'dye-sensitised' TiO_2 in order to form the pn junction central to the operation of the cell.[1,2] In this work, resonant photoemission at the Daresbury SRS is used to investigate the electronic structure of the prototype junction formed by depositing CuI from a getter source onto both rutile and anatase single crystal surfaces. Valence band resonant photoemission spectra at the Cu 3p-3d and Ti 3p-3d edges are monitored for a number of coverages and compared with data recorded for single crystal TiO_2 (rutile and anatase) and polycrystalline CuI. At the Cu 3p threshold, a very strong and prolonged resonance is observed, consistent with earlier observations from the copper halides[3]. Shifts in the resonance energies between the 'junction' and its component layers are interpreted in terms of Cu-3d/Ti-3d hybridisation at the interface.

[1] K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, and P.M. Sirimanne, Semicond Sci Technol, 10, (1995), 1689.

[2] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzert, and M. Grätzel, Nature, 395, (1998), 544

[3] T. Ishii, M. Taniguchi, A. Kakizaki, K. Naito, H. Sugawara, and I. Nagakura, Phys Rev B, 33, (1986), 5664. 1.

10:40am **PH-ThM8 Macroscopic and Microscopic Investigations of Dye Sensitization**, ***B.A. Parkinson***, Colorado State University, *N. Takeda*, Brookhaven National Laboratory, *C.B. France*, Colorado State University

Dye sensitization of large band gap semiconductors has been extensively studied both from a fundamental perspective and due to its practical importance. Electron injection from excited states of dyes into the conduction band of semiconductors is the principal processes of silver halide based photography and is also a key element of possible solar-to-electrical energy conversion devices. Photoelectrochemical methods have been used for many years to study the dye sensitization process but despite this a complete picture of the interfacial structure of the dye on the semiconductor surface is still lacking. We use a combination of scanning probe microscopies (AFM and STM), photocurrent spectroscopy and absorbance spectroscopy to obtain a more complete picture of the dye absorbance, sensitization efficiency and dye morphology on the semiconductor surface. Two semiconductors will be discussed, SnS_2 and TiO_2. SnS_2 has a bandgap of 2.2 eV is a useful model system for studying sensitization since atomically flat, reproducible surfaces can prepared. We have studied the morphology of several squaraine dyes on this material and were able to correlate it with the spectral response and the quantum yield for photocurrent generation. Quantum yield for electron collection per absorbed photon of 100% were observed with monolayer coverage of some dyes. The sensitization of titanium dioxide electrodes was also studied using both a ruthenium based sensitizer and a series of carbocyanine dyes with two pendant carboxylate groups to bind to the oxide surface. Rutile, anatase and brookite crystals were all investigated and the face dependence of the sensitized photocurrents was measured. The face dependence of photocurrent yield and the adsorption and desorption kinetics for a particular dye were explained by the ability of the carboxylate groups to both attach to binding sites on a given TiO_2 face.

Processing at the Nanoscale
Room: C-109 - Session PN+SS-ThM

Patterning and Functionalization
Moderator: W.N. Unertl, University of Maine

8:20am **PN+SS-ThM1 Carbon Nanotube Synthesis and Non-Covalent Surface Chemistry**, ***H. Dai***, Stanford University **INVITED**

This presentation will cover our latest results on, (1) Patterned growth of carbon nanotubes architectures on surfaces. Strategies for assembling nanotubes at their synthesis stage by self-assembly or external forces to orient nanotubes will be shown. (2) (2) Charge transfer interactions between small molecules and polymers with nanotube surfaces and the influence to the physical properties of nanotubes will be discussed. Charge transfer and photochemical effects will be presented. (3) Various non-covalent functionalization schemes for nanotubes will be described. Molecular and metal species can be attached to nanotube sidewalls by pi-stacking, van der Waals and hydrophobic interactions, electroless deposition, metal coordination chemistry. Functionalization by biological molecules will also be presented. The implications of controlled chemical synthesis and functionalization to future nano-electronics for chemical and biological applications will be discussed.

9:00am **PN+SS-ThM3 Thiol Diffusion in Dip Pen Nanolithography**, ***P.E. Sheehan**, S.E. Kooi, L.J. Whitman*, Naval Research Laboratory

Interest in the properties of nanometer scale objects has greatly increased in recent years and with it the desire for tools to create these objects. Dip Pen Nanolithography (DPN) is one promising tool because it is widely accessible, flexible in choice of materials, and capable of creating structures as small as 10 nm. Our research has expanded the range of molecules used in DPN and has calibrated the rate of their deposition and spread. Calibration of the deposition was performed by developing a model of the diffusive spread of thiols from an AFM tip.[1] To our knowledge, this model allowed the first direct determination of a diffusion coefficient for an alkanethiol on gold. The effect of alkane chain length and terminal on the diffusion coefficient was also studied, and we find that the length of the alkane chain significantly affects deposition. For instance, hexadecanethiol (16 carbons) deposits much more rapidly than the slightly longer octadecanethiol (18 carbons), indicating that chain-chain interactions strongly influence the deposition rate. A fundamental insight into the DPN deposition mechanism was also gained during these studies. It had been proposed that the water meniscus that naturally forms between an AFM tip and the scanned surface enables deposition. When we examined the effect of humidity on thiol diffusion, no correlation was found. Moreover, we find that deposition persists even after two days under dry nitrogen. For this reason, we propose that ODT is deposited directly onto the surface and does not require water as a medium.

[1] P. E. Sheehan and L. J. Whitman, Phys. Rev. Lett. 88 (2002) 156104.

9:20am **PN+SS-ThM4 Reversible Layer Phase Transition Controlled by the Scanning Tunneling Microscope Tip**, ***S. Berner**, M. de Wild, L. Ramoino, S. Schintke*, University of Basel, Switzerland, *H. Suzuki*, Kansai Adv. Res. Center, Japan, *A. Baratoff, H.-J. Guentherodt*, University of Basel, Switzerland, *T.A. Jung*, Paul Scherrer Institute, Switzerland

Sub-phthalocyanine (SubPc) on Ag(111) shows a complex phase behaviour of the growing first molecular monolayer. With increasing layer coverage, 2D lattice gas, condensed honeycomb superstructure and hexagonal close packed layers are observed. A previous study of SubPc on Ag(111) dealt with the coexistence of the honeycomb superstructure and the 2D lattige gas and showed the high mobility of individual SubPc molecules at room temperature.[1] The complex phase behaviour is a general consequence of the repulsive nearest neighbour interaction between individual molecules and the diffusion at room temperature. In this work we studied SubPc layers with a coverage in the order of 0.7 monolayers on Ag(111) with room temperature scanning tunneling microscopy (STM). On large terraces the SubPc molecules form a hexagonal close packed (hcp) superstructure. However, experimental sequences on confined terrace areas (vacancy islands with diameters of 30-80 nm introduced by sputter defects) reveal interesting details about the condensation and evaporation of molecular islands on a nanometer scale. In such vacancy islands reversible phase transitions between 2D mobile and 2D condensed (hcp) phases could be controlled by the STM tip. In addition, rotational flipping of the orientation of condensed islands between two different substrate lattice registries occurred. Different microscopic mechanisms are discussed in the context of this newly observed complex behaviour. .

[1] S. Berner, M. Brunner, L. Ramoino, H. Suzuki, H.-J. Guentherodt, and T.A. Jung, Chem. Phys. Lett. 348 (2001) 175.

9:40am **PN+SS-ThM5 Covalent Nanopatterning of Liquid Phase Organic Molecules to Silicon Surfaces using Conductive Atomic Force Microscopy**, *M.W. Such, C.R. Kinser, **M.C. Hersam***, Northwestern University

Electron stimulated desorption (ESD) with ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is a well-established technique for creating reactive patterns of dangling bonds on predominantly hydrogen passivated silicon surfaces. Gas phase surface chemistry occurs selectively with these nanopatterns, allowing for controlled deposition of materials down to the single molecule level. Although this approach is effective in UHV, it has not yet been utilized for the patterning of non-UHV-compatible materials. This paper describes an analogous means of creating reactive nanopatterns on hydrogen passivated Si(111) surfaces using conductive atomic force microscopy (cAFM) in liquid environments. Unlike cAFM patterning in air that induces oxidation on silicon surfaces, this approach suppresses oxidation through encapsulation of the tip-sample junction in an anhydrous organic solvent (e.g., toluene or dimethyl sulfoxide). Following ESD induced with cAFM, olefinic organic molecules suspended in the organic solvent environment spontaneously bind to the dangling bond patterns. To demonstrate this technique, exo-5-norbornene-2-ol has been patterned with 50 nm resolution on Si(111):H. Lateral force microscopy and force-distance spectroscopy confirm the hydrophilic nature of this molecule compared to the hydrophobic Si(111):H surface. Following deposition, these nanopatterned molecules have been subjected to a subsequent nucleophilic acyl substitution reaction with Lauroyl Chloride at 50°C for 24 hours. Consistent with the expected dodecyl ester modification of the adsorbed norbornene molecule, the resulting nanopattern appears hydrophobic in LFM analysis. The stability of these nanopatterns to subsequent chemistry suggests that the adsorbed molecules are covalently bonded to the silicon substrate. Further applications of this lithography for covalently nanopatterning polymers and biological molecules to silicon surfaces will also be discussed.

10:00am **PN+SS-ThM6 High Resolution Chemo-Mechanical Functionalization of Silicon Surfaces by Atomic Force Microscope**, ***R.C. Davis**, B.A. Wacaser, T.L. Niederhauser*, Brigham Young University, *I.A. Mowat*, Charles Evans & Associates, *M.R. Linford*, Brigham Young University

We describe a versatile high-resolution method for chemical functionalization of silicon surfaces. An atomic force microscope (AFM) probe is used to mechanically induce chemical functionalization thereby simultaneously patterning and functionalizing the hydrogen-terminated silicon. A 20 nm radius of curvature probe is used to scribe the hydrogen-terminated silicon. When the Si-H and Si-Si bonds are broken in the presence of unsaturated hydrocarbons a reaction occurs in which the hydrocarbon chain is covalently bonded to the Si surface. Using this technique we have produced patches and patterned lines of alkene molecules on a Si (111) substrate with line widths down to 100 nm. Time of flight secondary ion mass spectroscopy measurements verifying the high-resolution chemical functionalization will be presented.

10:20am **PN+SS-ThM7 Fabrication of Si Nanostructures by Scanning Probe Oxidation and Tetra-Methyl Ammonium Hydroxide Etching**, ***F.S.-S. Chien***, Center for Measurement Standards, Taiwan, *W.-F. Hsieh*, National Chiao-Tung University, Taiwan, *S. Gwo*, National Tsing-Hua University, Taiwan, *A.E. Vladar, J.A. Dagata*, National Institute of Standards and Technology

We demonstrated that the process of scanning probe microscope (SPM) oxidation and anisotropic tetra-methyl ammonium hydroxide (TMAH) etching is a low-cost and reliable method to produce smooth and uniform silicon nanostructures on a variety of silicon substrates. Etched structures with a pitch of 100 nm, positive- and negative-contrast structures, and features height greater than 100 nm have been produced on bare silicon, Si$_3$N$_4$-coated and silicon-on-insulator wafers. Evolution of hexagonal pits on two-dimensional grid structures were shown to depend on the pattern spacing and orientation with respect to Si(110) crystal directions. We successfully combined SPM oxidation with traditional optical lithography in a mixed, multilevel patterning method for realizing micrometer- and nanometer-scale feature sizes, as required for photonic device designs. The combination of SPM oxidation and TMAH etching is a promising approach to rapid prototyping of functional nano-photonic devices.

10:40am **PN+SS-ThM8 Charge Trapping in Oxide-Nitride-Oxide-Silicon Structures Studied by Electrostatic Force Microscopy**, ***S.-D. Tzeng**, Y.-C. You, S. Gwo*, National Tsing-Hua University, Taiwan, ROC

A novel approach of fabricating oxide-nitride-oxide-silicon (ONOS) charge storage structures is demonstrated by using the scanning-probe-induced oxidation process under ambient conditions. During the probe oxidation process, both positive and negative charges are injected and trapped inside the ONOS cell. By means of quantitative electrical force microscopy (EFM) measurements, we have investigated the trapping behavior of the probe-oxidation-induced charges. We found that the retention time of the negative charge is much shorter than the positive one. By measuring the decay lifetimes of these trapped charges after annealing at different temperatures, we have determined the trapping energies of both types of charges. We also found that, after high-temperature annealing, these trapped charges can be detrapped. The resulting ONOS cell can be used as a nonvolatile memory element with write/erase capability locally controlled by a biased scanning probe tip.

11:20am **PN+SS-ThM10 Ferroelectric Lithography for Multicomponent Nanofabrication**, ***D.A. Bonnell**, S.V. Kalinin, R.A. Alvarez, X. Lei, R. Shao, Z. Hu, J.H. Ferris,* University of Pennsylvania

In spite of the variety of approaches to the assembly of nanowires, nanoparticles, and organic/biological molecules, device functionality has been achieved in only a few select systems. The organization of dissimilar molecular or nanostructural constituents into predefined structures necessary to yield functionality remains a challenge. We report here a novel approach that controls atomic polarization of ferroelectric substrates to vary local electronic structure. It will be demonstrated that chemical reactivity involving electron transfer is domain specific due to surface band bending. The minimum feature size is on the order of 3 nm and resolution positioning 10-20 nm. When combined with chemistry associated with self assembly, nanostructure composites consisting of oxide substrates, metal nanoparticles, and organic/biological molecules can be fabricated in predefined configurations. This leads to the potential to make electronic or opto-electronic devices on the 10 nm size scale. The approach will be demonstrated with simple devices.

11:40am **PN+SS-ThM11 Size-Induced Ferroelectric Phase Transitions in PbTiO$_3$ and PbZrO$_3$ Nanotubes Formed by Sol-Gel Template Synthesis**, ***B.A. Hernandez**, K.-S. Chang, E.R. Fisher, P.K. Dorhout*, Colorado State University

Nanotubes of the perovskite ABO3 (A = Pb , B = Ti,Zr) have been prepared by sol-gel template synthesis. A size-induced ferroelectric phase transition for PbTiO3 and PbZrO3 nanotubes was observed by thermal analysis. The nanotubes were prepared within Whatman Anodisc templates (200 nm pore size) with a sol-gel method using titanium and zirconium alkoxides and lead acetate. Scanning electron microscopy demonstrated that the structures formed within the template were 50 Î¼m long tubes with 200 nm outer diameters. Transmission electron microscopy and electron diffraction revealed that the tubes were polycrystalline. Comparison of the d-spacing between electron and bulk powder X-ray diffraction patterns allowed assignment of the crystalline phase of the nanotubes as tetragonal for PbTiO3. Differential scanning calorimetery was used to monitor the ferroelectric phase transition temperature (Tc). Comparison between the bulk powders and nanotubes showed an anomalous decrease Tc. Values for PbTiO3 Tc were determined to be between 496.5°- 489.7°C for bulk powders with grain sizes of 75 and 35 nm respectively and 234.4°C for the nanotubes having a grain size of 11.2 nm. Preliminary results for PbZrO3 shows that the Tc decreases from 229.9 for bulk powder to 123.6 for nantRoom temperature Raman spectra also indicated structural size effects by monitoring the energies of the E1(TO) soft mode and relative intensities of the E2(TO) mode.

Plasma Science
Room: C-103 - Session PS+TF-ThM

Plasma Enhanced Deposition
Moderator: T.M. Klein, University of Alabama

8:20am **PS+TF-ThM1 The Correlations between Gas Phase Chemistry, Material Properties, and Device Characteristics of PECVD ZrO$_2$ Thin Films**, ***B. Cho**, J.P. Chang*, University of California, Los Angeles

We investigated ZrO$_2$ as a replacement dielectric film of SiO2 for dynamic random access memory (DRAM) capacitor. We used ECR-PECVD process to deposit ZrO$_2$ films on p-Si (100) wafers with zirconium tetra-tert-butoxide (ZTB; Zr(OC$_4$H$_9$)$_4$) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O$_2$ as an oxidant. Optical emission spectroscopy (OES), Langmuir probe, and quadrupole mass spectrometry (QMS) were used to characterize the plasma. Using QMS, we identified all oxidation states of Zr and found the compositional abundance shifted from Zr metal and monoxide to Zr dioxide and trioxide with the increase in O$_2$ /Ar flow rate ratio (O$_2$ /Ar). Based on the results, we proposed the oxidation and the decomposition reaction mechanisms of ZTB precursors. The as-deposited films obtained without any heating had monoclinic and tetragonal polycrystalline phases based on the grazing incidence x-ray diffraction analysis. High resolution transmission electron microscopy showed that the polycrystalline phase of ZrO$_2$ was interspersed with amorphous phase and that interfacial layer was formed between the ZrO$_2$ and the substrate Si. Static secondary ion mass spectrometry showed that Zr concentration was uniform across the bulk ZrO$_2$ film from both oxygen-rich and oxygen-deficient conditions but Si/Zr ratio was much higher in the interfacial layer obtained in the oxygen-rich condition. This suggested that the oxygen-rich condition resulted in more SiO$_2$-like interfacial layer. X-ray photoelectron spectroscopy (XPS) showed that stoichiometric ZrO2 film was obtained while an interfacial layer containing Si-O bond was formed even without any O$_2$ addition to the plasma.

8:40am **PS+TF-ThM2 Low-Temperature Plasma Migration Enhanced Epitaxy of CuInSe$_2$ on GaAs**, ***B.J. Stanbery**, S. Kincal, S. Kim, T.J. Anderson, O.D. Crisalle*, University of Florida

A comparison of migration-enhanced epitaxial growth[1] of CuInSe$_2$ on GaAs at 350°C with either a thermal cracker or ECR helicon plasma selenium source demonstrates both improved crystallinity and enhanced selenium incorporation using the plasma cracker. Mass spectrometric characterization of the flux from the effusion source coupled to a magnetic-mirror confined 2.45GHz plasma cracker shows 50% enhancement of the Se monomer to dimer flux ratio compared to the thermal double-oven with its cracking zone operating at 1200K, and no measurable ion flux outside the plasma source. Samples grown using the ECR plasma cracker were characterized by a number of differences from all other growth experiments that used the thermal source. The improvement of CuInSe$_2$ epilayer crystallinity is confirmed by the XRD data irrespective of the atomic [Cu]/[In] ratio of the resultant films, which exhibit an order of magnitude reduction in incoherent scattering compared to samples grown with the thermal source, particularly at low angles. Films grown with the plasma source that contain excess copper yield compositions that lie well into the selenium-rich domain of the equilibrium ternary phase field, with little indication of diffraction corresponding to the Cu$_2$Se binary compound which coexists in equilibrium with CuInSe$_2$ when the overall composition is copper-rich. In contrast, such a peak is always seen in significantly copper-rich layers grown with the thermal source. The higher level of selenium incorporation resulting from MEE growth with the plasma source is discussed in the context of a recent theoretical lattice defect model for CuInSe$_2$ that predicts a significant reduction in the electrical compensation ratio of indium-rich CuInSe$_2$ incorporating a stoichiometric excess of selenium.[2]

[1] Y. Horikoshi, et al., Jap. J. Appl. Phys. 25, L868 (1986).

[2] B.J. Stanbery, Ph.D. Dissertation, U. Fl.(2001).

9:00am **PS+TF-ThM3 2-Dimensional Plasma Simulation of Reactive Physical Vapor Deposition of Metal Nitride**, ***D. Zhang**, S. Samavedam, J. Schaeffer, R. Martin, P.L.G. Ventzek, P. Tobin*, Motorola Inc.

Reactive physical vapor deposition (RPVD) of metal nitride has been used for interconnect barrier and metal gate deposition due to its relative simplicity in process implementation and lower contamination compared to other deposition techniques requiring chemical precursors. As the electrical properties (e.g. work function, resistivity) of deposited film are sensitive to film characteristics (e.g. composition), optimal process control based on in-depth mechanistic understanding is critical for reactive PVD to meet product requirements. This has motivated our development of a 2-dimensional plasma model for RPVD of metal nitride films. The RPVD model is based on the 2-dimensional Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois.[1] Plasma is approximated as a fluid in HPEM. A target surface nitridation model (TSNM) has been developed to be self-consistently coupled with HPEM. The TSNM uses a site balance algorithm to address neutral adsorption, desorption by ion sputtering, and surface coverages. An effective sputtering yield for the target is used to account for the effect of target nitridation. The model has been applied to study reactive TiN and Ti$_x$Al$_y$N deposition using a parallel-plate PVD tool. It is found that athermal neutrals are the dominant source for deposition. Target nitridation impacts deposition rate by reducing sputtering yield. For Ar and N$_2$ source gases with a constant total flow, the model derived the dependency of deposition rate with N$_2$ flow that is in good agreement with experiments. Impact of various process parameters (gas mixture, power, pressure) on deposition characteristics will also be discussed in this work.

[1] P. Subramonium and M. J. Kushner, J. Vac. Sci. Technol. A 20, 325 (2002).

9:20am **PS+TF-ThM4 Expanding Thermal Plasma for SiO$_2$ Films: A Chemistry-controlled Process and an Insight into the Deposition Mechanism**, ***M. Creatore**, M. Kilic, K. O'Brien, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO$_2$ PECVD by means of organosilicon/O$_2$ mixtures has shown its versatility in many fields, as e.g. IC/MEMS, photonics, optics, mechanics, food packaging. However, some issues concerning the deposition process remain unresolved. For example, the deposition precursors have not been unambiguously identified, hampering a direct correlation between plasma species densities and film composition. The remote expanding thermal plasma (ETP) is introduced as a simplified approach to get insight into the hexamethyldisiloxane (HMDSO)/O$_2$ deposition process. HMDSO is injected downstream in the expanding argon plasma (generated in a dc cascaded arc) by means of a ring. Because of the expansion, the electron temperature drops to about 0.3 eV: electron-induced dissociations are negligible and the chemical activity is controlled by the (Ar$^+$, e$^-$) flow from the arc. The ETP has led to a step-by-step entirely chemistry-controlled process (no ion bombardment) from silicone-like to C-free and dense SiO_2 films, at competitive growth rates (8 nm/s). A multidiagnostics approach has been applied to study the fragmentation and reactions of HMDSO. Cavity Ring Down Spectroscopy (CRD) has been used for OH, CH and CH_3 radicals detection in HMDSO/O_2 plasmas. Together with Mass Spectrometry, CRD has shown that the Si-C bond in the HMDSO molecule appears to break only at very high Ar^+ flux (high arc Ar flow rate and current). Milder conditions favour the Si-O and C-H bond scissions. Films are characterized by means of IR absorption spectroscopy, in situ single wavelength ellipsometry and ex situ spectroscopic ellipsometry. In the presentation the relation between the film properties and the plasma characterization will be addressed.

9:40am **PS+TF-ThM5 Plasma Production of Silicon Clusters and Nanocrystalline Silicon Particles : A New Route for Nanostructured Silicon Thin Films**, ***P. Roca i Cabarrocas***, Ecole Polytechnique, France **INVITED**

The study of silane plasma deposition is important due to the large number of large area devices based on amorphous silicon. When transferring research results to production, deposition rate, uniformity, and powder formation are key issues. In this respect, the study of square-wave modulated discharges revealed that silicon nanocrystals (powder precursors) can be produced even at room temperature. This result has motivated for the work on plasma conditions near the onset of powder formation, to produce better-structured silicon thin films in which silicon clusters, and crystallites formed in the plasma contribute to deposition. Among the nanostructured materials we produced thus far, most work has focused on polymorphous silicon films because they share the high optical absorption of a-Si:H while having improved transport properties. In this presentation we review our recent work on the production, the characterization, and the study of devices based on this new material. The challenging issue of nanoparticle detection in the plasma is addressed with new techniques such as cavity ring down and impedance measurements. Moreover, in situ ellipsometry was used to study the growth and to determine the thermal gradient for which nanoparticles can reach the substrate. In conclusion, the precise control of the size and concentration of nanocrystalline silicon particles in the plasma opens the way to the nanoelectronics field in which the plasma-produced nanocrystallites can be passivated, coated, and incorporated into devices such as non-volatile memories. This is in our opinion an important challenge for the plasma community in the next few years.

10:20am **PS+TF-ThM7 Correlation between Cluster Amount and Qualities of a-Si:H Films for SiH_4 Plasma CVD**, ***K. Koga***, *K. Imabeppu, M. Kai, A. Harikai, M. Shiratani, Y. Watanabe*, Kyushu University, Japan

Recently, clusters below a few nanometers in size formed in SiH_4 high frequency discharges have been pointed out to be a possible cause of light-induced degradation of hydrogenated amorphous silicon (a-Si:H) films. Hence, suppression of cluster growth is an important issue for depositing high quality a-Si:H films at a high rate. To realize such suppression, we have developed a cluster-suppressed plasma CVD method utilizing gas flow and gas temperature gradient.[1] The following results have been obtained in our experiments. 1) Even under so-called device quality conditions, a large amount of clusters (> 10^4 cps) exist in the conventional plasma CVD reactor. 2) Microstructure parameter Rα of a- Si:H films decreases with decreasing the cluster amount. The developed cluster-suppressed plasma CVD reactor can decrease both Rα and cluster amount below detection limits of our measurement systems (Rα< 0.003 and cluster amount < 0.001 cps, respectively). These results suggest that a-Si:H films of high qualities can be prepared at a high deposition rate by suppressing the cluster growth. 3) A ratio of cluster amount to deposition rate for a discharge frequency of 60 MHz is 1/20 of that for 13.56 MHz, indicating that the VHF discharge is effective in suppressing cluster growth. 4) Preliminary evaluation of fill factor (FF) of a n^+Si/a-Si:H/Ni Schottky solar cell using a-Si:H films of Rα= 0.057 shows the high initial value FF_i= 0.57 and high stabilized value after-light soaking FF_a= 0.53, compared to FF_i= 0.51 and FF_a= 0.47 of cell using conventional device quality a-Si:H films of Rα~ 0.1.

[1] K. Koga, M. Kai, M. Shiratani, Y. Watanabe and N. Shikatani, Jpn. J. Appl. Phys., 41, L168 (2002).

10:40am **PS+TF-ThM8 Plasma and In Situ Film Diagnostic Study of Amorphous and Microcrystalline Silicon Deposition**, ***W.M.M. Kessels***, *J.P.M. Hoefnagels, Y. Barrell, P.J. Van den Oever, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

Our comprehensive investigation of the film growth process of amorphous silicon (a-Si:H) from a remote H_2/SiH_4 plasma has recently also been extended to microcrystalline silicon (μc-Si:H). This material is of particular interest for applications in thin film solar cells and thin film transistors because of its higher stability. In this contribution we will compare the absolute densities of the different silane radicals, as determined from cavity ringdown spectroscopy, for the two plasma regimes yielding the two different materials. Moreover, the surface reaction probability of the silane radicals will be presented as obtained under real deposition conditions (e.g., as a function of substrate temperature) by time-resolved cavity ringdown experiments. >From this information, it is, for example, revealed that Si, SiH, and SiH_3 radicals have approximately an equal contribution to μc-Si:H growth, unlike a-Si:H film growth which is almost completely governed by SiH_3. Furthermore, we will present 'film depth-information' with respect to hydrogen bonding, hydrogen concentration, and other structural film properties as has been obtained by in situ monitoring of film growth by attenuated total reflection infrared spectroscopy and spectroscopic ellipsometry. This powerful combination of diagnostics applied to the well-characterized plasma conditions has revealed a rather homogeneous hydrogen distribution throughout the film (also for μc-Si:H) apart from an initial incubation phase corresponding to interface/surface layer formation. The interface thickness and surface roughness increase with increasing deposition rate but decrease with increasing substrate temperature. New insights into the film growth process of both materials will be discussed.

11:00am **PS+TF-ThM9 Mechanism of Hydrogen-Induced Crystallization of Amorphous Silicon Thin Films**, ***S. Sriraman***, *E.S. Aydil, D. Maroudas*, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) films are used in solar cells, displays, and imaging devices. The a-Si:H films undergo chemically-induced structural transformation from a state of disorder to order (crystallinity) when exposed to H atoms from an H_2 plasma at temperatures lower than those required for thermal annealing; exposure to an H_2 plasma is used as a post-deposition treatment step for plasma-deposited a-Si:H films. In addition, nc-Si:H films can be grown during plasma deposition by heavily diluting the SiH_4 feed gas with H_2. Though several hypotheses have been proposed, the mechanism behind the H-induced disorder to order transition still remains unclear. The atomic-scale processes behind this structural transition are analyzed through molecular-dynamics (MD) simulations of repeated H atom impingement on a-Si:H films. These films were grown through MD by repeatedly impinging SiH_3 radicals on an initially H-terminated Si(001)-(2x1) surface. The evolution of the Si-Si radial distribution function during H exposure of the film showed gradual appearance of peaks corresponding to the coordination shells of crystalline Si, indicating a transition from disorder to order. Detailed structural analysis after H exposure revealed the presence of a nanocrystalline region embedded within the amorphous Si matrix. The structural transformation is mediated by H atoms that diffuse in to the a-Si:H film and insert into strained Si-Si bonds to form intermediate bond-centered H (Si-H-Si) configurations. This results in local structural relaxation of these strained Si-Si bonds. The energetics of H insertion into strained Si-Si bonds and its implications in the structural relaxation of the amorphous phase are discussed. The existence of bond-centered H(D) in a-Si:H films exposed to H(D) atoms from a $H_2(D_2)$ plasma also was verified experimentally through in situ infrared spectroscopy.

11:20am **PS+TF-ThM10 On the Roughness Evolution during Remote PECVD of Amorphous Silicon**, *M.C.M. Van de Sanden*, ***A.H.M. Smets***, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

The roughness evolution during the growth of hydrogenated amorphous silicon is studied in situ by means of single wavelength ellipsometry. The roughness measurements are corroborated by ex situ spectroscopic ellipsometry and Atomic Force Microscopy on films having thickness in the range from 30 up to 3000 nm. The films were deposited by means of the expanding thermal plasma, a remote plasma technique. Silane is injected downstream in an Ar/H_2 plasma. From detailed measurements in the gas phase it is established that the dominant radical contributing to the film growth is the silyl radical with minor contributions from other radicals such as Si, SiH and H. The self-bias is small which characterizes the a-Si:H growth from this dominantly SiH_3 source as purely chemical in origin. The roughness evolution is analysed by means of the scaling properties of the surface as first proposed by Family and Vicsek.[1] It is found that the surface width scales with film thickness d as $d^{ß}$. β, the dynamic scaling exponent, is determined as function of substrate temperature and growth rate. A cross-over from random deposition (β = 1/2) at low substrate temperatures, to a deposition process in which surface diffusion dominates the roughness evolution is observed. The scaling universality class of the roughness development of the growth of a-Si:H shows great similarity with, e.g., Molecular Beam Epitaxy of crystalline silicon. The activation energy from beta vs. substrate temperature is determined from comparing the data with a solid-on-solid model and is about 1 eV. This value is much higher than expected on basis of the conventional growth models for a-Si:H, in which the weakly adsorbed SiH_3 radical is assumed to rule the roughness evolution. The implications for the growth model of a-Si:H will be discussed.

[1] F. Family and T. Vicsek, J. Phys. A 18 L75 (1985).

11:40am **PS+TF-ThM11 Detailed Study of Chemistry of Ar/C_2H_2 Plasma and Consequences For the a-C:H Film Growth**, *J. Benedikt, R.V. Woen,* ***M.C.M. Van de Sanden***, Eindhoven University of Technology, The Netherlands

The role of hydrocarbon radicals during the deposition of a-C:H films is studied in an Ar/C_2H_2 remote expanding thermal plasma (ETP) reactor. C, C_2 and CH radicals are detected by means of cavity ring down spectroscopy (CRDS) at different plasma conditions and at different positions downstream from the thermal plasma source. A broadband absorption (BBA) is observed in the 250 - 520 nm region. Acetylene and diacetylene (C_4H_2) are monitored with a residual gas analyser. A simple plasma chemistry model is developed to explain measured data. The plasma chemistry is governed by argon ion induced dissociation of acetylene molecules. Main product of this reaction is the ethynyl (C_2H) radical, which can further react either with argon ions or with acetylene, depending on the ratio between the flux of argon ions and the flux of acetylene into the reactor. The BBA is due at least two species: most likely candidates are C_2H radical and C_4H_2 molecule. In-situ real-time ellipsometry was used to determine growth rate and refractive index of the films grown. Our preliminary conclusion is that C_2H radical is a growth precursor for high quality hard diamond-like a-C:H films; a-C:H films with slightly lower hardness but faster growth rate were also deposited using a C_4H_2 rich plasma. The loss probabilities of the ethynyl radical and diacetylene molecule are determined from time dependent CRDS. The probabilities can be used to monitor the relative importance of the ethynyl radical vs. diacetylene in the growth of a-C:H.

Surface Science
Room: C-112 - Session SS+EL+OF-ThM

Reactions and Patterning of Organics on Silicon
Moderator: S.F. Bent, Stanford University

8:20am **SS+EL+OF-ThM1 Fixation of Alkyl Groups on Si(111) Surface through C-Si Single Covalent Bond formed by Reaction of Grignard Reagent and H:Si(111)**, ***T. Yamada****, T. Inoue, K. Yamada, N. Takano, T. Osaka*, Waseda University, Japan, *H. Harada, K. Nishiyama, I. Taniguchi*, Kumamoto University, Japan

Alkyl adsorbates that are directly bonded to the outermost atoms of silicon wafer surfaces have prospective properties for application in nanometer-scale fabrication and surface functionalization.[1] Several methods have been proposed to deposit alkyl groups on hydrogen-terminated H:Si(111).[2] The conversion of the H-Si bonds in H:Si(111) into C-Si bonds caused by chemical processes is an important issue in preparing the organic adlayers. In this work, high-resolution electron energy loss spectroscopy (HREELS) was utilized to prove the formation of single covalent bonds between Si(111) surface atoms and alkyl groups by the chemical reaction of a Grignard reagent and hydrogen-terminated H:Si(111)(1x1).[2] The reaction was performed by heating a piece of H:Si(111) in 1M tetrahydrofuran (at 65°C) or diethylether solution (at 30°C) of desired alkylmagnesium halide for 18 hours under Ar atmosphere. By this reaction condition, somewhat 20% of the product surface were still covered with residual hydrogen. The bending vibration mode of the residual hydrogen (630 cm^{-1}) obscured the alkyl signals in the range of 600 - 700 cm^{-1}. By using deuterium-terminated D:Si(111), the vibration at 680 cm^{-1}, assigned to the C-Si bond, was isolated within the spectrum of CH_3-. The CH_3 groups were thermally stable at temperatures below 600 K. Similar features were observed for C_2H_5-, phenyl- and so on. The C-Si bonds are essential for enhancing the stability and lowering the mobility of alkyl moieties. Such properties of alkyl moieties of will lead to a new prospective science and technology in nanometer-scale fabrication.

[1] T. Yamada, N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, and T. Osaka, Jpn. J. Appl. Phys. 40 (2001) 4845.

[2] R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner, Langmuir 15 (1999) 3831.

8:40am **SS+EL+OF-ThM2 Chemomechanical Production of Sub-Micron Edge Width, Functionalized, ~20 Micron Features on Silicon**, ***M.R. Linford****, Y.-Y. Lua, T.L. Niederhauser, B.A. Wacaser,* Brigham Young University, *I.A. Mowat,* Charles Evans & Associates, *A.T. Woolley, R.C. Davis,* Brigham Young University, *H.A. Fishman*, Stanford University Medical School

We have recently reported that monolayers on silicon can be formed, and silicon substrates concomitantly patterned, when native oxide-terminated silicon is scribed with a diamond-tipped instrument in the presence of 1-alkenes,[1,2] 1-alkynes,[1,2] alkyl halides (chlorides, bromides, and iodides),[2,3] and alcohols.[3,4] Monolayers were prepared in the open laboratory with reagents that had not been degassed.[1-4] However, while this method is particularly facile, the features produced using a diamond scribe are coarse and irregular.[1] The high degree of edge and surface roughness in these features will no doubt limit the utility of our earlier work in some circumstances. Here we describe a substantial improvement in our earlier method by showing the production of sharp, well-defined, functionalized features on silicon that are invisible to the naked eye and very shallow. In contrast to the earlier procedure that used oxide-terminated silicon and a diamond-tipped scribe,[1-4] this new method consists of 1) cleaning and drying a silicon shard, 2) immersing the silicon in a fluoride ion etch to remove its native oxide and produce hydrogen-terminated silicon, 3) wetting the dry, H-terminated silicon surface with a reactive liquid, and 4) scribing the surface with a small tungsten carbide ball. Both Si(100) and Si(111) were successfully patterned and functionalized with this new method.

[1] Niederhauser, T. L.; Jiang, G.; Lua, Y.-Y.; Dorff, M. J.; Woolley, A. T.; Asplund, M. C.; Berges, D. A.; Linford, M. R. Langmuir 2001, 19, 5889-5900.

[2] Lua, Y.-Y.; Niederhauser, T. L.; Matheson, R.; Bristol, C.; Mowat, I. A.; Asplund, M. C.; Linford, M. R. In Press Langmuir 2002.

[3] Niederhauser, T. L.; Lua, Y.-Y.; Sun, Y.; Jiang, G.; Strossman, G. S.; Pianetta, P.; Linford, M. R. Chem.Mater. 2002, 14, 27-29.

[4] Niederhauser, T. L.; Lua, Y.-Y.; Jiang, G.; Davis, S. D.; Matheson, R.; Hess, D. A.; Mowat, I. A.; Linford, M. R. In press Angewandte Chemie 2002.

9:00am **SS+EL+OF-ThM3 Formation of Nanoscale Organic and Inorganic Features on Semiconductor Surfaces**, ***J.M. Buriak***, Purdue University **INVITED**

Integration of molecular devices and nanoscale materials with semiconductors, including silicon and germanium, is an area of intense interest, due to the potential for interfacing nanomaterials with the macroworld. We have developed a number of wet chemical routes which allow for covalent attachment of both organic functionalities, including molecular wires, and inorganic nanoparticles. For instance, a cathodic electrografting reaction between alkynes and hydride-terminated silicon surfaces results in alkynyl moieties bound directly through Si-C bonds, with no intervening oxide layer. The surfaces are air and water stable, and can withstand boiling pH 12 solutions. In order to pattern these alkynyl groups on the silicon surface in nanoscale regions, conducting probe lithography has been utilized to write the organic monolayers, with feature sizes as small as 30 nm. For inorganic structure patterning, electroless deposition has been combined with microcontact printing, dip pen nanolithography (DPN), and UV-mediated hydrometallation to produce nano- and micron-scale features. These approaches and others will be described.

9:40am **SS+EL+OF-ThM5 Structures, Dynamics, and Chemical Reactivity of Si (001) at Finite Temperatures: A First Principles Study**, *D. Pillay, Y. Wang,* ***G.S. Hwang***, The University of Texas at Austin

Imparting organic functions onto a well-defined functionality of semiconductor surfaces with atomic-scale precision provides an enormous opportunity to develop new molecular devices including chemical and biological sensors and molecular electronic devices. For semiconductor systems, the rates and pathways of chemical reactions are strongly influenced by local electronic structures determined by surface reconstructions and defects. Due to such complex structural effects, chemical dynamics on semiconductor surfaces has not been fully understood. To gain molecular-level control, therefore, first we must develop a detailed understanding of structures, dynamics, and chemical reactivity of clean, defective, or modified (with various adsorbates) surfaces at finite temperatures, along with the structures and bonding of organic compounds onto the surfaces. In this talk we will present first principles quantum mechanics [Density Functional Theory with plane-wave basis sets and pseudopotentials] simulations for structures, dynamics, and chemical reactivity (towards organic species) of (001)-faced Si and Ge surfaces at finite temperatures. This includes the dynamics of buckled dimers on clean and defective surfaces and their effects on adsorption dynamics of various organic molecules.

10:00am **SS+EL+OF-ThM6 Superexchange Interactions in STM-Organic-Semiconductor Systems**, ***L.C. Teague****, J.J. Boland*, University of North Carolina at Chapel Hill

The incorporation of organic layers and individual molecules into existing semiconductor technologies requires a thorough understanding of surface/molecule reactions. Although numerous studies have focused on the reaction of individual molecules with the Si(100) surface, the specific reaction mechanisms remain poorly understood. The similarity of the Si(100)-2 x 1 surface chemistry with that of C=C systems opens up the possibility of a wide range of organic chemistry reactions. Here, a combination of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) calculations are used to study and interpret the reaction of 1,3-cyclohexadiene (1,3-CHD) with the bare Si(100)-2 x 1 surface. Because STM probes the local density of states (LDOS), the local bonding geometry of 1,3-CHD can be inferred from the location of the π bond in the adsorbed molecule. Other groups have reported similar observations.[1,2] However, DFT calculations indicate the π^* orbital is located several eV above the Fermi Energy and should be energetically inaccessible under typical bias conditions. Here, we show that these images can be understood by considering the interaction between the STM tip and the molecule-surface system. The superexchange mixing of the tip dangling bond state with the filled π state on the molecule produces a new state within the tunneling window. This state is responsible for the observed image contrast and suggests superexchange effects of this type may be important in understanding the charge transfer that occurs through these molecular systems.

[1] Hamaguchi, K.; Machida, S.; Nagao, M.; Yasui, F.; Mukai, K.; Yamashita, Y.; Yoshinobu, J.; Kato, H. S.; Okuyama, H.; Kawai, M.; Sato, T.; Iwatsuki, M. J. Phys. Chem. B 2001, 105, 3718.

[2] Hovis, J. S.; Liu, H.; Hamers, R. J. J. Phys. Chem. B, 1998, 102, 6873.

10:20am **SS+EL+OF-ThM7 Modifying the Semiconductor Interface with Organonitriles**, ***M.A. Filler***, *C. Mui, C.B. Musgrave, S.F. Bent*, Stanford University

Organic functionalization of group-IV semiconductor surfaces has recently garnered considerable attention and applications in the areas of molecular electronics, biological recognition, and reagentless micropatterning have been proposed. If these and other concepts are to become technologically feasible, however, the creation of an ordered and selectively grown layer as well as the ability to successively attach additional organic monolayers will be necessary. Organonitrile compounds were studied as potential candidates for first and subsequent layer surface reactions on Si(100)-2x1 and Ge(100)-2x1. Bonding is investigated experimentally with infrared spectroscopy and theoretically with density functional theory. We find that acetonitrile does not react on the Ge(100)-2x1 surface at room temperature and explain this result with kinetic and thermodynamic arguments. A [4+2] cycloaddition product through the conjugated π system and a [2+2] C=C cycloaddition product through the alkene are found to be the dominant surface adducts for the multifunctional molecule 2-propenenitrile. While the non-conjugated molecules 3-butenenitrile and 4-pentenenitrile are not expected to form a [4+2] cycloaddition product, both show vibrational modes characteristic of this adduct and we propose the possibility of a surface catalyzed reaction. Pathways directly involving only the nitrile functional group are thermodynamically unfavorable at room temperature on Ge(100)-2x1 and the conversion of the remaining nitrile functionality as well as its use in additional surface reactions will also be presented.

10:40am **SS+EL+OF-ThM8 Adsorption and Reaction of Allyl- and Ethyl-amine on Germanium and Silicon Surfaces**, *P. Prayongpan*, ***C.M. Greenlief***, University of Missouri-Columbia

The adsorption and reaction of allyl- and ethyl-amine with the Ge(100) and Si(100) surfaces is examined. These processes are followed by a variety of surface sensitive techniques including ultraviolet photoelectron spectroscopy and temperature programmed desorption. Possible adsorption structures are also examined by theoretical methods. Density functional theory calculations are used to help interpret the photoelectron spectroscopy data. The calculated molecular orbital energies (within Koopmans' approximation) are used to help identify adsorbed molecular species, as well as, reaction intermediates. The interaction of these nitrogen-containing molecules with surface dimmer bonds and ordering of the resulting surface layers will be discussed.

11:00am **SS+EL+OF-ThM9 Adsorption Chemistry of Cyanogen Bromide and Iodide on Silicon (100)**, ***N.F. Materer***, *P. Rajasekar, E.B. Kadossov*, Oklahoma State University

The adsorption of cyanogen iodide (ICN) and bromide (BrCN)on a silicon (100) surface is studied by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and thermal desorption spectroscopy (TPD). After submonolayer exposures, XPS indicates that the CN triple bond of both ICN and BrCN emains intact upon adsorption at 100K. The UPS spectrum of these molecules contains two peaks assigned to the pi electrons in the CN triple bond. The splitting of these levels, due to the interaction between the pi electrons on the cyanogen and the halide, show that some portion of the initially adsorbed cyanogens halide also remains intact upon low temperatures adsorption. In contrast, the UPS spectrum of ICN and BrCN adsorbed at room temperature on Si(100) contains only one peak due to the pi electrons in the carbon nitrogen triple bond. The lack of splitting in the room temperature UPS spectrum is a result of XC (X=Br, I) bond dissociation. Thus, the XC bonds breaks while the CN bond remains intact during room temperature adsorption on Si(100). Upon annealing the Si(100) surface to higher temperatures, the UPS spectra indicates that the C-N triple bond remains intact until approximately 700 K. Simultaneous changes in the C 1s photoelectron peak are consistent with the idea that C-N bond cleavage in the cyanogen halides is correlated with silicon carbide fomation.

11:20am **SS+EL+OF-ThM10 Theoretical Adsorption Studies of ICN on the Si(100) Surface**, ***E.B. Kadossov***, *P. Rajasekar, N.F. Materer*, Oklahoma State University

Ab initio quantum calculations have been used to study the adsorption and surface reactions of ICN on the Si(100) surface represented by Si_2H_{12} single-dimer cluster. At low temperatures, experiments show that some faction of the initially exposed ICN is molecularly absorbed to the surface. Calculations of the molecularly absorbed species support the formation of end-on configuration with the N forming a dative bond with the lone pair on the Si(100) surface. Upon annealing, experiments reveal that the remaining molecular adsorbed ICN species dissociate to produce I and CN species on the surface. Calculations show that this process can take place directly or through a stable side-on adsorption intermediate. The transition barrier to form the side-on intermediate species is slightly lower than for the direct reaction (12.82 vs. 17.26 kJ/mol). After dissociation, the CN is bound to the silicon surface through either the C or the N ends. The C bound species possesses the lowest energy and is consistent with experimental XPS results. In addition, these two possible structures are separated by an activation barrier of 107.39 kJ/mol, easily overcome by the excess adsorption energy. An alternate pathway for the ICN side-on species is to isomerize into an INC structure through a 212.26 kJ/mol activation barrier. However, the activation barrier between this new species and the dissociated state is 5.53 kJ/mol. This transition barrier is even lower than the 84.05 kJ/mol barrier between side-on ICN surface species and the dissociated state.

11:40am **SS+EL+OF-ThM11 Infrared Study of Adsorption of C_6H_6 onto Si(100)(2x1)**, *M. Shinohara, H. Watanabe, Y. Kimura, H. Ishii*, ***M. Niwano***, Tohoku University, Japan

The interaction of benzene with the (100) and (111) surfaces of silicon has proven to be an interesting model system for molecular adsorption on semiconductor surfaces. The adsorption of benzene on the Si(100)(2x1) surface has been expensively studied in recent years both experimentally and theoretically. Previous elaborate theoretical calculations predicted that adsorption of benzene onto the Si(100)(2x1) surface leads to two different adsorption structures: One corresponds to benzene adsorbed on top of a dimer row between two adjacent Si dimers. This structure has four C atoms of benzene bonded to four Si atoms from two adjacent dimers. The other corresponds to the benzene molecule that sticks on top of the dimer row and has two of its C atoms bonded to two Si atoms of a single surface dimer. However, there still is a controversy regarding which structure is more favored. In this study, we have investigated the adsorption of benzene C_2H_6 on the Si(100)(2x1) surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) and the so-called hybrid density-functional theory (DFT) to determine the most preferred adsorption structure of benzene on Si(100)(2x1) at room temperature. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. We analyzed IRAS spectra in the C-H stretching vibration region to determine the detailed adsorption structure of benzene. The central result is that benzene adsorbs in different manners depending on the surface coverage of benzene: at low coverage the molecule adsorb on the surface to favor the formation of benzene adsorbed on two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface to generate benzene adsorbed on a single dimer. We also discuss the reason why the adsorption structure depends on surface coverage.

Surface Science
Room: C-110 - Session SS+EL-ThM

Structure of Semiconductor Surfaces & Interfaces
Moderator: C.J. Palmstrom, University of Minnesota

8:20am **SS+EL-ThM1 Strain Control of the Ge(105) Surface via Hydrogen Adsorption**, ***Y. Fujikawa***, *M. Kawashima, T. Nagao, T. Sakurai*, Tohoku University, Japan, *M.G. Lagally*, University of Wisconsin-Madison

Controlling the size and shape of Ge quantum dots formed on the Si(001) substrate is of great technological importance for their potential application in future semiconductor devices. Surfactant effects on this system are regarded as a promising method to achieve the controlled growth of quantum dots. Among them, hydrogen adsorption, which has been studied intensively, is known to suppress the formation of Ge "huts", pyramidal nanocrystals bounded by four Ge{105} facets.[1] We have investigated hydrogen adsorption on a Ge(105) surface formed on a Si(105) substrate using STM to elucidate the role of surface strain on the stability of Ge(105) under hydrogen-adsorption conditions. The STM images of Ge(105) surfaces with adsorbed hydrogen atoms are understood based on the newly-established atomic structure of Ge(105).[2] We observe the stability of hydrogen-covered Ge(105) for different amounts of Ge initially deposited on the Si(105) surface. We find that hydrogen adsorption on Ge(105) surfaces formed from deposited amounts of Ge less than 1.5 ML makes the surface remarkably unstable and results in the formation of local defects. This fact indicates that hydrogen adsorption on Ge(105) increases the surface strain by arresting the strain-relief mechanism that would ordinarily occur on clean Ge(105) with the formation of sp^2-hybridized dimers. Thus, the formation of Ge(105) will be unfavorable and suppressed in the presence of adsorbed hydrogen. This work is supported by NSF.

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[1] Kahng et al., Phys. Rev. Lett. 80, 4931 (1998).

[2] Fujikawa et al., Phys. Rev. Lett. 88, 176101 (2001).

8:40am **SS+EL-ThM2 A LEEM Study of the Ge(001)-(2x1)-(1x1) Phase Transition; Domain Wall Proliferation and Dimer Break-up**, *E. van Vroonhoven, H.J.W. Zandvliet, **B. Poelsema***, University of Twente, The Netherlands

The Ge(001) surface exhibits two phase transitions. At low temperatures it is c(4x2) reconstructed, evolving with increasing temperature into (2x1). The origin of the reconstruction is dimerization of the surface: the number of dangling bonds is reduced from two per surface atom, for a bulk terminated surface, to only one. In the c(4x2) phase the dimers are buckled in an anti-symmetric way; in the (2x1) phase the dimers rapidly switch between the two buckled orientations and appear symmetric. Due to the diamond structure of Ge, the dimer rows on neighboring terraces are rotated by 90°. At high temperature the (2x1) phase disappears and the (1x1) phase emerges. Two conflicting models have been proposed in literature. One model suggests that this phase transition is driven by vacancy pair creation and dimer break-up on the Ge(001) surface. The other claims that the phase transition involves (2x1) domain wall (step) proliferation rather than dimer break-up. Our results demonstrate that domain wall proliferation sets in around 950 K, leading to a complete loss of contrast in LEEM around 1050 K. The dimers, however, remain clearly visible up to about 1130 K. The dimer concentration is a strong function of the substrate temperature between 1030 and 1130 K. Our combined microscopy and diffraction data are only consistent with the first model. It is even possible for the first time to directly extract the free energy gain of dimerization, being 1.6 eV per pair. This value compares perfectly with calculations performed for silicon after scaling with the melting temperature. We estimate the temperature to be accurate with ± 25 K and thus the dimerization energy with ± 5%.

9:00am **SS+EL-ThM3 Encapsulation of SiGe Quantum Wells and Quantum Dots**, ***G.G. Jernigan**, P.E. Thompson*, US Naval Research Laboratory

Semiconductor device characteristics are dependent on the chemical and structural properties of the electrical interface. As such, we are interested in SiGe quantum wells and quantum dots grown in Si. Heterojunctions between Si / SiGe / Si are chemically smeared due to Ge segregation, but little is known about the structural nature of the heterojunctions. We will present an STM study of the encapsulation of a Si$_{0.8}$Ge$_{0.2}$ alloy grown in Si at 500, 650, and 800 °C. Alloy deposition induces a rougher morphology than the inital Si surface. Intermixing of Ge from the alloy with the Si substrate is observed to happen immediately to produce a rough surface. The amount of intermixing increases with increasing growth temperature, and at 800 °C the surface roughness exceeds the thickness of deposited alloy. After intermixing, Ge segregates out from the alloy, and the surface Ge leads to an island growth mechanism, which further increases the surface roughness. At 500, 650, and 800 °C the alloy surfaces obtain a steady-state value for surface roughness, which has been characterized as 2D planar, rippled, and hutted, respectively. Encapsulation of the alloy layer with Si attempts to restore a smooth morphology. At 800 °C where the height of the huts are ~40 nm, a 5 nm Si layer reduced the hut height to ~10 nm, and after 20 nm of Si, the huts are gone. Remnants of the underlying alloy morphology can still be seen on the surface in the form of square pits where material did not fill in between the huts. For lower growth temperatures, less Si is needed to reduce the surface roughness, and square pits are still observed from the underlying alloy. The square pits arise from Ge segregation modifying the S$_A$ and S$_B$ step-edge sticking coefficient of Si to produce equal sized S$_A$ and S$_B$ terraces. A structural model for the heterointerfaces based on the STM observations will be presented.

9:20am **SS+EL-ThM4 First Atomic-Resolution Ultrahigh Vacuum Scanning Tunneling Microscopy Study of GaSe/Si(111) Ultrathin Films**, ***T. Ohta**, A. Klust, J.A. Adams, Q. Yu, M.A. Olmstead, F.S. Ohuchi*, University of Washington

Gallium-selenide thin films deposited on Si(111) are of increasing interest for applications, both in their own right as optoelectronic structures, and as non-reactive, low surface energy, high band gap buffer layers for subsequent nanostructure formation. Gallium selenide crystallizes into two crystal structures, layered GaSe and cubic Ga$_2$Se$_3$ with bandgaps of 2.0 and 2.6eV, respectively. Crystal structure and stoichiometry of the deposited Ga$_x$Se$_y$ can be controlled by the substrate temperature during deposition. We present the first atomic-resolution ultrahigh vacuum scanning probe microscopy study of GaSe/Si(111) ultrathin films. When GaSe thin films are deposited at substrate temperature 520°C, atomically flat surfaces consisting of a single molecular layer of GaSe with altered step structures of 7*7-Si(111) were observed. These surfaces have no dangling bonds to react with residual gases, or to provide nucleation sites for subsequent growth. We also observed occasional point defects causing long-range alterations of the local band bending, but no sharp states revealed by the tunneling spectroscopy. At lower substrate temperatures, Ga$_x$Se$_y$ multilayers with flat surface and triangle features with 3-4nm sides were formed. Height difference of the atomic steps suggests that the multilayers have a cubic structure. These triangles are likely associated with Ga or Se vacancies in the Ga$_2$Se$_3$.

This work was partially supported by the M. J. Murdock Charitable Trust and NSF Grant DMR 0102427.

9:40am **SS+EL-ThM5 Electronic and Structural Properties of Aluminum Selenide Ultrathin Film on Si(111)**, ***J.A. Adams**, A.A. Bostwick, T. Ohta, A. Klust,* University of Washington, *E. Rotenberg,* Advanced Light Source, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

The wide band gaps of aluminum selenide and gallium selenide make them appealing candidates for blue-green opto-electronics, and they are closely lattice matched to silicon making them compatible in silicon-based structures and devices. However, very little is known about the properties of aluminum selenide heteroepitaxial films. Bulk aluminum selenide, a defected wurtzite structure, has a 3.1 eV band gap, and its hexagonal lattice constant is about 1.3% larger than Si(111). Unlike gallium selenide, which is stable in both layered GaSe and defected zincblende Ga$_2$Se$_3$ structures, layered AlSe has not been reported in either bulk or thin film form. We investigated varying thicknesses of ultrathin films of aluminum selenide grown epitaxially on Si(111) including sub-monolayer growth, a single bilayer, and the subsequent initial stages of growth on the bilayer. The AlSe/Si interface forms a bilayer structure similar to GaSe-terminated Si, although the temperatures for bilayer formation and for Se-evaporation from the film are higher for AlSe than for GaSe. The reactivity of the AlSe terminated Si(111) surface with both residual gases and for subsequent film growth is much higher than that of GaSe. Further deposition of aluminum selenide produces films that resemble the bulk stochiometry Al$_2$Se$_3$. Electronic band-structure for AlSe/Si was investigated using angle resolved photoelectron spectroscopy (ARPES). Unlike GaSe/Si, the AlSe bilayer appears to have a true surface state. Si-Al bond lengths and Al-Se bond lengths were measured by energy dependent photoelectron diffraction (EDPD). Initial results indicate that the Al-Si bond is 8% larger that in Al/Si(111)-($\sqrt{3}$x$\sqrt{3}$). Heterostructures of AlSe/GaSe on Si(111) will also be discussed. Funded by NSF Grant DMR-0102427.

10:00am **SS+EL-ThM6 Ga Surface Segregation in ErAs (100)/GaAs (100)**, ***H.K. Jeong**, T. Komesu, C.-S. Yang, P.A. Dowben,* University of Nebraska-Lincoln, *B.D. Schultz, C.J. Palmstrom*, University of Minnesota

Surface segregation has now been characterized by angle resolved x-ray photoemission for NiMnSb, a variety of perovskites, and a number of binary alloys. Using angle-resolved x-ray photoemission spectroscopy (ARXPS), the surface composition of the sample can be roughly established since the effective probing depth is shorter at large emission angles with respect to the surface normal. Epitaxial thin films of the rare earth pnictide ErAs(100) can be grown on GaAs(100), but at elevated temperatures the ErAs film degrades. Ga segregation through the ErAs to the surface has been identified by angle-resolved X-ray photoemission spectroscopy, following extensive annealing. The angle-resolved XPS data indicates that the segregation of Ga is extensive throughout the ErAs thin film and is not restricted just to the surface layer.

10:20am **SS+EL-ThM7 Absolute Orientation-Dependent TiN(001) Step Energies from Two-Dimensional Equilibrium Island Shape and Coarsening Measurements on Epitaxial TiN(001) Layers**, ***S. Kodambaka***, *S.V. Khare, V. Petrova,* University of Illinois, *A. Vailionis,* Stanford University, *I. Petrov, J.E. Greene*, University of Illinois

In situ high-temperature (1030-1185 K) scanning tunneling microscopy was used to determine the equilibrium shapes of two-dimensional TiN vacancy islands on atomically-smooth terraces of epitaxial TiN(001) layers. Inverse Legendre transformations of the equilibrium island shapes yield relative step energies as a function of step orientation within an orientation-independent scale factor λ, the equilibrium chemical potential of the island per unit TiN molecular area. We then use quantitative TiN(001) adatom island coarsening measurements to determine λ and, hence, absolute orientation-dependent step energies β and step stiffnesses b̃eta. For <110> and <100> steps on TiN(001), we obtain: β_{110} = 0.21±0.05 eV/Å, β_{100} = 0.25±0.05 eV/Å, b̃eta$_{110}$ = 0.9±0.2 eV/Å, and b̃eta$_{100}$ = 0.07±0.02 eV/Å. From the b̃eta values, we calculate kink formation energies ε_{110} = 0.40±0.2 eV and ε_{100} = 0.11±0.1 eV based on the unrestricted terrace-step-kink model.

10:40am **SS+EL-ThM8 Scanning Force Microscopy Measurements on Ionic Crystals at Low Temperatures and Comparison to Atomistic Simulations**, ***R. Hoffmann***, *M.A. Lantz,* University of Basel, Switzerland, *L.N. Kantorovich,* University College London, UK, *A. Baratoff, H.J. Hug,* University of Basel, Switzerland, *A.L. Shluger,* University College London, UK, *H.-J. Güntherodt*, University of Basel, Switzerland

Alkali halide surfaces were the first insulating materials to be imaged by scanning force microscopy (SFM) with true atomic resolution. Although atomic resolution images on alkali halides have been obtained by several groups, the tip-sample interaction above specific sites has so far been studied only theoretically.[1] Knowing this interaction force provides insight into atomic resolution image mechanisms and allows to study bonding interactions on a surface on the atomic scale. Recently, site-specific force-distance experiments have been performed for the first time at low temperatures on the Si(111) 7x7 surface.[2] Here we report similar measurements on the KBr (001) and the NaCl (001) surface in which we study the interaction forces and the imaging mechanism. The short-range forces have been calculated using atomistic simulations. The magnitude of the calculated forces agrees well with the experimental data, although for KBr the calculated corrugation is larger than the measured one even when the long-range forces are included. For NaCl also the corrugation is in good agreement to the experiment.

[1] L. N. Kantorovich et al. Surf. Sci. 445, 283 (2000)

[2] M. A. Lantz et al. Science 291, 2580 (2001)

11:00am **SS+EL-ThM9 Core-level Spectroscopy Study of the Clean c(4x2) and the Hydrogenated 2x1-H Phases on the 3C-SiC(001) Surface**, ***L.S.O. Johansson***, *S.M. Widstrand, K.O. Magnusson, M.I. Larsson,* Karlstad University, Sweden, *H.W. Yeom,* Yonsei University, Korea, *S. Hara, S. Yoshida*, AIST, Japan

We report a core-level spectroscopy investigation of the clean Si-terminated 3C-SiC(001)-c(4x2) surface and the hydrogenated 3C-SiC(001)2x1-H surface. The 2x1-H surface was formed by exposing the clean c(4x2) surface to excited hydrogen gas. Desorption of the hydrogen at 900° C led to the restoration of the c(4x2) periodicity. Higher hydrogen exposures led to the formation of diffuse 1x1 and mixed 3x1/2x1 phases, as observed by low-energy electron diffraction (LEED). This behaviour is remarkably similar to hydrogen adsorption on the Si(001)2x1 surface. Si 2p core-level spectra from the clean c(4x2) surface displayed the characteristic surface peak shifted by 1.4 eV to lower binding energy, which in previous studies has been attributed to Si adatoms on top of a Si-terminated surface.[1,2] The formation of the 2x1-H surface lead to dramatic changes in the Si 2p lineshape, where the main surface components now appeared closer to the bulk peak. Detailed decompositions of the spectra are presented and are discussed in relation to the suggested structural models for the c(4x2) surface[3,4] and to previous core-level studies.[1,5].

[1] M.L. Shek, Surf. Sci. 349, 317 (1996).

[2] A. Catellani, G. Galli, and F. Gygi, Appl. Phys. Lett. 72, 1902 (1998).

[3] P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli, and C. Joachim, Phys. Rev. Lett. 78, 907 (1997).

[4] W. Lu, P. KrÃ¼ger, J. Pollmann, Phys. Rev. Lett. 81, 2292 (1998).

[5] V. Yu. Aristov, H. Enriquez, V. Derycke, P. Soukiassian, G. Le Lay, C. Grupp, and A. Taleb-Ibrahimi, Phys. Rev. B 60, 16553 (1999). .

11:20am **SS+EL-ThM10 The Anomalous Effective Surface Debye Temperature of ErAs(100)**, ***T. Komesu***, *H.K. Jeong, P.A. Dowben,* University of Nebraska-Lincoln, *B.D. Schultz, C.J. Palmstrom*, University of Minnesota

We have recently explored the surface electronic structure of ErAs(100), as well as the compositionally stability, but the vibrational modes are a key contribution to both electronic structure and compositional stability. Consistent with a surface electronic structure different from the bulk, here we show that the surface vibrational modes are different from the bulk from our estimates of surface and bulk Debye temperature using LEED (low energy electron diffraction) and XPS (X-ray photoemission spectroscopy). This could contribute to the very large temperatures dependence of transport effects across ErAs interfaces.

11:40am **SS+EL-ThM11 CRN Models of Covalent Amorphous Materials and Their Interfaces**, ***D. Yu***, *G.S. Hwang*, The University of Texas at Austin

Understanding the structural properties of covalent amorphous (semiconductor and dielectric) materials and their interfaces as well as defect-dopant dynamics in the disordered systems is an outstanding problem of great importance for microelectronic and optoelectronic applications. Significant advances in Continuous Random Network (CRN) models have made it possible to generate the amorphous and interface structures that are in good agreement with experiments. This further allows us to address the behaviors of defects and dopants in the disordered structures. In this talk we will present our newly developed CRN models and some recent results on i) the diffusion and clustering dynamics of vacancies and self-interstitials in a-Si and the amorphous-crystalline interface, ii) the structures of a very thin amorphous SiO_2 layer and its interfaces with Si, and iii) thermal stability of Si/Ge nanoclusters in SiO_2.

Surface Science
Room: C-108 - Session SS-ThM

Electronic Structure and Stimulated Processes
Moderator: R. Bartynski, Rutgers University

8:20am **SS-ThM1 Electronic Structure of Atomic Chains on Vicinal Silicon**, ***J.N. Crain****, University of Wisconsin - Madison, *K.N. Altmann,* Synchrotron Radiation Center, *Ch. Bromberger,* Philipps - University, Germany, *A. Kirakosian, J.-L. Lin, J.L. McChesney, F.J. Himpsel,* University of Wisconsin - Madison

Surface states on semiconductors provide a unique opportunity to study low-dimensional electron systems. States at the Fermi level are in the band gap and thus do not couple to the bulk states. Thereby, truly two- and one-dimensional metals can be achieved. An example of a 2D metal is Si(111)-√21x√21(Ag + Au) which exhibits two distinct Fermi surfaces associated with Ag and Au.[1] By growing chains of gold atoms on Si(111), Si(557), Si(335), and Si(337) we demonstrate the capability of engineering one-dimensional metallic states with varying inter-chain spacings and electron count. In addition, we find a new Si(111)-5x2 Gadolinium reconstruction akin to a lattice of 1D spin chains. Using a combination of STM and angle resolved photoemission we map the real-space and momentum-space electronic structures for these atomic chains. By locking the atoms to the silicon lattice the Peierls transition is overcome. The resulting metallic bands exhibit novel properties including the formation of two half-filled metallic bands in place of a single semiconducting band and a continuous 1D to 2D transition within a single band.[2,3,4] The engineering of 1D metals is instrumental in the search for exotic electron behavior like the Luttinger liquid.[5]

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[2] R. Losio, K. N. Altmann, and F. J. Himpsel, Phys. Rev. Lett. 85, 808 (2000).

[3] R. Losio, K. N. Altmann, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, and F. J. Himpsel, Phys. Rev. Lett. 86, 4632 (2001).

[4] K. N. Altmann, J. N. Crain, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, F. J. Himpsel, and R. Losio, Phys. Rev. B 64, 035406 (2001).

[5] J. Voit, Rep. Prog. Phys. 58, 977 (1995).

8:40am **SS-ThM2 Origin of the Negative Shift Observed in the XPS Spectra of Cu and Ag Cations having d^{10} Electronic Configuration**, ***D.A. Kukuruznyak***, *J.G. Moyer, A.L. Ankudinov, J.J. Rehr, F.S. Ohuchi*, University of Washington

We discuss the phenomenon of the negative chemical shift in the XPS spectra, where an oxidized ion appears to be chemically reduced. The effect is illustrated in the the Cu^{1+} cation within a spinel crystal structure and in Ag^{1+} in silver fluorides, AgF and AgF_2. We have found that the negative chemical shift of the core levels is caused by similar shifts of the ions 3-d and 4-d Valence Bands. We therefore modeled the experimental valence band photoemission spectra by theoretical DOS of the d-levels using an ab initio FEFF8 code. This code is based on a relativistic Greens function real

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* Morton S. Traum Award Finalist

space full multiple scattering formalism and allows accurate determination of the position of the levels with respect to the Fermi energy. We have determined that the negative shift of the d-levels is not caused by a long-range electrostatic interaction (Madelung potential). The amount of the total charge on the Cu^{1+} cation in the spinel structure was similar to that of copper in Cu_2O, thus charging is not the cause of negative shift either. It was also found that only Cu 4s and 4p electrons participate in the chemical bonding. Completely filled d^{10} shells of the copper in spinel structure do not form a band, but were localized, having an atomic-like character. The 3d-level therefore appeared as a false valence band edge in the spectrum. A similar effect was observed for the silver compounds. We claim that the negative chemical shift is not due to charging or splitting effects, but occurs when a completely occupied non-bonding d^{10} shell appears on the XPS spectra as a false valence band edge.

9:20am **SS-ThM4 Electronic Band Structure of Sn/Si(111)**, ***J. Lobo***, *A. Tejeda*, Universidad Autonoma de Madrid, Spain, *A. Mugarza*, Universidad del Paés Vasco, Spain, *E.G. Michel*, Universidad Autonoma de Madrid, Spain

We report an investigation on the electronic band structure of the Sn/Si(111)-$(\sqrt{3}x\sqrt{3})R30°$ phase using angle-resolved photoemission, in the coverage range between 1/6 and 1/3 ML, both at room and at low temperature, with special emphasis in the analysis of its metallic character and in the evolution of the surface states as a function of temperature and coverage. The photoemission experiments have been performed at HASYLAB (Hamburg, Germany). This phase has deserved widespread attention since the discovery of a temperature induced phase transition to a low temperature (3x3) phase. Several different models have been put forward to explain the nature of the phase transition, that is observed only in the case of Ge(111): formation of a surface charge density wave, stabilized by correlation effects or defects; dynamical fluctuations, that destroy the (3x3) phase at RT; or existence of a soft phonon. There is no indication of a (3x3) pattern at low temperature for Sn/Si(111), but several features of the (3x3) phase are found in the valence band. We present also an analysis on the influence of the defect density in the surface state behavior and metallic character. The results found for the ideal $(\sqrt{3}x\sqrt{3})R30°$ phase at 1/3 ML coverage support the dynamical fluctuations model for the phase transition. While a (3x3) phase is not observed in the temperature range accessible, the system exhibits a behavior similar to the one found in Sn/Ge(111) (split surface state band that survives at RT). The existence of a semiconductor to metal transition has been investigated in detail.

9:40am **SS-ThM5 Electron Confinement in Metallic Ultrathin Films**, ***Z.Q. Qiu***, University of California at Berkeley **INVITED**

Electron confinement or quantum well (QW) state manifests in metallic thin films as the film thickness is reduced to nanometer scale. Photoemission provides the most direct observation of QW states in k-space. The unique capabilities now available at the Advanced Light Source (ALS) at Berkeley make it possible to image QW states on the atomic scale. The photoemission results from ALS on Cu thin films grown on fcc Co(100) are presented using single- and double-wedge samples. First, we will discuss how the QW states are formed in the Cu film and how to describe it using the phase accumulation model. Second, we will show how the QW states result in the oscillatory interlayer coupling between two ferromagnetic Co layers across a thin Cu layer.

10:20am **SS-ThM7 Dominance of the Final State in Photoemission Mapping of the Fermi Surface of Co Thin Films**, ***R.L. Kurtz***, *X. Gao*, Louisiana State University, *A.N. Koveshnikov*, Simon Fraser University, Canada, *R.L. Stockbauer*, Louisiana State University

The Fermi surface of tetragonally-distorted fcc Co grown on Cu(001) has been investigated with angle-resolved photoemission and compared with first-principles calculations. Photoelectron angular distributions were obtained with a display-type ellipsoidal-mirror analyzer at the LSU CAMD synchrotron light source for electrons emitted from E_F using photons in the energy range of 20-80 eV. These angular distributions show distinct patterns that vary with photon energy as different regions of the Brillouin zone are sampled. In order to evaluate the correspondence to Fermi surface contours, we have computed the band structure of tetragonally-distorted Co. We have used WIEN97.9 to perform a spin-polarized gga FLAPW calculation including spin-orbit interactions for a pseudomorphic fcc structure with an in-plane lattice constant that of Cu while the vertical lattice parameter is reduced by 5%. From this, the resulting Fermi surfaces have been extracted and cross-sectional contours were produced corresponding to the various photon energies used in the measurements. We find that there is rather poor agreement between these contours and the structures seen in photoemission. To investigate this further, we have computed the momentum matrix elements using the final states produced in the band calculation. In the case of Co, the resulting angular distributions that we predict are in much better agreement with our data, and even reproduce the photon polarization effects that are observed. These observations suggest that comparison with first principles calculations are extremely important, particularly in the case of flat-band materials such as the d-bands of Co seen here. The slow dispersion of the occupied states, when coupled with the rapid dispersion of the final state, produces angular distributions whose contours are heavily influenced by the final state.

10:40am **SS-ThM8 Spin-Resolved Photoemission of Surface States in H on W(110)**, ***E. Rotenberg***, Lawrence Berkeley National Laboratory, *M. Hochstrasser*, *J.G. Tobin*, Lawrence Livermore National Laboratory, *S.D. Kevan*, University of Oregon

Surface states of metals can be split due to the spin-orbit-coupling (SOC) interaction, as first shown experimentally by LaShell et al for Au(111) surface states.[1] Their conjecture was that the surface states could be split by SOC when the bulk inversion symmetry was broken at the vacuum/metal interface. Later we found a similar splitting for W(110) and Mo(110) surfaces and furthermore that this splitting could be enhanced with hydrogen or alkali metal adsorption.[2] In the present work, the hydrogenated surface electronic states on W(110) have been measured using spin-resolved photoemission. The origin of the splitting is confirmed to be spin-orbit-coupling. In confirmation of the conjecture by LaShell et al, we observe 100% polarization of these states in local regions of momentum space. The spins are aligned in the plane of the surface, perpendicular to the electronic momentum relative to the S-bar symmetry point.

[1] S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett. 77, 3419 (1996).

[2] E. Rotenberg, J. W. Chung, S. D. Kevan, Phys. Rev. Lett. 82, 4066 (1999).

11:00am **SS-ThM9 Ultraviolet Laser Interactions with Single Crystal Sodium Nitrate: Wavelength Dependence of Photodesorbed Products**, ***L. Cramer***, *J.T. Dickinson*, Washington State University, *W.P. Hess*, Pacific Northwest National Laboratory

Sodium nitrate is a wide bandgap ionic material containing an oxyanion. Single crystals show a strong absorption band in the ultraviolet due to a π to π^* transition in the nitrate. Previous work has suggested that a number of neutral emission products are due to direct excitation of this band. In this study we compare the laser induced ion and neutral atom/molecule emissions from single crystal $NaNO_3$ at three wavelengths: at the band maximum (193 nm) and two minima on either side of the maximum (248 nm and 157 nm). Surprisingly, little correlation with the π to π^* absorption is observed, including molecular species derived from the nitrate. Our results are better explained by defect mediated processes attributed to anion vacancies. These results are corroborated by simultaneous laser induced photoelectron emission measurements that are very sensitive to low densities of electron trap defects at insulating surfaces.

11:20am **SS-ThM10 Low Dimensional Metallic States in Heavily Irradiated CaF_2 Thin Films on Si(111)**, ***A.A. Bostwick***, *J.A. Adams*, *A. Klust*, University of Washington, *E. Rotenberg*, Advanced Light Source, *M.A. Olmstead*, University of Washington

Calcium fluoride is a wide band gap ionic insulator that undergoes photosimulated desorption of fluorine. It has been previously reported by Karlsson et al.[1] that heavily irradiated thin (2.5 â€“ 4 triple layers) CaF2/Si(111) films show a sharp metallic defect state associated with an ordered array of surface fluorine vacancies. We find two additional states in thicker, irradiated films (5-10 triple layer), one at higher binding energy and one at lower energy than the surface state. These states also cross the Fermi level dispersing upwards from normal emission. The zone-center energies of these states depend on the thickness of the initial CaF2 film, hinting that the electrons are confined in the growth direction. The upper state could lie within the band gap of the silicon substrate, but the lower state, which is more than 1.5 eV below the Fermi level at the zone-center, does not. These states are observed after prolonged irradiation, much longer than that necessary to produce the surface state. We postulate that these new states are due to the formation of fluorine vacancy clusters (Ca metal quantum dots) within the CaF2. Funded by DOE grant DE-FG03-97ER45646/A0003.

[1] Karlsson et al., Phys. Rev. Lett. 57,1247 (1986).

11:40am **SS-ThM11 Ion Emission from Ultrathin Resists during Exposure to Metastable Atom Beams**, ***Y. Yamauchi***, *X. Ju*, *T. Suzuki*, *M. Kurahashi*, National Institute for Materials Science, Japan

The combination of ultrathin resists and slow metastable atom beams has attracted attention because of its potential for downscaling the semiconductor lithography beyond the diffraction limit, proximity effect, or transmission of conventional exposure radiations, i.e., ultraviolet light, electron beam, and soft x-ray. Slow metastable atoms carrying fairly large excitation energy in their electronic system interact only with topmost atoms at surfaces because the kinetic energies of the atoms are so low that they are reflected above surfaces. These extreme surface sensitivity and damage-free feature to under layers are desirable for an exposure radiation in lithography. Since Berggren et al.[1] had suggested the atom lithography, several groups have reported their success on pattern transfer employing metastable atom beams for ultrathin resists (self-assembled monolayer (SAM) of alkanethiolate,[1] hydrogen passivation on silicon surface[2] followed by wet chemical etching. As to the fundamental phenomena of resists caused by the irradiation of metastable atoms, however, are not well understood. Recently metastable-atom-stimulated desorption (MSD) was discovered for water and alkali coadsorbed surfaces.[3] We have investigated MSD of positive ions from alkanethiolate-SAMs and from hydrogen-passivated Si(111) surfaces. The MSD data show H^+ and CH_x^+ desorption from of the alkanethiolate-SAMs and H^+ desorption from the hydrogen-passivated Si(111) surfaces, which provide direct evidence for the dissociation of alkanethiolate-SAMs and of silicon hydrides by metastable helium atom beams at the initial stage of the pattern transfer.

[1] K. K. Berggren, et al., Science 269 (1995) 1255.

[2] S. B. Hill, et al., Appl. Phys. Lett. 74 (1999) 2239.

[3] M. Kurahashi and Y. Yamauchi, Phys. Rev. Lett. 84 (2000) 4725; T. Suzuki, et al., Phys. Rev. Lett. 86 (2001) 3654.

Vacuum Technology
Room: C-104 - Session VT-ThM

Gas Dynamics and Flow

Moderator: R. Dobrozemsky, University of Vienna, Austria

8:20am **VT-ThM1 Cryopump Pumping Performance Estimation Using Flow Meter Method**, *H.-P. Cheng*, ***Y.-C. Lu***, National Taipei University of Technology, Taiwan, *M.-K. Hsu*, World Hold Engineering Consultants, LTD

The pumping performance of cryopump, ULVAC CRYO-U10PU, is estimated by the flow meter method, which is widely used in the estimation of the pumping capacity of the turbo molecular pump for inlet pressure greater than 1.0E-04 Pa. The test dome is designed according to the instruction of JVIS-005 and connected directly with the cyropump. The inner diameter of the test dome is the same as the inlet port of the pump. The PIRANI gauge (ULVAC GP-1000, range 0.4 to 2700 Pa) and the ION gauge (ULVAC GI-1000 WIT, range 1.3E-05 to 6.7E-01 Pa) are equipped on the peripheral of the test dome to measure the test dome pressure according to the instruction of the JVIS-005. Four flow meters (Sierra 820 series, ranges 25 SCCM, 500 SCCM, 10 SLM, and 50 SLM) hybrid the needle valves are used to control the inlet gas throughput of the pump and two types of gas, nitrogen and argon are introduced. The variations of the temperature of the first stage (80K) of the cryopump and the test dome pressure relative to the operating time of cryopump are discussed. The pumping speed and throughput of the cryopump versus to the test dome pressure that is considered as the inlet pressure of cyropump are plotted and compared to the values described in the catalog of ULVAC. Finally, the residual gas analysis is made to investigate the residual gas in the whole system. And the temperature recovery time is recorded after the cryopump is turned off. According to the measurements, the temperature of the first stage of cryopump is in the steady state condition after two hundred minutes of the starting of the cryopump. The pumping speed for nitrogen is near to the value shown in the catalog of ULVAC and the argon is nearly twice than the catalog. The main residual gases are hydrogen and water at the status of the ultimate pressure operating condition. The recovery time from normal operating temperature of the cryopump to the room temperature is over three hundred minutes after the pump turned off.

8:40am **VT-ThM2 Developing of Calculation Methods of Diffusion Vacuum Pumps' Characteristics**, *M.G. Sapeshinsky,* Bauman Moscow State Technical University, Russia, ***B.N. Kemenov***, NPK INTELVAC, Russia

Results on 3-dimensional mathematic simulations of processes in an inlet chamber of diffusion vacuum pumps, of interaction between pumped out gas and steam molecules are presented. Description of algorithmus and of a calculation programs complex for characteristics of diffusion vacuum pumps is given. Using the developed calculation programs the influence of parameters and form of a steam flow, geometry of a body, as well as of an oil reflector and protecting screens, on operation rate and on reverse oil flow of diffusion pumps is investigated. Rated and experimental data are compared. The concept of optimisation of an inlet chamber of diffusion pumps is developed

9:00am **VT-ThM3 Comparison between Monte Carlo and Analytical Calculation of the Conductance of Cylindrical and Conical Tubes**, ***J. Gómez-Goñi***, *P.J. Lobo*, Universidad Politécnica de Madrid, Spain

The accurate calculation of transmission probabilities of ducts in the molecular flow regime has become a need of vacuum standards on the ultra high vacuum region. The usual approach is to simulate a molecular flow of molecules with a Monte Carlo method, because of the difficulties that arise trying to find a solution of the Clausing integral equation in a system of a given geometry. As modern computers increase their speed, the accuracy of Monte Carlo methods is higher and higher. So it becomes important to compare simulation results with data obtained by other methods to check that random number generators used in the Monte Carlo are not biased. Moreover, with numerical methods we can obtain the density of molecules along the tube. This density is important in molecular beam formation studies. We have applied both a Monte Carlo method and numerical solutions of the Clausing integral equation for cylindrical and conical tubes. In the case of cylinders, we have found very accurate transmission probabilities solving numerically Clausing integral equations. The method consists in an approximation of the Clausing function with Chebyshev polynomials using a subroutine made by the Numerical Algorithm Group (NAG).[1] Comparing with other values found in the literature[2] made by a variational method, we have obtained values near the upper bound and quite far away from the lower bound. In the case of cones, we obtain values which agree with values found in the Literature[3] to a high degree of accuracy.

[1] NAG Subroutine D05AAF.

[2] R.J. Cole, J. Inst. Maths. Applics. 20, 107-115 (1977).

[3] R.P. Iczkowski, J.L Margrave and S.M. Robinson, J. Phys. Chem. 67,229 (1963)

9:20am **VT-ThM4 Modeling Molecular Drag Pumping in the 20th Century: A Personal View**, ***J.C. Helmer***, Consultant **INVITED**

In the last decade we have had a renaissance in molecular drag pumping, led by the design of hybrid turbopumps that exhaust at pressures above 10 Torr, to oil-free forepumps. The exhaust stages, which operate in laminar flow, may be of the Gaede, Holweck, or Siegbahn type. While Gaede provided the underlying model in 1913, upon which all are based, the Gaede design was not developed as a commercial pump until it was revived by Varian SpA, in Turin, in 1992. The neglect of the Gaede design was accompanied by 80 years neglect of the molecular drag model, in deficiencies which Gaede himself identified in his original papers. Pumps operate in continuum flow, which is a new field in vacuum science, extending the classical field of molecular flow. The appropriate mathematical tools have been developed in the fields of fluid mechanics (CFD), aerodynamics (RGD) and molecular simulation (DSMC). It is a challenge to extract from these fields a subset of theory that is appropriate and useful to molecular pumping. Many papers miss the fact that molecular drag pumps operate in the classic analytic regime of Couette-Poiseuille flow, and results need to be compared with the characteristics of this type of flow. Even G.A. Bird, author of the famous DSMC method, recommends that numerical simulations be guided by analytic models. Useful theory has been developed in the design of gas (journal) bearings, and floating magnetic recording heads. For molecular pumping, the inertial term in the viscous equations should not be neglected. Some papers calculate solutions with a form of slip-flow that has no physical correspondence, since in practice the molecules have full accomodation to the surface. This is an emerging field which has many opportunities for student research.

10:00am **VT-ThM6 Mathematic Simulation of Processes in Flow Parts of Hybrid Turbomolecular Vacuum Pumps**, ***M.G. Sapeshinsky***, *A.V. Ponomarev*, Bauman Moscow State Technical University, Russia

Results on 3-dimensional mathematic simulation of processes in flow parts of hybrid turbomolecular pumps (TMP) are presented. Description of algorithms and of a calculation programs complex for characteristics of hybrid turbomolecular pumps with molecular and drum forcing channels is given. The influence of geometric parameters of a flow part on an operation rate and a maximal compression degree of pump channels is investigated. The concept of optimisation of hybrid pumps under restrictions of controlled parameters is developed.The optimal variants of a flow part are given. Rated and experimental data are compared. There is developed an algorithm of optimization of a TMP flow part with axial and axial-radial gas flow under functional restrictions on controlled parameters, ensuring the desired TMP operation rate at fixed suction pressure for a chosen gas, and also the desired operation rate for several gases using the algorithm of slipping access and the absolute penalty functions metod. It is found out, that within the investigated operation rate's range an axial-radial scheme has better mass-size characteristics compared to that of an axial scheme. Decrease in volume of a flow part with optimal geometric parameters makes from 36 % (S=0.5 m^3/sec) to 53 % (S=20 m^3/sec) due to decreasing the axial rotors number. Here the external diameter of axial rotors increased from 35 % (S=0.5m^3/sec) to 5 % (S=20m^3/sec). More preferable is the axial-radial scheme with periphery-center flow direction. It is found out, that if ensuring the desired raised evacuation characteristic for light gases, the flow part volume of all the three schemes increases due to increase in axial rotors number and smoother changing of geometric parameters over rotors, and mass-size characterictics of axial-radial schemes come worse. Decrease in the flow part volume comparing to that of an axial scheme makes for the scheme with periphery-center flow 24 % ($S=20m^3/sec$, $P=10^{-5}$ Pa, $S=15\ m^3/sec$ and $P=10^{-3}$ Pa). The volume of an axial scheme raised on 93 %, of axial-radial schemes - on 163 % and 150 % compared to the computation results when ensuring the desired operation rate only for nitrogen.

10:20am **VT-ThM7 Two-Dimensional and Three-Dimensional Monte Carlo Simulation on the Pumping Performance of a Turbomolecular Pump with Rough-Surface Blades**, *M. Yabuki*, ***T. Sawada***, *W. Sugiyama*, Akita University, Japan, ***M. Watanabe***, Osaka Vacuum Ltd., Japan

The elements of a turbomolecular pump (TMP) are sometimes coated with ceramic (SiO_2) film for the purpose of preventing corrosion on the TMP. The blades coated with SiO_2 have relatively rough surfaces, and it has been confirmed by previous experiments that the SiO_2-coated TMP gives a higher maximum-compression ratio than the non-coated TMP. This paper describes the Monte Carlo simulation on the effects of the surface roughness of blades on the pumping performance of a TMP. The surface roughness was measured by SEM, and then the distribution of roughness slope angles was obtained from the surface roughness data. The surface roughness was modeled by statistically located circular-conic peaks and dimples of the same base radius and various base angles. The base angles were sampled in a statistical manner so as to accord with the measured slope angle distribution. Both the 2D and 3D Monte Carlo simulations were done in the free molecule flow regime and the simulated maximum-compression ratios were compared with the previously measured values. The 3D simulation naturally showed a better agreement with the measured values than the 2D simulation. However, it was proved that the 2D simulation gave reasonable results with much less computation time than the 3D simulation when the ratio of blade height to pitch was larger than the unity.

10:40am **VT-ThM8 Experimental Analysis of Tapered Gaede Pumps**, ***S. Giors***, *R. Gotta*, *J.C. Helmer*, Varian S.p.A., Italy

In 1993 Varian S.p.A. revived the Gaede design and developed it for commercial hybrid turbomolecular pumps. The Gaede stages exhaust at pressures above 10 Torr, operating in laminar viscous flow. Classical Gaede stages are characterized by uniform cross section of the channel, from inlet to exhaust. Both modelling and experimental analysis agrees in showing that the maximum compression in the viscous regime is inversely proportional to the square of the height h between disk and channel surface, while channel pumping speed is proportional to the inlet cross section of the channel and hence to h. From this reasoning comes the simple idea that tapering the height h of the channel from inlet to exhaust, keeping the same entrance section, can greatly increase compression, without compromising the pumping speed of the channel. An experiment was designed to test these concepts. A uniform channel and one with a 3:1 taper, with the same inlet channel section, are compared in viscous conditions. Results show that the channels must be compared not just in terms of maximum compression and maximum speed, but in terms of the complete speed vs. compression characteristics. Actually the tapered channel shows a slight decrease in maximum pumping speed, but that is highly compensated by increased compression and improved shape of the speed vs. compression characteristics. Another promising advantage of the tapered channel with respect to the uniform one, is reduction in power dissipation with the same exhaust pressure and flow. Comparison of experimental results with model calculations, indicates some ways in which the Couette-Poiseuille model needs to be improved.

11:00am **VT-ThM9 Pumping Performance Investigation of a Turbo Booster Vacuum Pump Equipped with Spiral-Grooved Rotor and Inner Housing by CFD Method**, ***H.-P. Cheng***, *C.-P. Chien*, National Taipei University of Technology, Taiwan, *C.-P. Lee*, China Engineering Consultants, INC

This paper estimates the pumping performance of a turbo booster vacuum pump equipped with spiral-grooved rotor and inner housing by CFD method. The computational domain hybrids the flow channels in the rotor and inner housing, thus the gas can flow continuously from the inlet of rotor through the outlet then into the inlet of inner housing and exist. The pumping characteristics for the spiral angle of the rotor, and the groove number and the spiral angle of the inner housing are detailed investigated. The spiral angle, 15 degrees, of rotor can adequately increase the effective pumping length of the flow channel and overcome the following increased friction force, therefore the pumping performance can be enhanced. Similarly, the spiral-grooved inner housing with 5 grooves and spiral angle 27 degrees can also have the better pumping performance. The results also indicate that there is an axial vortex dominated the spiral-grooved flow channel of both rotor and inner housing. The back stream from rotor channel to the vacuum chamber is evident. Otherwise, the detailed three-dimensional velocity vector, axial velocity contour, and pressure fields are shown in the paper. The arithmetic axial pressure distribution, compression ratio are also discussed. The pumping performance of two prototypes are also measured and shown in the paper. The discrepancies among experiments, simulation, and expected target are discussed.

Thursday Afternoon, November 7, 2002

Applied Surface Science
Room: C-106 - Session AS-ThA

Practical Surface Science II
Moderator: B. Beard, Akzo Nobel Chemicals, Inc.

2:00pm **AS-ThA1 Transferring Classical UHV Techniques into Ambient Pressure - Is the Gap Bridged for Electrons?**, ***A. Vollmer***, University of Cambridge, UK, *J.D. Lipp, G.E. Derbyshire,* Rutherford Appleton Laboratories, UK, *H. Weiss,* Universität Magdeburg, Germany, *D. Herein,* ACA, Berlin, Germany, *T. Rayment*, University of Cambridge, UK

Most traditional surface science methods are restricted to studies of model systems under 'ideal' conditions, most prominently single crystals in ultra-high vacuum (UHV). The interest in the development of surface science methods for investigations of systems with a more immediate, practical relevance (e.g., heterogeneous catalysts) remains strong, especially with a view to the difficulties in delineating relationships between interfacial behaviour under conventional "surface science" and "practical" conditions, i.e. high pressure environments. In the field of heterogeneous catalysis the terms "pressure gap" and "material gap" have been coined to describe the relationship between surface science and practical catalysis. Under UHV conditions, gas-surface-interactions are widely studied by means of electron detection (LEED, UPS, XPS, XAS and many more) while in gaseous environments electrons are strongly scattered and quickly attenuated. Until recently,[1] an efficient mode for energy-selective electron detection at ambient pressure was not available. We have now explored the possibilities of gas microstrip detectors (GMSD) as a promising tool for bridging the pressure gap between surface science and 'real world' conditions. We will show that energy-selective electron detection and depth profiling is possible for various systems operating under practical pressure conditions, including powders, layered structures, metals as well as insulators. Investigated systems include partial oxidation catalysts based on Vanadium oxides and phosphates. We will also report upon an ambient pressure surface sensitive scanning X-ray microprobe working under reaction conditions.

[1] T. Rayment et al, Rev. Sci. Instrum. 71 (2000) 3640.

2:20pm **AS-ThA2 Plan to Maximise Information Retrieval from the XPS Survey Scan**, ***J.E. Castle***, The University of Surrey, UK

The work to be described concerns the implementation of procedures designed to extract the maximum information possible from the initial survey scan typically made at the outset of XPS analysis of an unknown surface. The procedures resulted from detailed expert discussion of the issues at the recent 'IUVSTA Workshop No.34'. The procedures devised are intended to give guidance for those developing data systems having a degree of inbuilt inferencing capability. Here we have assessed the recommended procedures using off-line processing where necessary but have, as far as currently possible, mimicked the operation of a hands-off system. We will show in this paper the extent to which information retrieval can be enhanced and discuss the possibilities for this to be implemented in future datasystems.

2:40pm **AS-ThA3 Real World Surface Analysis**, ***W.R. Nieveen***, *T.F. Fister, P. Lindley*, Charles Evans & Associates - Evans Analytical Group **INVITED**

In todays short R&D-to-product cycle, there is often an oversimplification of the use and valuation of surface analysis. The dividing line is usually chosen between academic/institutional versus industrial or production environments and the most common divider is typically time. Both arenas are equally "real", but the utilization of equipment and instrumentation is typically quite dissimilar. Consequently, methodology between the two divisions is also substantially different. The outcome of any particular surface analytical experiment may have different significance depending on the environment in which it is conducted. The process by which decisions within the analysis are determined and the resulting decisions from the experiment's conclusion can greatly affect the way a particular analysis is performed. These intangibles frequently affect the perceived success or value of surface analysis. In this talk, we will look at the differences in methodology between typical industrial or production situations compared to the R&D or academic use of surface analysis. We will contrast the deadlines, purpose, and goals of typical R&D projects with the demands, timelines, and expectations of a production problem. We will examine the role of the analyst and the affect his/her experience within and outside the framework of surface analysis has on the results. Current real world examples (from both types of environments) using multiple technique surface analysis will be presented to illustrate the processes. Time permitting, examples of surface analytical methods as a research technique for materials characterization, a method for problem solving and/or failure analysis, and a metrology and/or QA/QC tool will be given. The incorporation of these different environments, the analytical decision processes, and the utilization of the results will be important for "expert system" development in surface analysis.

3:20pm **AS-ThA5 Nanoscale Tomography with the Focused Ion Beam**, ***R. Hull***, University of Virginia **INVITED**

We describe the use of focused ion beam sputtering to create tomographic reconstructions of objects at length scales ranging from tens of nanometers to tens of microns. This is achieved by imaging (with secondary electrons or secondary ion mass spectroscopy, SIMS) the sputtered surface at different depths in the sample. Computer interpolation of successive images then enables reconstruction of the 3D structure and chemistry. The final reconstructions typically contain several million independent voxels of data. We will describe experimental strategies for optimizing the realizable spatial resolution, for example by minimizing generation of topography arising from differential sputtering rates. We will also describe implementation of computer algorithms for interpolating between experimental images. The simplest algorithms employ linear interpolation of pixel intensities between successive images, but these techniques work well only where structures are relatively uniform along the normal to the sputtered surface. For structures with high curvature along the sputtering direction, we employ shape-based interpolation techniques (as developed for the medical tomography field) that enable complex geometrical forms to be reconstructed. Spatial resolution is defined primarily by the probe size and the lateral spread of the incident Ga ions in the sample for lateral resolution, and the implant depth for incident Ga ions and escape depth for secondary electrons/ions for vertical resolution. We have confirmed predicted resolution of order 20-30 nm by direct lateral and vertical detection of 22 nm layers in InAlP/InGaP heterostructures. Chemical sensitivities are greatly limited by the low ionization efficiency of most materials by primary Ga ions. Accordingly, we are exploring photon-based techniques for post-sample ionization of sputtered neutrals. This work is done in collaboration with A. Kubis and G. Shiflet (UVa), D. Dunn (IBM) and D. Backman (GE).

4:00pm **AS-ThA7 Electromigration Behavior of Single Crystal Copper**, *C.M. Contino, S.M. Schwarz,* ***L.A. Giannuzzi***, University of Central Florida

A preliminary report on the electromigration behavior of single crystal copper will be presented. A focused ion beam instrument was used to prepare single crystal copper samples oriented along [100] and [110]. Electromigration results of the single crystal samples indicate that the [100] oriented sample had better electromigration properties than the [110] oriented sample.

4:20pm **AS-ThA8 XPS Analysis under External DC and AC Bias**, ***S. Suzer***, *B. Ulgut*, Bilkent University, Turkey

Charging is a nuisance in XPS analysis and is usually circumvented by flooding the sample with low energy electrons. External biasing is an easier/cheaper alternative and can even give additional static or dynamical information about charging which can in turn be related to composition of the sample. In this contribution, we will present XPS spectra of Au/SiO2/Si system under various DC and AC (square-wave) bias conditions and discuss the issues related to charging and/or composition.

Biomaterials
Room: C-201 - Session BI-ThA

Cell Patterning to Engineer Function
Moderator: G.J. Leggett, University of Sheffield

2:00pm **BI-ThA1 Analysis of Cell Adhesion Strengthening Using Micropatterned Substrates**, ***N.D. Gallant***, *A.J. García,* Georgia Institute of Technology

Cell adhesion to fibronectin (FN) involves integrin receptor binding and subsequent adhesion strengthening, which includes integrin clustering, interactions with cytoskeletal and signaling components to form focal adhesions (FAs), and cell spreading. We applied micropatterning methods to control FA size and position and decouple FA formation from gross changes in cell morphology in order 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 µm dia.) within a non-adhesive background.[1] 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.[2] 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, independently of cell spreading. 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.

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[1] N.D. Gallant et al., "Micropatterned surfaces to engineer focal adhesions for analysis of cell adhesion strengthening," Langmuir (in press).

[2] A.J. García et al., "Force required to break $\alpha_5\beta_1$ integrin-fibronectin bonds in intact adherent cells is sensitive to integrin activation state," J. Biol. Chem. Vol. 273, pp. 1098-10993, 1998.

2:20pm **BI-ThA2 Micropatterning of Polymer Surfaces for Controlled Cell Adhesion and Spreading Processes**, ***C. Satriano***, University of Catania, Italy, *S. Carnazza*, *S. Guglielmino*, University of Messina, Italy, *A. Licciardello*, *G. Marletta*, University of Catania, Italy

The prompting of cell adhesion and spreading processes onto polymeric surfaces activated by ion beam irradiation is a phenomenon observed for several polymers. In particular, in the case of carbon-based polymers and silicon-based polymers, the enhancement of cytocompatibility of the ion-irradiated surfaces has been mainly related to the formation of amorphous phases of hydrogenated carbon or SiO_2-like clusters, respectively. In this work the physico-chemical properties of two representative polymers of the two classes above mentioned, i.e., poly(ethyleneterephtalate) (PET) and poly(hydroxymethylsiloxane) (PHMS) were modified in a graded and controlled way with a micrometric spatial resolution. Namely, irradiated patterns with stripes of width ranging between 10 and 100 microns were obtained on the two polymer surfaces by using finely focused ion beams, with a total ion dose of $1x10^{15}$ ion/cm^2. The surface chemical structure and composition of the ion-modified surfaces were characterized by TOF-SIMS and Small Spot XPS, the micro-topography and the morphology were measured by AFM, finally, the surface free energies were calculated by wettability measurements. Fibroblast cells were used to test the cell adhesion and viability on the various micropatterned surfaces. Optical Microscopy was employed to characterize the importance of the lateral resolution effect respectively in PET and PHMS. Epifluorescence Microscopy evidenced the occurrence a specific cell morphology and mitotic activity for the different patterned surfaces. Furthermore, preferential cell alignment effects were observed depending on the type of irradiated polymer.

2:40pm **BI-ThA3 Designing In Vitro Patterned Neuronal Networks**, ***B.C. Wheeler***, University of Illinois, Urbana-Champaign **INVITED**

Through the use of microstamped patterns of polylysine against covalently linked backgrounds of polyethylene glycol, we have been able to maintain patterns of neurons for up to a month in culture. We have demonstrated the ability to use patterning technology in combination with planar microelectrode arrays to confine the neurons to narrow (10 um or 40 um) tracks which intersect the electrodes and to record spontaneous electrical activity (action potentials) from them. Work is in progress to determine how sparse a network can be and still maintain functional electrical activity. This work is intended to provide a technological basis for robust, repeatable and designable neural networks from which one could study basic neuroscience or construct a neural biosensor. Supported by NIH grants R21 NS 38617-01 and R55 RR13320-01 and NSF EIA-0130828. This work is done in collaboration with Dr. Gregory J. Brewer, Dept. of Medical Microbiology, Southern Illinois University School of Medicine.

3:20pm **BI-ThA5 Development of a High Throughput Cell Printing Platform**, *M.V. Deshpande*, *E.A. Roth*, Clemson University, *A. Gutowska*, Pacific Northwest National Laboratory, ***T. Boland***, Clemson University

High throughput cell printing has a potential to be a very valuable technique in the field of tissue engineering and genomics. A single nozzle cell pen and multi nozzle cell printer have been designed and developed to explore this area. New techniques are being developed to apply these tools for precise placement of cells with high throughput capabilities. The printer nozzles can be loaded with a known concentration of cells in solution or a pre-polymerized hydrogel solution. Pressure created by low power piezoelectric signals will push the cell solution onto a substrate in a programmed design. The cell printer was designed to print cell suspensions to media of any thickness. The body of the printer is made from PMMA with off the shelf printing components (logic board, encoder, etc.). The printer is equipped with a newly designed print head connected to sterile stainless steel hypodermic needles (gauge 30). The needles are individually addressable through piezo driven transducers. Finally, the software drivers were custom written to allow for computer-controlled delivery of single drops. In single-pass mode, the new printer is able to print 80pl drops onto substrata of varying thickness up to 1 inch. Preliminary results indicate a success in developing an array of cells. The cells are alive and healthy as determined by the green stain of the live/dead assay. This indicates the potential of printing small sheets of cells. Other techniques will be investigated to extend the use of the printer to print fluid hydrogel solutions into patterns for use as cell culture templates. Current investigation emphasizes characterizing and comparing temperature sensitive hydrogel mediums. Collagen I, a PLGA based biodegradable gel, and PIPAaM are being investigated. We will present this single cell platform technology and discuss the extension of the technology for two and three-dimensional cultivating systems of varying geometries.

3:40pm **BI-ThA6 Spatially Patterned Tissue for Retinal Cell Transplantation**, *C. Lee*, ***S.F. Bent***, *P. Huie*, *M.S. Blumenkranz*, *H.A. Fishman*, Stanford University

Patterning of tissue for selective placement of cells is currently being investigated in a novel treatment for age-related macular degeneration (AMD). The transplantation of human retinal pigment or iris pigment epithelial cells (RPE or IPE) on a carrier substrate is a proposed method for rescuing the diseased retina in AMD. We have examined the use of autologous tissue as a carrier substrate for the cells because it offers several advantages over synthetic substrates. Human lens capsule is readily available through ocular surgery and can coexist in the subretinal space without inducing immune rejection. To control the adhesion and morphology of the RPE cells, we have spatially modified the tissue surfaces using microcontact printing techniques. We have micropatterned inhibitory molecules such as poly (vinyl alcohol) (PVA) on lens capsule and have examined RPE cells subsequently cultured on the surface. We show that micropatterning these molecules via microcontact printing and related flow methodologies confines RPE cells to cuboidal structures that closely mimic the natural RPE layer. The cell inhibition by PVA was found to be stable in culture over a period of weeks. The cells have been successfully patterned on human tissue to circular patches as large as 50 microns and as small as 15 microns in diameter, separated by only a few microns. However, we find that the pattern size strongly affects the probability of cell adhesion and subsequent cell spreading. Overall, micropatterning PVA appears to be a promising and reproducible method for confining cells to high density and to a single morphology. We will discuss the potential for these methods to create a precise and organized transplanted cell layer for the treatment of patients suffering from macular disease.

4:00pm **BI-ThA7 Synaptic Connectivity in Geometrically Defined Neuronal Networks**, ***A. Vogt***, MPI for Polymer Research, Germany, *A. Offenhaeusser*, Research Center Juelich, Germany, *W. Knoll*, MPI for Polymer Research, Germany

One of the major problems in the study of neuronal network behaviour lies in the enormous complexity of the vertebrate brain. A promising approach to this problem is the creation of simplified neuronal circuits in vitro as a model system. A simplified circuit can be achieved by growing neurons on micropatterned substates which impose geometrical constraints upon the forming network, such that the amount of possible cellular contacts is greatly reduced. Additional advantages of such a system are the clear definition of the connections formed as well as a high reproducability of the network shape. We grew rat embryonic cortical neurons on micropatterned substrates made by microcontact printing of ECM proteins onto a hydrophobic background. The pattern applied was a grid pattern with 6 µm wide lines and nodes that were 14 µm in diameter. The cells aligned with the geometry of the structure and formed simple circuits. Cell density was low enough to observe single cell contacts resulting in the formation of functional synapses along the lines of the pattern; this was shown by triple patch-clamp measurements. The synapses we found did not differ significantly from the synapses found on homogeneous control substrates in average synaptic failure and EPSP height. We therefore believe that our system is suitable as a model for neuronal networks and has multiple potential applications in basic biological research as well as in pharmaceutical testing, neurological implants, neuro-electronics and cell-based biosensors.

4:20pm **BI-ThA8 Oral Keratinocyte Attachment to Chemical Surfaces**, ***R.E. Rawsterne***, UMIST, UK, *G.J. Leggett*, University of Sheffield, UK, *S. Kothari*, UMIST, UK

The control of surface chemistry and topography are key factors in the design and development of next generation biomaterials and prostheses.

The importance of surface chemistry has been well established for a variety of cell types, and the importance of surface topography is also gaining momentum. Whilst these are now recognised as being influential in initial cell attachment and growth, and both have been studied independently, there has been little work on examining their combined effects. Furthermore, the effect of these parameters on the behaviour of oral keratinocytes has not been studied. In order to ascertain which chemical functionality would best promote oral keratinocyte attachment, self-assembled monolayers (SAMs) of alkanethiolates on gold with varying chain lengths and acid (COOH), alcohol (OH) or methyl (CH_3) terminal groups were used. To introduce chemical cues to these surfaces SAMs were exposed to UV light through a mask resulting in selective oxidation of specific regions. Following photooxidation, samples were placed in a solution of a contrasting thiol, resulting in the displacement of the oxidised SAM in the exposed region with fresh thiols from solution. Samples exhibiting both single functionality and patterned chemistry were incubated with an oral keratinocyte cell line. For samples with a single functional group, the numbers of attached cells were counted at various time points up to 24h. Attachment to all surfaces was also observed using an inverted microscope and images recorded using a digital camera. It was found that hydroxyl terminated SAMs were the preferred surface for attachment of oral keratinocytes, in contrast to results for the attachment of fibroblasts. This was further investigated by observing the attachment of keratinocytes to patterns comprising of OH/CH_3 and OH/COOH terminated SAMs.

4:40pm **BI-ThA9 The Adaptation of Hydrogel Scaffolds to Three Dimensional Tissue Construction of Cylindrical Vessels**, ***E.A. Roth***, Clemson University, *A. Gutowska,* Pacific Northwest National Laboratory, *T. Boland*, Clemson University

This study investigates the ability of hydrogels to establish patterns for cell growth and their application to the construction of three-dimensional tissues. A variety of hydrogels are being investigated for this application including a collagen based hydrogel and Poly-N-Isopropyl Acrylamide (polyNIPAAm) based copolymers, which undergo liquid-gel transformations in response to temperature changes. The end goal is to construct viable cylindrical vessels that maintain stability, after hydrogel absorption or removal has occurred. A high-throughput cell printing system is under development that allows for accurate cell placement in pre-designed patterns. In this system, bioabsorbable hydrogels and cellular solutions are precisely deposited by needles connected to piezo electric pumps programmed through a software interface. A second method employs a mold consisting of two concentric cylinders, which has been designed to create vessels consisting of smooth muscle cells propagated in a hydrogel matrix. The outer surface of the annulus acts as a structural component during hydrogel stabilization and cellular proliferation. To allow for mold removal, this surface is grafted with poly NIPAAm so that upon slight cooling, the tissue can detach with all cellular junctions intact due to a decrease in hydrophobicity of the polymer. The inner surface of the annulus, composed of an inert nanoporous material, allows for nutrient diffusion from a media reservoir contained in the center of the mold. After sufficient culture time the mold is removed leaving a freestanding cylindrical vessel. Results from both of these methods will be discussed.

5:00pm **BI-ThA10 Integration of Cells and Silicon Devices via Surface Microengineering**, ***J. Hickman***, *M. Das, P. Molnar,* Clemson University

The long-term research goal of our group is to learn how to handle and prepare biological cells as components for microdevices and engineered tissues, and then to demonstrate the practicality of this approach by manipulating them to build hybrid systems and engineer functional tissues. The idea is to integrate microsystems fabrication technology and surface modifications with cellular components, with the aim of initiating and maintaining self-assembly and growth into biologically, mechanically and electronically interactive functional multi-component systems. The ability to control the surface composition of an in vitro system, as well as controlling other variables, such as growth media and cell preparation, all play important roles in creating a defined system for hybrid device fabrication. We are using self-assembled monolayers (SAMs) to control the intrinsic and geometric properties of surfaces in contact with these cellular systems. We have used the geometric control of the surface composition afforded us by SAMs to create in vitro circuits of rat hippocampal neurons. We have also demonstrated functional control of these systems by recording the electrophysiological signals on the patterned SAMs in response to stimuli and demonstrated geometric control of synaptic development. We have used geometric only cues to define axonal/dendrite polarity in developing hippocampal neurons which is a key step in creating engineered neuronal networks. Summed together these all represent a growing set of tools for building hybrid cellular systems. We are using this ability to integrate biological systems with silicon-based systems to create cell-based sensors for high throughput drug discovery and functional genomic assays as well as for hybrid neuronal/silicon systems to study biological computation. We are also using what we learn for a more fundamental understanding of cellular development and neuronal regeneration.

Dielectrics
Room: C-107 - Session DI+EL-ThA

Processing and Properties of Dielectric Materials
Moderator: C.J. Palmstrom, University of Minnesota

2:00pm **DI+EL-ThA1 Plasma Etch Processes for Ferroelectric Memory Integration**, ***F.G. Celii***, *M. Thakre, S. Summerfelt, S. Aggarwal, J.S. Martin, K.R. Udayakumar, T.S. Moise*, Texas Instruments

Embedded ferroelectric memory has the potential to enable increased functionality, reduced power, and potentially lower cost for portable electronics applications. In recent years, several companies have demonstrated lateral scaling of ferroelectric capacitors needed to realize high-density capacitor arrays consistent with low-cost requirements. In this paper, we summarize our current status towards integration of FeRAM capacitors into a CMOS flow, with emphasis on the etch processes. We review the various schemes for FeRAM integration and highlight our selected multi-height Via approach. In this approach, we define the Ir / PZT / Ir capacitors by a combination of hardmask and capacitor stack etches. Following encapsulation and interlevel dielectric deposition, the Via-0 pattern is applied and etched, utilizing a high-selectivity oxide etch to give the bi-level Via-0 etch profile. Electrical results from integrated and non-integrated capacitors will be presented.

2:20pm **DI+EL-ThA2 Electrical Properties of the $Bi_{4-x}La_xTi_3O_{12}$ Films Etched in Cl_2/Ar Inductively**, ***D.P. Kim***, *C.I. Kim, K.T. Kim,* Chung-Ang University, Korea, *A.M. Efremov*, Ivanovo State University of Chemistry and Technology, Russia

For last decade, Bi-layered perovskites materials including $SrBi_2Ti_2O_9$ and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) show high resistance to polarization fatigue due to Bi_2O_2 layers, which reduce space charges and the unpinning of domain walls. The BLT of 200 nm was spun-coated on the Pt/Ti/SiO_2/Si substrate by MOD. Pt thin films, which used as not only the top electrode but also as physical mask, were deposited on the BLT films. However, there is no report on the electrical characteristics of BLT thin films after etching process. BLT thins films were etched in Cl_2/Ar using ICP due to easy control bias power. The etch rates and selectivity of BLT thin films were investigated as a function of gas mixing ratio, rf power and dc-bias voltage. With adding 20 % Cl_2 in Ar 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 the ions of Ar were investigated in Cl_2/Ar plasma 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. According to our experiment, the etch rate of BLT highly depends on removing etch-product ($LaCl_2$: Tm = 2700 °C) effectively. After etching process, we obtained low remnant polarization value and high leakage current density compared with virgin sample. The degraded electrical properties of BLT were recovered after annealing at 800 °C for 1 hour.

Acknowledgement This work was supported by grant No. R01-2001-00268 from the Korea Science & Engineering Foundation.

2:40pm **DI+EL-ThA3 Formation of Al Oxynitride Alloys by Low-temperature Remote Plasma Nitridation**, ***C. Hinkle***, *G. Lucovsky*, North Carolina State University

Remote rf plasma nitridation of plasma deposited Al_2O_3 films was studied. Online Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and nuclear resonance profiling (NRP) are used to characterize the composition and spatial distribution of the resultant films. Al_2O_3 films were deposited by remote plasma enhanced chemical vapor deposition (RPECVD). Nitridation was carried out using 30 W rf power and a substrate temperature of 300 C. Nitrogen was introduced upstream diluted with Helium in a 60:160 ratio, and the process pressure was varied from 0.0325 Torr to 0.3 Torr. Nitridation at lower process pressures allows the plasma to extend into the processing chamber and results in greater nitrogen incorporation. Previous studies of nitrided SiO_2 have shown different fundamental nitridation mechanisms depending on process pressure and identified through different nitridation kinetics. In those experiments, low pressure nitridation in the plasma glow resulted in top surface nitridation by

N_2^+ ions while high pressure nitridation with the plasma confined in the generation tube produced uniform nitridation throughout the film via N atoms. A kinetics study of the plasma-nitrided Al_2O_3 films shows the data to fit an expression of the form, $[N] = A \{1\text{-}\exp(-Bt_N)\}$, where A increases inversely and exponentially with process pressure, B is a time constant that remains constant (within 10%) as process pressure changes, and t_N is the nitridation time in minutes. The fact that the time constant remains constant suggests that there is a single mechanism for the nitridation of Al_2O_3 that is associated with the N_2^+ ions that impinge on the oxide film.

3:00pm **DI+EL-ThA4 Heterostructured Cu-Based Electrode for High-Dielectric Constant Oxide Thin Film Devices**, ***W. Fan***, Northwestern University, *O. Auciello, S. Saha, J.A. Carlisle, D.M. Gruen,* Argonne National Laboratory, *R.P.H. Chang*, Northwestern University, *R. Ramesh*, University of Maryland

Copper (Cu) has recently been introduced as an interconnect material in integrated sub-micron circuit technology, due to its low resistivity and high electro- and stress-migration resistance. The main problems inhibiting its application as an electrode material in high-dielectric constant (k) thin film capacitors are the Cu oxidation and diffusion during the growth of the high-k layer at relatively high temperature in an oxygen environment. To overcome these problems, heterostructured Ti-Al/Cu/Ta multilayers were fabricated on SiO2/Si substrates using ion beam sputtering deposition. The Ta layer acts a diffusion barrier to prevent high temperature-induced diffusion of Cu into the Si substrate, while the amorphous Ti-Al alloy layer provides the protection against oxidation of the Cu film during growth of the high-k materials. The diffusion and oxidation resistance of the Cu-based heterostructured electrode layer was investigated using a variety of complementary characterization techniques, including x-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and four-point probe sheet resistance measurements. Analytical results showed that the Cu/Ta heterostructure remained intact through the annealing in 6 mTorr oxygen up to 600 °C. A thin oxide layer, formed on the Ti-Al surface, effectively prevented the oxygen penetration toward underneath layers. To test the feasibility of the proposed heterostructured electrode integrated with high-k thin films, complex oxide $(Ba_xSr_{1-x})TiO_3$ (BST) layers were then deposited on Ti-Al/Cu/Ta by magnetron sputtering. Polycrystalline BST film was obtained at 500 °C and 600 °C, and the measured permittivity and leakage current density were 170 ~ 330 (at zero bias) and $10^{-6} \sim 10^{-9}$ A/cm^2 (at 100 kV/cm) respectively.

3:20pm **DI+EL-ThA5 Investigation of the Interfacial Region of $(Ba,Sr)TiO_3$ Thin Films Deposited on Pt Substrates by MOCVD**, ***T.C. Kaspar***, University of Washington, *L.V. Saraf, C.L. Aardahl, J.W. Rogers, Jr.*, Pacific Northwest National Laboratory, *T.S. Dory*, Intel Corporation

Thin films of $(Ba,Sr)TiO_3$ (BST) have been extensively investigated as high-permittivity materials for microelectronics applications such as dynamic random access memory (DRAM) and advanced packaging components. By controlling the bottom electrode composition, electrode/film interface, and film stoichiometry and structure, the dielectric properties of the film can be tailored. In this study, BST thin films are deposited by MOCVD at low temperatures (500-575°C) using liquid delivery of metalorganic β-diketonate precursors on Pt/Ti/Si(100), Pt/Cr/Si(100), and MgO(100) substrates. A $(Ba,Sr)TiO_3$ film deposited on Pt/Ti/Si with a bulk composition of (Ba+Sr)/Ti = 57 / 43 forms a thick titanium-rich interfacial region at the platinum interface, with a composition of (Ba+Sr)/Ti = 36 / 64, which adversely affects the dielectric properties of the film ($\varepsilon_r = 84$). Since titanium enrichment is not observed in deposition on MgO substrates, the unique precursor chemistry that occurs on the platinum surface plays a role in the formation of the interfacial region. To better understand the effect of titanium non-stoichiometry on the dielectric properties, a BST film was deposited with a titanium-rich composition of (Ba+Sr)/Ti = 35 / 65. After annealing at 750°C, the film exhibited a low dielectric permittivity of $\varepsilon_r = 92$ and a leakage current density of $J_L = 8.7\times10^{-5}$ A/cm^2. The mechanisms of excess titanium incorporation in the interfacial region, its effect on the dielectric properties, and its reduction or elimination are discussed.

3:40pm **DI+EL-ThA6 Reduction of the k Value of the Low k Polyimide Film by Plasma Hydrogenation**, ***Y. Kuo***, *T. Chung*, Texas A&M University

For advanced VLSICs, the multi-level interconnection structure requires two types of materials: a low k dielectric and copper metal. Polyimide is one of the few dielectrics that have a low k value, e.g., < 3, and can stand a high annealing temperature, e.g., > 350°C. Previous, it was reported that when a polymer thin film was exposed to a hydrogen plasma, its material properties were drastically changed.[1] The hydrogenated film can be applied to many new areas. In this paper, authors report a plasma hydrogenation method that improves the dielectric characteristics of a low k polyimide thin film. We investigated the influence of the plasma process parameters to physical properties, such as the k value, the leakage current, and morphology, and chemical structure, such as the composition and bonding states, of a fluorinated polyimide film. The result shows that the k value was lowered from 2.7 to 2.3 after the hydrogenation process while the leakage current was still low, e.g., 10^{-9} Amp. Hydorgenation is an effective method in improving the dielectric characterists of the low k polyimide film. The process is compatible with current semiconductor processes.

[1] Y. Kuo, "Plasma Swelling of Photoresist," Jpn. J. Appl. Phys., 32(1), 1AB, L126, 1993.

4:00pm **DI+EL-ThA7 Materials Transformation and Kinetics in the Formation of Porous Low-K Polymer Dielectrics for Advanced Interconnect Technology**, ***P. Lazzeri***, *L. Vanzetti, M. Bersani, M. Anderle,* ITC-irst, Italy, *J.J. Park, Z. Lin, G.Y. Yang, R.M. Briber, G.W. Rubloff,* University of Maryland, *R.D. Miller*, IBM Research

The advance of Si ULSI technology requires the integration of very low K materials (i.e., low dielectric constant) into Cu Damascene interconnect schemes. To produce such low-K materials spin-casting and curing of multi-component polymeric precursor materials to form nanoporous films through selective degradation of one of the components (termed the porogen) is an attractive option, but process reproducibility and control, microstructure, and sensitivity to contaminating ambients during processing all present serious manufacturability challenges. We have used time-of-flight SIMS (ToF-SIMS) and XPS to investigate the chemical composition of a leading low-K candidate, polymethylsilsesquioxane (PMSSQ), and porous versions of PMSSQ, as a function of curing treatment to characterize reaction kinetics which accompanies formation of the low-K matrix and evolution of the volatile porogen to form a nanoporous microstructure. The PMSSQ matrix, with an average composition of Si(CH3)O1.5, shows only small changes in chemical composition upon curing. The formation of the nanoporous PMSSQ involves the degradation of the added porogen, poly(methylmethacrylate-co-dimethylaminoethylmethacrylate) (PMMA-co-DMAEMA) at elevated temperatures. The degradation products of the porogen are also evaluated by means of ToF-SIMS. The loss of the porogen and the evolution of the contaminants upon curing are observed to primarily occur in the range 125-450°C. These results show that such surface analysis methods may reveal the kinetics of critical materials transformations in these complex inorganic-organic hybrid systems, which are required for establishing the manufacturability of porous low-K dielectrics.

4:20pm **DI+EL-ThA8 Fluorinated Amorphous Carbon Films Prepared by Plasma Enhanced Chemical Vapor Deposition for Solar Cell Applications**, ***L. Valentini***, University of Perugia, Italy, *V. Salerni,* University of L'Aquila, Italy, *I. Armentano, J.M. Kenny,* University of Perugia, Italy, *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

Amorphous carbon a-C or a-C:H and/or diamond-like-carbon (DLC), has attracted attention as an environmentally benign and economically viable optoelectronic device material over others such as amorphous silicon (a-Si and/or a-Si:H) due to various advantage and therefore possibility to replace the existing technology based on the a-Si/a-Si:H.[1] Heterojunction diodes fabricated by plasma enhanced chemical vapor deposition of n-type fluorine-doped amorphous carbon (a-C:H:F) on p-type silicon are analyzed in terms of their electronic and photoresponse properties. The nature of heterojunction is confirmed by the rectifying current-voltage characteristic of a-C:H:F/p-Si junction. The photovoltaic behavior of the junction is presented as a function of both fluorine incorporation and thermal treatment of the a-C:H:F films after the deposition. The diodes made show a behavior dependent on the amount of the fluorine content. A better photovoltaic effects was observed from annealed a-C:H:F heterojunction structures. The optical and structural characterization performed by Raman spectroscopy and UV-VIS transmittance on films after the thermal treatment indicates that this behaviour is most likely due to an extended graphitization.

[1] H. A. Yu, Y. Kaneko, S. Yoshimura, and S. Otani, Appl. Phys. Lett. 68 (1996) 547.

4:40pm **DI+EL-ThA9 Dopant Penetration Studies in Hf Based Gate Dielectrics from Doped Polysilicon Films: Effect of Nitrogen in Penetration Robustness**, ***M.A. Quevedo-Lopez***, *H. Zhang, M.J. Kim, M. El-Bouanani, B.E. Gnade, R.M. Wallace,* University of North Texas, *M.R. Visokay, A. Li-Fateau, J.J. Chambers, A.L.P. Rotondaro, L. Colombo*, Texas Instruments Inc.

As the aggressively scaling of CMOS technology continues, high-κ gate dielectrics become one of the solutions in providing increased capacitance without remarkable increase in gate leakage current. However, issues such as thermal stability[1] and dopant penetration still require further study. Hf based films have been proposed as suitable candidates for advanced gate dielectric applications.[2] However, dopant penetration (B, As, P) following dopant activation annealing needs to be investigated. Recently, nitrogen incorporation in $HfSi_xO_y$ has been shown to be an efficient way to improve the thermal stability of Hf-silicate films, without compromising the electrical performance.[3] Dopant penetration studies (experimental and modeling) of boron, arsenic, and phosphorous from doped poly-crystalline silicon (poly-Si) through 4-5 nm thick $HfSi_xO_y$ and $HfSi_xO_yN_z$ into Si after aggressive annealing will be presented. XPS, HRTEM, RBS, and DSIMS results are presented. Dopant diffusivities in the dielectric films are calculated by fitting the dopant profile in the Si substrate to a reported model.[4] Implications for the use of these films as high-κ gate dielectrics on CMOS processing are also discussed. This work was supported by the Texas Advanced Technology Program, the Semiconductor Research Corporation, Texas Instruments, and DARPA.

[1] M. Quevedo-Lopez, M. El-Bouanani, S. Addepalli, J. L.Duggan, B. E. Gnade R. M. Wallace M.R.Visokay, M. Douglas, M.J. Bevan, and L. ColomboAppl. Phys. Lett. 79 (2001) 2958.

[2] For a review, see: G.D. Wilk, R.M. Wallace, and J. M. Anthony. J. Appl. Phys. 89, 5243 (2001).

[3] M.R. Visokay, J.J. Chambers, A.L.P. Rotondaro, A. Shanware, and L. Colombo, Appl.. Phys. Lett. 80, 3183 (2002).

[4] C. T. Sah, H. Sello, and D. A. Tremere, J. Phys.:Condens. Matter. 11, 288 (1959).

5:00pm **DI+EL-ThA10 Nanoporous MSSQ Films Characterised by Surface Acoustic Wave Spectroscopy and Brillouin Light Scattering**, ***C.M. Flannery***, Colorado School of Mines, *T. Wittkowski, K. Jung, B. Hillebrands*, Universitaet Kaiserslautern, Germany, *M.R. Baklanov*, IMEC, Belgium, *D.C. Hurley*, National Institute of Standards and Technology

Nanoporous methylsilsesquioxane films are a leading candidate for low dielectric constant (low-κ.) materials for microelectronic interconnect. However, mechanical strength reduces rapidly with lower density.(increasing porosity), yet there is a lack of techniques to characterize these properties in the κ~2 range. This work reports application of surface acoustic wave spectroscopy and Brillouin light scattering to characterization of the density/porosity and Young's modulus for a range of methylsilsesquioxane films from different manufacturers. Dispersion of laser-generated surface acoustic waves detected by both piezoelectric and optical methods yields density and stiffness measurements which are independently verified by specular X-ray reflectivity, ellipsometric porosimetry and Brillouin spectroscopy. Brillouin results also show that attenuation is related to pore size. Nanoindentation measurements consistently overestimate stiffness and we discuss why this is so. The behaviour of 3 sets of films show different stiffness-porosity relationships, the initially stiffer materials declining more rapidly with increasing porosity than the softer materials. This has important consequences for stiffness properties in the κ<2 region.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+NS-ThA

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

2:00pm **MI+NS-ThA1 Atomic-scale Surface Magnetic Structures of Mn_3N_2 Observed by Spin-polarized Scanning Tunneling Microscopy**, ***H. Yang***, *A. Smith*, Ohio University

The development of spin-polarized scanning tunneling microscopy (SP-STM) has made possible the imaging of surface magnetic structures in real space down to the atomic scale.[1] In this talk, we will discuss the magnetic structure of Mn_3N_2 (010) surface investigated using SP-STM with antiferromagnetic (AFM)-coated tungsten (W) tips. The Mn_3N_2 film was grown by molecular beam epitaxy. The surface structure of the film was studied in-situ. Normal STM images of Mn_3N_2 (010) obtained using W tips reveal row structures, corresponding to Mn atoms at the intersection of surface and N vacancy planes which occur every third atomic layer.[2] By using AFM-coated W tips, we observed a modulation in the height of the rows, which is attributed to the spin-polarized effect in which the tunneling current has a component which depends on the angle between the surface and tip magnetic moments. The row modulation implies that the Mn moments are ferromagnetic within a row but AFM from row to row. We show, using a new method, that it is possible to extract the magnetic component, which is proportional to the integrated local magnetization density of states.[3] The extracted magnetic component is compared with various surface spin models, which will be discussed. This work is supported by NSF under Grant No.9983816.

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[2] H. Yang, Hamad Al-Brithen, Arthur R. Smith, J. A. Borchers, R. L. Cappelletti, and M. D. Vaudin, Appl. Phys. Lett., 78, 3860 (2001).

[3] D. Wortmann, S. Heinze, Ph. Kurz, G. Bihlmayer, and S. Blugel. Phys. Rev. Lett., 86, 4132 (2001).

2:20pm **MI+NS-ThA2 Spin-Orbit Effects on Fe/W(110) Revealed by Scanning Tunneling Spectroscopy**, ***M. Bode***, University of Hamburg, Germany, *S. Heinze*, IBM Research Division, *A. Kubetzka, O. Pietzsch*, University of Hamburg, Germany, *X. Nie, G. Bihlmayer*, Forschungszentrum Jülich, Germany, *S. Blügel*, Universität Osnabrück, Germany, *R. Wiesendanger*, University of Hamburg, Germany

We have studied the dependence of the spin-averaged tunneling current on the direction of the magnetization experimentally on the well-defined model system Fe/W(110) with its well-known magnetic structure at the nanometer scale.[1,2] We found by scanning tunneling spectroscopy (STS) and first-principles calculations that the surface electronic structure of an Fe double layer on W(110) depends on the orientation of the magnetization. From a detailed analysis of the electronic structure we deduce how the signature of the magnetization direction is imprinted via the spin-orbit interaction. Our analysis reveals that it is not the splitting of bands but changes of the orbital character of certain bands which affects the tunneling current. As an important implication of this effect the magnetic nanostructure of surfaces can be investigated with a conventional nonmagnetic tip, similar to an earlier proposal by Bruno et al.[3] The underlying physics of the spin-orbit dependent differential conductivity can be considered as the static limit of the magnetic linear x-ray dichroism or the ballistic or tunneling analogon of the anisotropic magnetic resistance of ferromagnets.

[1] O. Pietzsch et al., Phys. Rev. Lett. 84, 5212 (2000).

[2] M. Bode et al., Phys. Rev. Lett. 86, 2142 (2001).

[3] P. Bruno, Phys. Rev. Lett. 79, 4593 (1997).

2:40pm **MI+NS-ThA3 Magnetic Imaging and Spectroscopy of $Fe_xNi_{(1-x)}$ Thin Films on Cu(111)**, ***Y. Sato***, *T.F. Johnson, S. Chiang*, University of California, Davis, *M. Hochstrasser, J.G. Tobin*, Lawrence Livermore National Laboratory, *A. Scholl*, Lawrence Berkeley National Laboratory, *J.A. Giacomo, D.B. Hoffman*, University of California, Davis

We are studying the system of FeNi/Cu(111) to understand the surface/interface magnetism relevant to the application of the giant magnetoresistive effect to magnetic recording heads. We have used X-ray Magnetic Linear Dichroism (XMLD) and Photoemission Electron Microscopy (PEEM) at the Advanced Light Source, and Low Energy Electron Microscopy (LEEM). Using XMLD, the dichroism signals from both the Fe and Ni peaks were measured, and the asymmetries were calculated. Both the Fe and Ni asymmetries as a function of temperature have been fit to the theoretical curve to extract the critical exponent β. Preliminary analysis indicates that for thicker films, the values are consistent with 3D mean-field magnetic models. As a function of Fe concentration x, the total weighted asymmetry, $A_T = xA_{Fe}+(1-x)A_{Ni}$, where A_{Fe} and A_{Ni} are the respective elemental asymmetries, shows a monotonic increase from 2% to a maximum of 8.5% for x~65%, near the bulk Invar concentration. For higher x, the asymmetry is quenched, indicating a magnetic transition taking place in the film system. This magnetic instability for high x agrees with the trends in Curie temperature as a function of x, as measured from XMLD spectra, PEEM data, and previous work on FeNi/Cu(100).[1] The PEEM images show a change in the domain structure of the films for x~42-55%. The domain structures are defined well by 180° domain walls, and their size is much bigger than for other concentrations. The magnetization appears to align along one of the crystal axes. Low Energy Electron Microscopy images of the growth of the films will also be shown.

[1] F.O.Schumann, S.Z.Wu, G.J.Mankey, R.F.Willis Phys.Rev.B 56, 2668 (1997).

3:00pm **MI+NS-ThA4 Falicov Award Presentation**

3:20pm **MI+NS-ThA5 Magnetic Resonance Force Microscopy at Millikelvin Temperatures**, ***H.J. Mamin***, *R. Budakian, D. Rugar*, IBM Almaden Research Center **INVITED**

Magnetic resonance force microscopy (MRFM) offers the promise of combining the spectral resolving power and three-dimensional imaging capabilities of magnetic resonance with the high resolution of scanning probe techniques. The greatest payoffs are expected once it is possible to detect and manipulate individual spins. There is now evidence that one of the greatest obstacles to reaching this goal is that of thermally-driven fluctuations in the magnetic tip, which interfere with the quantum state of the spins. For this reason, we have begun an effort to perform MRFM at millikelvin temperatures in a dilution refrigerator. Some essential technical improvements have been incorporated, included detection of the cantilever displacement with ultralow optical powers, and ultra-efficient generation of microwave fields using a superconducting resonator. Using this newly developed apparatus, we have successfully demonstrated MRFM on an ensemble of electron spins at millikelvin temperatures. We are investigating various nonequilibirum effects, including spin relaxation times, which will have important implications for the feasibility of single spin detection.

4:00pm **MI+NS-ThA7 Magnetic Force Microscopy Study of Various Lithography Patterned Magnet Arrays**, ***X. Zhu***, *P. Grutter,* McGill University, Canada, *V. Metlushko,* University of Illinois at Chicago*, B. Ilic,* Cornell University*, Y. Hao, F. Castano, S. Haratani, C.A. Ross, B. Vogeli, H.I. Smith,* Massachusetts Institute of Technology

Magnetic force microscopy (MFM) with in-situ magnetic field has been used to study lithography pattered magnet arrays: elongated elements, rings, disks, empty squares and sub 100 nm pseudo spin valve structures (PSV) (NiFe/Cu/Co). Great care has been taken to reduce the MFM tip stray field induced irreversible distortion by choosing a constant height mode, using small magnetic moment tips, operating in vacuum, and using a digital PLL.[1] This allows us to study the details of magnetic structures. For example, the nature of the head-to-head domain wall in a permalloy ring can be revealed, and the vortex structure with a core singularity in a permalloy disk can be found by high resolution imaging. In the PSV structures, the parallel and two different antiparallel configurations for both magnetic layers (NiFe and Co) in an element can be distinguishable. A local hysteresis loop technique has been developed to study the switching behavior of individual elements.[2] In a permalloy disk, the abrupt switching due to a nucleation or annihilation process has been revealed by monitoring cantilever frequency shift at a fixed location above the disk while sweeping the external magnetic field. In a PSV structure, the abrupt switching for both individual layers is clearly distinguishable. The hysteresis loop of patterned arrays can be obtained by MFM in the presence of an external magnetic field. The anisotropy induced by interdot coupling can be found in a closely packed square lattice disk array which shows a much smaller nucleation field along the (100) direction than the (110) direction. In the PSV structures, the layer coupling and the broad switching field distribution have been investigated through major and minor hysteresis loop obtained by MFM.

[1] X. Zhu, et al., J. Appl. Phys., May (2002).

[2] X. Zhu, et al., to be published in Appl. Phys. Lett.

4:20pm **MI+NS-ThA8 Magnetic Dipoles in Patterned Magnetic Metal Dot Arrays**, ***T.-H. Kim***, *J.H. Choi, Y. Kuk*, Seoul National University, South Korea

Magnetic dipole arrangement was studied with scanning tunneling microscope and magnetic force microscope (MFM) in patterned magnetic metal dot arrays. Magnetic dot arrays on silicon substrate were made by following procedures: (1) electron beam lithography, (2) shadow mask deposition, (3) electro-chemical anodizing of aluminum layer and successive deposition of magnetic metals. MFM image reveals individual magnetic dipole with small dot-dot interaction. The correlation between the shape anisotropy with the direction of magnetization will be discussed.

Microelectromechanical Systems (MEMS)
Room: C-210 - Session MM-ThA

Fabrication, Integration, and Packaging Techniques for MEMS

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

2:00pm **MM-ThA1 Addressing MEMS Reliability Through Innovative Fabrication, Integration, and Packaging Techniques**, ***V.M. Bright***, University of Colorado, Boulder **INVITED**

MEMS research at the University of Colorado in Boulder (UCB) has been focused on MEMS reliability through innovative design, materials, and fabrication. The UCB has applied techniques from other fields in a novel way to solve reliability issues in MEMS. This approach has improved the reliability of more traditional silicon-based MEMS. It also has resulted in a number of innovative new MEMS designs and applications. As the silicon-based MEMS manufacturing techniques mature and products transition from the R&D phase to production, the reliability aspects of MEMS design, fabrication, and packaging become more of a reality. It is known that MEMS reliability problems are related to nano-scale interface phenomena. One approach to solve MEMS reliability challenges is through novel materials and/or fabrication methods. Another approach is to improve MEMS reliability through proper design, which takes into account interface phenomena such as adhesion or charging. The barriers to MEMS reliability include: thin film structure susceptibility to adhesion due to large contact surface area and/or dielectric charging; limited life-time of microstructure due to friction and wear at micro-scale; multilayered structure change in curvature during thermomechanical loading or fabrication/packaging processes that require temperature cycling; multilayered structure stress relaxation over time, which may result in changing device functionality. In order to build reliable devices, advanced design knowledge must emphasize interactions among thermal, mechanical, chemical, and atomic effects bridging the necessary nano- and micro-scales. The fabrication must focus on nano-scale materials synthesis, characterization, material processing and packaging technologies that are critical to assure device reliability. The technologies that this talk is focused on include: atomic layer deposition of coatings, self-assembly of MEMS using surface tension forces, flip-chip MEMS assembly and packaging.

2:40pm **MM-ThA3 Development of Individually Addressable Micro-Mirror-Array for Space Applications**, ***S.B. Dutta***, NASA, Goddard Space Flight Center **INVITED**

MEMS is a strategic technology thrust area for NASA's missions of the 21st century. It will enable development of sensors and actuators for communication, navigation, propulsion and optical subsystems with low mass and power that operate in space environment. Currently, NASA is supporting MEMS technology development for the Next Generation Space Telescope (NGST), successor of the Hubble Space Telescope (HST) to be launched in 2009. NGST would have a Near InfraRed Multi Object Spectrometer (NIRMOS) that would use programmable slits to select multiple stars and galaxies for simultaneous observation. A team at NASA, Goddard Space Flight Center (GSFC), has developed aluminum, bi-state Micro-Mirror-Array (MMA) operating at 30K that could be used as programmable slits, to support science objectives of NGST. MEMS technology permits fabrication of MMA with self-contained actuation mechanism and direct interfaces to digital electronics. 32x32 MMA has been designed and fabricated using standard CMOS and surface micro-machining processes. The unit cell of MMA contains a square mirror on 100µm pitch and tilts by ± 10 °. The MMA are built on top of CMOS driven address and driver circuit for individual addressing and a CMOS compatible MEMS process has been implemented for compact design. The tilting of the mirrors is achieved by electrostatic attraction between two parallel plate aluminum electrodes. A pair of thin aluminum torsion straps is used so that the voltage required for tilting is less than 20V. The array has been tested successfully to operate at room temperature and at 30K for over 10^6 cycles. Operation of mirror elements has been simulated extensively. Experimental data are in good agreement with model predictions. For optimal operation of MMA, different alloy materials were studied for mirror fabrication. Electro-mechanical modeling, material property studies, fabrication, packaging and optical characterization of the MMA will be presented.

3:20pm **MM-ThA5 Transformer Coupled Plasma Etching of Polycrystalline 3C-SiC Films for MEMS Applications**, ***D. Gao***, *M.B.J. Wijesundara, C. Carraro, R.T. Howe, R. Maboudian*, University of California at Berkeley

Polycrystalline 3C-SiC films were etched by oxygen-mixed sulfur hexafluoride transformer coupled plasmas (TCP) in a commercial LAM TCP 9400 etcher for MEMS applications. The SiC films were grown by single-source CVD at 850°C using 1,3-disilabutane as the precursor.[1] Low-temperature CVD SiO_2 and plasma-enhanced CVD SiO_2 were employed as etching masks, which avoided micromasking phenomena and chamber contamination commonly involved when using metals as masks in most SiC etching processes. The SiC etch rates changed slightly with O_2 percentage, reaching maximum of 3800 Å/min at 16% O_2. Etching rate ratio of SiC/SiO_2 increased with O_2 percentage, reaching 2.6 at 50% O_2. By integrating the etching process into micromachining techniques, SiC-based micromechanical structures were fabricated. The etching profile and the chemical components of etched SiC surfaces were examined by cross sectional SEM and X-ray photospectroscopy respectively.

[1] C.R. Stoldt, et al., Proceeding of Transducers 01, the 11th International Conference on Solid-State Sensor and Actuators, Munich, Germany, June 10-14, 2001, pp. 984-987.

3:40pm **MM-ThA6 MEMS-based Gray-scale Technology**, ***C.M. Waits***, *A. Modafe, R. Ghodssi*, University of Maryland

Micro-electro-mechanical systems (MEMS) fabrication technologies originated directly from integrated circuit (IC) fabrication, consisting of primarily planar techniques. Consequently, structures fabricated for MEMS devices have been traditionally designed with nominally vertical sidewalls (dry anisotropic etching), undercut sidewalls (wet isotropic etching), or sidewalls with limited angles due to the crystallographic orientation of the substrate (wet anisotropic etching). There exists a breadth of potential applications for a fabrication technique that can achieve 3-D structures (arbitrarily sloped sidewalls) in silicon suited for small and large high aspect ratio MEMS structures. A micromachining technique using gray-scale lithography along with dry anisotropic etching enables the development of 3-D structures in silicon. The gray-scale lithography allows the fabrication of a differential-height photoresist-masking layer. The key components in gray-scale lithography include (a) design of the optical mask and (b) use of a projection lithography system. A sub-resolution optical mask and a photolithography stepper system together locally modulate the intensity of ultraviolet light through diffraction. The modulated light exposes a photoresist film to specified depths where a gradient height profile remains once developed. This method results in the fabrication of differential-height photoresist masking layers with up to 22 different height levels. The masking layers are then used in Reactive Ion Etching (RIE) to successfully transfer the structures in silicon, resulting in various shaped 9-micron tall silicon structures with sloped sidewalls ranging from 5 to 90 degrees with respect to the silicon surface. The results of preliminary characterization for both gray-scale lithography and RIE etching in silicon are presented.

4:00pm **MM-ThA7 Thick and Thermally Isolated Si Microheaters for Preconcentrators**, ***W.-C. Tian***, *S.W. Pang*, The University of Michigan

Thick, thermally isolated microheaters in Si are fabricated using high aspect ratio etching technology. These thick microheaters with large surface area provide large adsorbent capacity needed for high sensitivity preconcentrators in a micro gas chromatography system (µGC). Microheaters in this work are different from previous work which consisted of mostly thin poly-Si or metal microheaters (<2 µm) on top of the dielectric membranes. Instead, thick microheaters (>500 µm) surrounded by air gaps are generated to provide large surface area and good thermal isolation, which are important for high sensitivity, low power preconcentrator in a µmGC system. A 520 µm thick Si microheater with good thermal isolation has been made and its backside is anodically bonded to a pyrex glass substrate. To provide good thermal isolation, a 500 µm wide air gap around the microheater, thin poly-Si interconnects on top of dielectric membrane, and air gap isolation from the bottom glass substrate are used. Microheaters with 500 µm air gap can be heated up 50% faster to a temperature of 270 °C compared to those with 100 µm air gap, while the power consumption is 25% less and there is a larger temperature difference between the microheater and the bonding area. Operating the microheater in vacuum results in lower power consumption. At 250 °C, 38% less power is needed at 1.2 Torr compared to atmosphere pressure. Power consumption is further reduced by minimizing the contact area with the heater support substrate. Up to 33% power reduction has been demonstrated by placing heaters on thin membrane or etching trenches in supporting substrate. This is the first demonstration of using thick Si microheaters with air gap isolation for µmGC system. These thick, thermally isolated Si microheaters can provide good power efficiency, large adsorbent capacity, and high mechanical strength as preconcentrators.

4:20pm **MM-ThA8 Silicon Nitride Micromesh Bolometric Detectors for Planck**, ***M. Yun***, *T. Koch, J. Bock, W. Holmes,* Jet Propulsion Laboratory, *A. Lange*, California Institute of Technology

We report on the design, fabrication and testing of the bolometric detectors for the High Frequency Instrument (HFI) on the Planck Surveyor, ESA mission designed to image the Cosmic Microwave Background that is scheduled for launch in 2007. The bolometric detectors consist of NTD Ge thermistors indium bump-bonded to a fine mesh of silicon nitride. The mesh is metalized to efficiently absorb mm-wave radiation. Unmetalized support becomes excellent thermal isolation from the heat sink. The absorber geometries are of 2 types: one sensitive to both linear polarizations and optimized for background-limited sensitivity at 100, 143, 217, 353, 545 and 857 GHz, the other sensitive to a single linear polarization and optimized for background-limited sensitivity at 143, 217, 353 GHz. The detectors have NEP ~ 10^{-17} W/(Hz)$^{0.5}$ and time constants of several msec.

4:40pm **MM-ThA9 Piezoelectric MEMS for RF Filter Applications**, ***A. Wickenden***, *B. Piekarski, L. Currano, J. Pulskamp, R.G. Polcawich, E. Zakar, R. Piekarz, D. Washington, J. Conrad, M. Dubey,* U.S. Army Research Laboratory

Resonator arrays for RF filter devices operating in the GHz frequency range are of interest for lightweight, low power, high precision frequency selection applications. A high quality factor (Q) is required to reduce phase noise and ensure stability against frequency-shifting phenomena. MEMS-based resonator devices offer potential advantages in size, weight, and power consumption over surface wave acoustic wave (SAW) or bulk acoustic resonators currently used for frequency filtering applications. Piezoelectric electromechanical resonator devices should demonstrate advantages over equivalent electrostatic devices for high frequency applications, since they are less sensitive to degraded coupling strength as the device dimensions are reduced.[1] Resonant frequency response is determined by both device geometry and materials properties. PZT is attractive for piezoelectric filters due to its high piezoelectric coupling coefficient, although the operating frequency of PZT resonators is limited to the MHz range by the large acoustic time constant of the material. Piezoelectric materials such as aluminum nitride (AlN), zinc oxide (ZnO), and related alloys are of interest because their fast acoustic response times translate to theoretical maximum frequencies of >100 GHz.[2] Models are being developed to predict the response of piezoelectric MEMS resonators. These models are currently being validated using PZT resonator devices with beam lengths ranging from 400µm to 20µm, with natural frequencies in the MHz regime. Deviation from standard mechanical models has been observed in the measured response of these devices having lengths less than 50µm. The fabrication, testing, and modeling of piezoelectric PZT resonator devices will be discussed, and the extension of the predictive models to alternate materials systems and submicron geometries for GHz applications will be outlined.

This work is supported in part by DARPA

[1] D.L. DeVoe, Sensors and Actuators A 88, 263-272 (2001)

[2] A. Ballato, "Micro-electro-acoustic Devices for Wireless Communication," IEEE Sarnoff Symposium on Advances in Wired and Wireless Communications (March 1999)

5:00pm **MM-ThA10 Micro-Thermal Conductivity Detector for Chemical Sensing**, ***D. Cruz***, UCLA and Sandia National Laboratories, *J.P. Chang*, University of California, Los Angeles, *F. Gelbard, R.P. Manginell, S.K. Showalter, L.J. Sanchez, S.S. Sokolowski, M.G. Blain*, Sandia National Laboratories

Microsensors are essential for detecting biological and chemical warfare agents in state-of-the art micro chemical analytical systems. We have designed and fabricated a micro thermal conductivity detector to analyze the effluent from a gas chromatography column (GC). The TCD can be integrated with a micro-GC column to form a complete "lab-on-a-chip" separation-detection scheme. The TCD consists of a two-flow cell Wheatstone bridge circuit where the resistor elements are suspended by a thin SiN$_x$ membrane in pyramidal and trapezoidal shaped flow cells. A four-flow cell detector can also be constructed for doubling of sensitivity. Rapid computational prototyping by simulating the heat transfer in the TCD with a Boundary Element Method enables a cost-effective way of optimizing the TCD geometries yielding the greatest sensitivity. Two flow patterns, six operating temperatures, five heater sizes, and five channel widths were theoretically investigated, and the optimal geometry along with eight additional promising geometries was fabricated. The change in heat flow versus the change in gas thermal conductivity (dQ/dk) of He was first determined to verify the simulation results. Nitrogen and a carbon-fluorocarbon were added as effluents to the He gas stream. The voltage response in the Wheatstone bridge changed by approximately 40% and 70% respectively. A four-cell detector was used, where He was flowed at 5 sccm through 2 reference resistors and a mixture of the carrier gas (He) and effluent was flowed through the other two resistors. The measured voltages yielded heat flux values that consistent with the theoretical values. In addition; results verified that convection became a dominant effect over conduction when the carrier gas was flowed at a rate greater than 10 sccm.

[1] 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.

Nanometer Structures
Room: C-207 - Session NS-ThA

Nanowires
Moderator: D.A. Bonnell, University of Pennsylvania

2:00pm **NS-ThA1 Biofunctionalized Nanowires for Biosensing and Assembly**, ***C.D. Keating***, The Pennsylvania State University **INVITED**

This presentation will focus on the characterization, derivatization, and some applications of segmented metallic nanowires having stripes of different metals along their length. These particles are prepared by sequential electrodeposition of metals (e.g. Au, Ag, Pd, Pt, Co) within the pores of alumina or polycarbonate templates, and typically range from 30-300 microns in diameter and up to 10 microns in length. They can be released from the template and derivatized with proteins or nucleic acids for use in sensing or assembly. The metal segments can be used as an optical barcode to enable multiplexed bioanalysis or as a chemical pattern to spatially control (bio)chemical derivatization along the length of the particle. Both multiplexed bioanalytical applications and DNA-directed nanowire assembly will be discussed.

2:40pm **NS-ThA3 Aligned Dielectrophoretic and Electrophoretic Deposition of Single Wall Carbon Nanotubes**, ***P.E. Pehrsson***, Naval Research Laboratory, *J.W. Baldwin*, NRC/NRL Postdoctoral Fellow, Naval Research Laboratory

Carbon nanotubes offer real promise for a variety of nanotechnology applications such as resonator arrays for RF electronics, sensors, and other devices. We use dielectrophoresis (DEP) and electrophoresis (EP) to position nanotubes on surfaces and then measure their electrical conductivity. We vary the solution concentration and sonication procedures to control tube aggregation. We also use functionalized single-wall nanotubes (SWNTs), e.g. fluorinated, oxidized or with attached organosilanes. Functionalization can introduce potentially charged species such as carboxylic acid and may also change the nanotube's conductivity and permittivity, both of which may enhance its susceptibility to dielectrophoresis. The resistance across a gap spanned by a few tubes is typically above a MΩ, but resistance across the gap drops sharply (to 10-20 kΩ) at higher tube densities, possibly due to formation of a continuous percolation network. Tube purity is critical for good deposition. Contaminant particles in the suspension alter the deposition under specific deposition conditions. Some particles are unassociated with nanotubes and respond to the electric fields like other dielectric particles. Other particles (possibly leftover Ni nanocatalyst or amorphous carbon) are attached to the tubes and may pull them along in response to the fields. We are evaluating the interplay between surface chemistry on the nanotubes and at the electrode/liquid interface and the forces governing DEP and EP. DEP makes particles move in the direction of higher or lower electric field depending on the relative frequency-dependent conductivity and permittivity of the solvent and particle, and the particle size, shape, and surface chemistry. It could ultimately solve two of the biggest problems impeding the exploitation of carbon nanotubes; 1) separation of metallic and semiconducting nanotubes; and 2) removal of non-nanotube contaminants without the need for aggressive acid cleaning.

3:00pm **NS-ThA4 Functionalizing Molecular Lines on H-Si(100)**, ***P. Kruse***, *D.D.M. Wayner*, *R.A. Wolkow*, National Research Council of Canada

SPM-based lithography on H-terminated Si(100) and Si(111) surfaces has received considerable attention in recent years. It is based on stepwise controlled removal of H-atoms and subsequent reaction of molecules with the resulting Si-radicals (dangling bonds). Previously, we have reported the remarkable capacity of styrene to induce a chain reaction on these surfaces, resulting in self-directed line growth along dimer rows in the case of the Si(100) surface.[1] We have now examined a number of avenues for creating lines with built-in functionality. The incorporation of heteroatoms such as nitrogen in vinyl pyridine would be desirable, but the facile interaction of the lone electron pair of the nitrogen atom with the silicon dangling bonds prevents line growth. Aldehydes such as benzaldehyde are shown to undergo the same line growing mechanism as their vinyl compound analogues such as styrene. This offers the unique opportunity to create functionalized molecular lines by exposing the surface to dialdehydes. It is shown that in a rigid molecule such as terephthaldicarboxyaldehyde only one aldehyde group per molecule reacts with the surface whereas the other group is available for further reactions. This study seeks to open avenues for customizing molecular lines from self-directed growth for a wide variety of applications. Lines with preserved reactive groups or metal-complexing abilities can serve as devices or conducting wires on the surface and become building blocks of molecular electronics.

[1] G.P. Lopinski, D.D.M. Wayner, and R.A. Wolkow, Nature 406, 48 (2000).

3:20pm **NS-ThA5 Growth, Properties and Applications of Semiconductor Nanowires[1]**, ***L. Samuelson***, Lund University, Sweden **INVITED**

One-dimensional (1D) semiconductors, or nanowires, have interesting physical properties and may offer possibilities to realize ultra-small electronic and photonic devices[2] as well as new kinds of circuitry.[3] Well defined nanowires (or nanowhiskers) can be formed using size selected catalytic nanoparticles to induce growth. By locating individual nanoparticles on predefined locations on a substrate also the position of the nucleation of individual nanowires may be controlled.[4] It was recently shown that not only homogeneous nanowires, but also multi-heterostructures with good electronic properties may be formed within a nanowire, even for combinations of materials having large differences in their lattice constants.[5] I will describe results from our studies of the electronic properties of heterostructures and will present examples of 1D heterostructure nanoelectronic devices created in nanowire systems.

@super 1@ I want to ackhowledge contributions from a number of students and colleagues (see author lists in refs. 5 and 6), especially Jonas Ohlsson on whisker growth, Mikael Bj@um o@rk on physics investigations and Prof. Reine Wallenberg on transmission electron microscopy.

@super 2@ K. Hiruma et al., "GaAs p-n junction formed in quantum wire crystals", Appl. Phys. Lett. 60, 745 (1992)

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4:00pm **NS-ThA7 Metal-Catalyzed Nanowires for Integrated Devices and Interconnections**, ***T.I. Kamins***, *X. Li*, *T. Ha*, *R.S. Williams*, Hewlett-Packard Laboratories

As integrated-circuit technology progresses, interconnections between active devices become more important in determining overall circuit and system density and performance. Without special circuit techniques, interconnection delays can degrade circuit performance even if the device speed improves. Defining multiple levels of fine wires by conventional lithography becomes increasingly difficult as dimensions decrease, and defining wires by advanced techniques becomes attractive. Wires can be formed at the nanoscale by nanoimprint lithography or by self-assembly techniques such as anisotropic lattice-mismatched epitaxy or metal-catalyzed nanowire growth. The latter is especially attractive because the surfaces are formed by growth, rather than by etching, which can cause crystal damage. The catalyzing nanoparticles can be in the liquid phase or possibly in the solid phase during growth. Nanowires formed by self assembly can be used as interconnections between devices, and devices can also be formed within the nanowires, allowing close integration of the nanowires and devices. If the nanowire is uniformly doped, tradeoffs must be made between the series resistance in the interconnection and the ability to deplete the wire in the device region, limiting performance. Requiring the maximum depletion region to be at least half the wire diameter limits the conductance of the interconnection, and therefore the charging time of the device, to possibly unacceptable values. If portions of the wire can be selectively doped, the interconnecting region and the device can be separately optimized.

4:20pm **NS-ThA8 Gadolinium Silicide on Si(100)**, ***B.C. Harrison***, *J.J. Boland*, University of North Carolina at Chapel Hill

The fabrication and characterization of nanoscale structures is motivated by the desire to produce materials and devices with novel optical, structural, and electronic properties. A large part of this effort involves discovering ways to replace current microelectronic technology with faster and cheaper nanostructures. One system of current interest is lanthanide silicide nanowires that spontaneously self-assemble on the Si(100) surface.[1,2,3] The high aspect ratio, large mechanical strength, micrometer length scales, and metallic character[3] suggest applications as nanoscale interconnects. However, these wires cannot be successfully used in electronic circuits until the morphology and placement is controlled and their electrical properties are well characterized. This study focuses on the morphology and electrical properties of Gadolinium silicide since this silicide has the smallest lattice constant mismatch in the wire growth direction of any of the available lanthanide silicides. Scanning Tunneling Microscopy (STM) is used to study the atomic structure of the nanowires and the wetting layer that grows by a Stranski-Krastanov mechanism while the local electrical properties of these structures are probed by STS.

[1] Chen, Y.; Ohlberg, D. A. A.; Williams, S. J. Appl. Phys. 2002, 91, 3213.

[2] Chen, Y.; Ohlberg, D. A. A.; Medeiros-Riberio, G.; Chang, Y. A.; Williams, S. Appl. Phys. Lett. 2000, 76, 4004.

[3] Nogami, J.; Liu, B. Z.; Katkov, M. V.; Ohbuchi, C.; Birge, N. O. Phys. Rev. B 2001, 63, 233305-1. .

4:40pm **NS-ThA9 Atomic Structure and Electronic Properties of Rare Earth Silicide Epitaxial Nanowires on Si(001)**, ***J. Nogami***, Michigan State University

Several groups have recently reported growing nanowires of rare earth (RE) metal silicides on the Si(001) surface.[1,2,3] These nanowires grow by self assembly during the deposition of the RE metal on the Si(001) surface. They have many desirable properties such as crystalline structure, metallic conduction, and micron scale length. Recent STM and STS results on Dy and Ho silicide nanowires will be shown. Metal coverage, growth temperature, substrate step density, and post growth annealing duration all have strong effects on the nanowire morphology and surface density. Macroscopic transport measurements on nanowire networks will also be discussed.

[1] C. Preisenberger et al, J. Phys. D 31,L43 (1998)

[2] Y. Chen et al, Appl. Phys. Lett. 76, 4004 (2000)

[3] J. Nogami et al, Phys. Rev. B 63, 233305 (2001).

5:00pm **NS-ThA10 Fabrication of Low-dimensional Nanostructured Substrates**, ***M. Yoshimura***, Toyota Technological Institute, Japan, *K. Ojima*, NIMS, Japan, *K. Ueda*, Toyota Technological Institute, Japan

A clean Si(110) surface is reconstructed into so-called "16x2" superstructure, where pentagonal silicon clusters (hereafter, "pentagons") form one-dimensional up-and-down terrace structure with monatomic layer (0.2 nm) in height and about 5 nm in periodicity. This structure is expected to be a novel template for low-dimensional nanostructures. Since high step-density in this surface is due to relaxation of surface stress caused by formation of pentagons, it is possible to control the terrace width by modifying surface stress intentionally. Recently we succeeded in increasing terrace width by about 50% in Sn/Si(110) system. In this surface, Sn atoms form trimers, which are inserted into the pentagons. Then the spacing between pentagons is increased, giving lower surface stress and lower density of steps. Thus the arrangement of pentagons dominates surface structure in Si(110). However, the atomistic processes of rearrangement have not yet been clear. Here we first demonstrate the control of dimensionality of Si(110)-16x2 surface, namely, single or double domain, by using tilted wafers. We found that the epitaxial growth of metals on these surfaces was completely different from each other. Secondly, we examined adsorption of other metals on Si(110) to see how the pentagons change their positions and how the surface stress is relaxed. In contrast to Sn/Si(110), the up-and-down terraces immediately annihilate on Ag/Si(110) system. Lastly we compare the case of Ge(110), which forms a similar 16x2 structure, and discuss the mechanism of stress relaxation in (110) surface based on above results.

Photonic Materials Topical Conference
Room: C-111 - Session PH-ThA

Optical Lightguides
Moderator: S. Shankar, Intel

2:00pm **PH-ThA1 Tunable Microfluidic Optical Systems**, ***J.A. Rogers***, Bell Laboratories, Lucent Technologies **INVITED**

This talk describes some of our recent work on pumped microfluidic networks for new classes of dynamically tunable fiber and integrated optical components. It presents two different types of devices. The first combines microstructured, or "holey", silica fiber with microfluidic plugs that can be tuned and pumped back and forth in the fiber using thermal pumps formed directly on the fiber surface.[1] We present two examples of devices that use this microfluidic optical fiber design. One relies on dual-fluid plugs and long period fiber gratings; this component provides variable, wavelength-tunable attenuation for dynamic gain equalization in wavelength division multiplexed optical networks. The other uses fiber tapers; it provides a broadband variable attenuator that can be useful at add/drop nodes. The second class of system combines electrowetting pumps and recirculating planar microfluidic channels with fiber and integrated optical structures. We describe the fluidic and optical physics of these devices, and we demonstrate the performance of several different components that use this design.[2]

[1] P. Mach, C. Kerbage, M. Dolinski, K.W. Baldwin, R.S. Windeler, B.J. Eggleton, J.A. Rogers, "Tunable Microfluidic Optical Fiber," Applied Physics Letters, in press.

[2] P. Mach, T. Krupenkin, S. Yang, J.A. Rogers, "Dynamic Tuning of Optical Waveguides with Electrowetting Pumps and Recirculating Fluid Channels," Applied Physics Letters, submitted.

3:00pm **PH-ThA4 A New Generation of Plastic Optical Fiber**, ***W.R. White****, L.L. Blyler, R. Ratnagiri*, OFS Laboratories **INVITED**

During the last few years, there have been revolutionary advances in plastic optical fiber (POF) technology as a result of fibers based on perfluorinated polymers, especially poly(perfluorobutenylvinylether), commercially known as CYTOP.[1,2] Due to these new materials, the attenuation obtainable in POF has plummeted from 160 dB/km to less than 20 dB/km, and wide transmission windows have been opened in the commercially desirable wavelength range between 850 and 1300 nm. Moreover, graded-index POF(GI-POF) has been shown[3,4] to have unexpectedly large bandwidths, due to subtle interplay between low material dispersion,[4,5] high mode coupling,[4,5] and differential mode attenuation.[6] How can the remarkable properties of perfluorinated GI-POF be harnessed to deliver an extremely simple, longer reach, high bandwidth medium? To meet this goal, perfluorinated GI-POF must offer aspects of both older POF technologies and silica fiber technologies. From the POF tradition, it is important to retain simplicity of fiber termination and connector attachment. From the silica fiber tradition, we must replicate not only low attenuation and high bandwidths, but also low loss connectors and sophisticated cable designs. In this talk, I will discuss some highlights of our work to develop practical technologies for fabricating, cabling, terminating, and connectorizing perfluorinated GI-POF.

[1] Y. Koike, Proceedings of ECOC '96, v.1 p.141 (1996).

[2] K. Koganezawa and T. Onishi, Proceedings of POF Conference 2000, p.19 (2000).

[3] G. Giaretta, W.R. White, M. Wegmuller, and T. Onishi, IEEE Photonics Tech. Lett., v.12, p.347 (2000).

[4] G. Giaretta, et al, Proceedings of ECOC '99 (1999)

[5] W. R. White, M. Dueser, W. A. Reed, and T. Onishi, IEEE Photonics Tech. Lett., v.11 p.997 (1999).

[6] T. Ishigure and Y. Koike, Proceedings of POF Conference 2000, p.14 (2000).

4:20pm **PH-ThA8 Influence of Ge Content and Process Parameters on the Optical Quality of Low Temperature PECVD Deposited Silica Waveguides**, ***M. Dainese****, L. Wosinski, H. Fernando, X. Cao*, Royal Institute of Technology, Sweden

Silica-on-Silicon technology for Planar Lightwave Circuits, based on Plasma-CVD, is a candidate for monolithic optoelectronic integration due to its potential compatibility with VLSI technology. But the standard fabrication process, that includes a final high temperature (≥1000°) consolidation step, is not compatible with this purpose. We propose a modified, full low temperature, PECVD-based process that has been optimized to obtain an as-deposited material with high optical quality. Using a capacitively coupled reactor, with 380kHz RF power supply and platen temperatures between 250° and 300°, we have investigated the properties of the as-deposited material, with emphasis on germanium doped silica glass, which forms the light guiding layer. The set of characterisation techniques includes: prism coupler, wet etch rate, FTIR, XPS, ERDA. The results show that, for pure silica, stoichiometry is controlled by the N_2O/SiH_4 flow ratio, whereas RF power affects the material structure and homogeneity, together with by-products release during surface processes. For a given SiH_4 flow and flow ratio, there is an optimum value for the deposition pressure which maximise the deposition rate (here 1750Å/min). In case of germanium doping (up to 6.5at%), the high reactivity and low surface mobility of germane radicals make the deposition more sensitive to platen temperature and produce films with higher porosity and co-ordination disorder, compared to pure silica. We demonstrate that increasing the flow ratio is not enough anymore to obtain correct stoichiometry and RF power becomes a critical variable with respect to this. The final result is a material with low optical losses (0.3dB/cm at 1.55µm), with no absorption due to higher order harmonics of either Si-H or N-H bond vibrations. Examples of photonic devices will be presented.

4:40pm **PH-ThA9 High Density Plasma Enhanced Chemical Vapor Deposition of SiOxNy for Optical Applications: Influence of Process Parameters**, ***P. Bulkin****, D. Daineka, G. Girard, J.-E. Bourée, B. Drévillon*, CNRS, Ecole Polytechnique, France

Rapid development of integrated optics made necessary the development of the technology for fast deposition of high quality optical films that can be used as a base for waveguide fabrication. Such process shall not only produce silica films with low scattering and absorption in the communication window (1.3-1.6 microns) but also allow doping of the silica in order to create graded refractive index profiles and, maybe even convert it to active media. High-density plasma sources for PECVD, such as ECR, helicons and inductively coupled sources, are prime candidates considered for those applications. However, a process window for high density PECVD needs to be optimised for the deposition of films with thickness of several tens of microns. The deposition systems should also incorporate self-cleaning capabilities. We report in this work on extensive studies of a recently developed matrix distributed electron cyclotron resonance (MDECR) concept for the deposition of silica and silicon oxynitride films. We investigated influence of substrate temperature, microwave power, position and type of gas injection, gas composition and bias on the properties of material grown in such deposition system. Self cleaning by C2F6/O2 plasma was also studied. We show that the MDECR concept can be a technology of choice for the deposition of waveguide structures for integrated optical components.

Processing at the Nanoscale
Room: C-109 - Session PN-ThA

Charged Particle Patterning and Emission

2:00pm **PN-ThA1 Nanoscale Electron Beam Stimulated Processing**, ***P.D. Rack****, R.C. Burns, Y. Deng, Y. Choi, D.C. Joy*, University of Tennessee

The ability to manipulate materials at the nanoscale is critical for the nanotechnology revolution that is occurring. To intelligently design and or repair nanoscale devices requires techniques to selectively and nanoscopically deposit and remove material in a controllable fashion. Current techniques to selectively deposit or etch microscopic features utilize ion beam deposition and etching, laser ablative etching using far field and near field optics, and mechanical abrasion using a fine microtip. In this paper we will discuss electron stimulated nanoscale processing. The experimental set-up for the process will be presented and experimental results for electron stimulated nanoscale processing will be shown. The relevant electron-solid, electron-gas, and gas-solid interactions that are critical for nanoscale electron beam processing will be discussed. The effect that the beam energy has on the reaction rate for stimulated deposition and etching will be illustrated and the growth kinetics will be discussed. To minimize the effective spot size, strategies to control surface diffusion as well as electron-gas scattering will also be discussed.

2:20pm **PN-ThA2 Electron Beam Patterning with Carboneous Contamination Rezists below 10 nm Linewidth**, ***M. Malac***, University of Alberta, Canada, *J. Lau,* Brookhaven National Laboratory, *R. Egerton, M. Freeman,* University of Alberta, Canada, *Y. Zhu*, Brookhaven National Laboratory

We have studied the processes determining the resolution limits of contamination patterning in a transmission electron microscope (TEM) as a means to produce magnetic nanostructures. By optimizing the exposure parameters we achieved linewidth of 7 nm. Sputter etch was used to transfer the pattern to cobalt, permalloy and bismuth films on silicon nitride membranes. Previously the resolution of the technique was determined by the crystallite size of the patterned film.[1] We have investigated patterning of our structures within one large crystallite and we have studied the limitations dictated by the kinetics of the surface diffusion processes. A comparison of pattern writing at conditions when importance of surface diffusion is suppressed (high dose rate and high writing speed) with diffusion controlled writing (slow writing at low dose rate) was made. We have explored the reproducibility and suitability of different types of materials for precontaminating the samples. Transmission electron microscopy, electron holography, electron energy loss spectroscopy and high resolution TEM was used to characterize structure and to study properties of such structures.

[1] Broers et al, Appl. Phys. Letters 29 (9), 1976 page 596.

2:40pm **PN-ThA3 A Study of PMMA EBL Cross-sections Prepared by a Novel Process**, ***W. Hu***, *T. Orlova, G.H. Bernstein*, University of Notre Dame

We have developed a novel technique of silicon cross-section preparation with high breaking precision with which we have studied cross-section profiles of sub-50 nm electron beam lithography (EBL) patterns in PMMA resist, including post-exposure aging effects. This technique enables us to break our samples along a desired axis with about 1 µm precision, and gives cross-sections allowing imaging with scanning electron microscope (SEM) at any angle. This is a complementary method to cleaving, wedge-polishing and focused ion beam, the last two of which create damage to the surface of the exposed edges. The precise breaking of the wafer or small sample was accomplished by high-aspect-ratio plasma etching of a 2~10 µm wide line in an inductively coupled plasma etcher using the Bosch process (Alcatel 601E) with small sample areas in the line unetched for EBL. After EBL, wafers were broken along the etched line using a simple mechanical. Cross-section studies can provide improved information on the nanometer scale about PMMA EBL profiles, development contrast, and the metal or molecule liftoff process. However, damage to PMMA by the SEM imaging, cross-section preparation and sample metal coating interfere with data analysis. We have developed an optimized process which enables us to obtain nearly original PMMA EBL profiles by coating samples with AuPd alloy using thermal evaporation first and followed by a plasma sputter coating. The fully-covered PMMA trenches are broken along the desired axis and imaged with our Hitachi S-4500 cold cathode field emission SEM. Using these techniques, we studied the aging effect of PMMA resist before development of EBL, which is seldom taken into consideration in fabrication processes. Our cross-section results of PMMA EBL trenches indicate a loss of contrast due to one week aging prior to development, and will result in unsuccessful liftoff. Other cross-sectional views of EBL in a variety of resists will be discussed.

3:00pm **PN-ThA4 Nanometer Scale Patterning of Dielectric Surfaces with Combined Electron/laser Beams and Chemical Exposure**, ***K.H. Nwe***, *J.T. Dickinson*, Washington State University

We examine the nanometer scale patterning of insulating surfaces exposed to simultaneous beams of radiation and reactive chemicals. Specifically, we show that ionic crystals in the presence of low pressure water exposure leads to rapid material etching in self-organized patterns under UV laser or keV electron irradiation. Radiation effects on reactive layers on single crystal inorganics are poorly understood. We find that dense ordered arrays of highly oriented nanoscale conical structures, with aspect ratios greater than 200, are produced under such exposure. We show that the nanostructure formation mechanism involves photo/electron stimulated decomposition of the matrix via defect mediated interactions. Using time resolved mass spectroscopy we are able to provide detailed kinetics for these electronic etching processes.

3:20pm **PN-ThA5 Field Emitter Arrays with Sharp Tips for THz Microwave Source**, ***C. Peng***, *S.W. Pang*, The University of Michigan

Ballistic tunneling transit time device consists of a field emitter cathode, a drift region, and a collecting anode. These new transit time devices can produce mW level power in THz range with optimized operating voltage and anode to cathode separation. The field emission devices also need to have sharp tips, high emission current, low threshold voltage, and small dimensions for high packing density. In this work, nanofabrication technology to generate large arrays of sharp Si field emitters is developed. Sharp Si tips with tip radius of 20 nm are fabricated by dry etching with Cl_2 in an inductively coupled plasma system. The tip sharpness, height, and profile are controlled by balancing the lateral etch rate of the SiO_2 mask and the vertical etch rate of the Si substrate. It is found that tip height and tip radius vary with rf power applied to the plasma source and the etch time. Tip height decreases with rf power and increases with etch time, while tip radius increases with source power and decreases with etch time. Uniform, large arrays of Si field emitters are formed with tip density of $1.1x10^7$ tips/cm^2 and tip height varying from 2 to 4 µm. For these field emitters to function as THz microwave source, close tip to anode spacing in the range of 0.5 to 2 µm is needed. Etch time, spacer, and bonding technology are used to provide flexible and precise control of the tip to anode distance. In addition, emitter tip sharpening by oxidation and coating the tips with low work function materials will be studied to improve the emission current characteristics.

3:40pm **PN-ThA6 Structure and Field Emission Properties of SiC Nanotip Arrays Fabricated by Electron-cyclotron-resonance Plasma Process of Monolithic Si Wafer**, ***L.C. Chen***, National Taiwan University, *H.C. Lo, J.S. Hwang, J.S. Hsu,* Institute of Atomic and Molecular Sciences, *C.F. Chen,* National Chiao-Tung University, Taiwan, *D. Das, K.H. Chen*, Institute of Atomic and Molecular Sciences

Fabrication of SiC nanotip arrays of a few microns in height and around 1 nm in diameter at the tip and of density as high as 10^{12}cm^{-2} is reported. The mechanism of the nanotip formation by electron cyclotron resonance (ECR) plasma process and detailed structure analyses using high resolution TEM will be presented. It is concluded that the tips are primarily composed of SiC. The nanotip arrays showed magnificent field emission property with typical field emission current of 0.5 mAcm^{-2} at an applied field as low as 0.8 V/µm. Furthermore, the nanotip arrays also exhibited excellent stability, as evident by temporal evolution of the emission current at a constant applied voltage measurement which showed less than 3% fluctuation in one hour. The SiC nanotip array produced by ECR-plasma process of monolithic Si wafer offers a reliable, economic field emission electron source alternative to carbon nanotubes. Formation of the SiC nanotip on top of a Si cantilever has also been demonstrated. Such geometry provides potential applications in ultrahigh resolution SPM and field emission microscopy.

4:00pm **PN-ThA7 Field Emission from Well-Aligned Heterojunctions of Carbon Nanotubes and Silicon Nanowires**, ***M. Lu***, *M.-K. Li, H.-L. Li*, Lanzhou University, P.R. China

Silicon nanowires (SiNWs) has recently attracted much attention due to its unusual properties. However, it is easily oxidized in air, which can hurt the uniformity and the efficiency of electron emission. It is our motivation to design nanowire/tube growth process and fabricate well-aligned CNTs/SiNWs heterojunctions by chemical vapor deposition (CVD) based on AAO template-synthesis method.[1] It is clearly observed from SEM and TEM images the junctions consist of a core-sheath structure and have a highly-orientation. The filling material is proved to be a polycrystalline Si from SAED pattern. Field emission measurements show the turn-on field of the junctions decreases to ~7 V/µm from ~14 V/µm (pure SiNWs) and the maximum emission current density increases to ~35 mA/cm^2 from ~3 mA/cm^2 (pure SiNWs). A significant improvement in the turn-on field, the total emission current and the emission stability is apparent from the junctions compared with pure SiNWs. We also notice that the threshold field is in the range of 22-25V/µm for the junctions. The Fowler-Nordheim plot almost follows a linear relationship that indicates the field emission from the junctions is a barrier tunneling, quantum mechanical process. Moreover, the field emission increased with decreasing diameter of the junctions. During 24 h of continuous operation at 5 mA/cm^2, the current fluctuation was as low as ±4% and the average current did not decrease over this period. When a sample was found to air for weeks after it was grown, it exhibited essentially the same emission behavior as the freshly grown surface. This suggests that the sheath of CNTs is indeed stable and chemically inert.

[1], C.W. Wang, M.K. Li, and H.L. Li, Science in China 44(2), 234 (2001)

4:20pm **PN-ThA8 Evolution of Surface Morphology and Microstructure during Ion Sputtering of Diamond**, ***D.P. Adams***, *T.M. Mayer, M.J. Vasile*, Sandia National Laboratories

This work investigates the morphology and structure of diamond surfaces that evolve during focused ion beam (FIB) sputtering and chemically amplified processes. We include a detailed study of morphology for a broad range of ion incidence angles (0-88 deg) and dose. A single ion (Ga) and incident energy (20keV) are used. For incidence angles between 30-75 degrees referenced from substrate normal, we observe the formation of ripple patterns. Ripples form with a wavevector aligned to the incident beam direction over this range of angles, similar to that predicted by Bradley-Harper for small theta. In order to develop an understanding of the mechanisms underlying a rippled topography, we analyze the evolution of morphology for increasing dose. AFM is used to quantify changes in ripple wavelength and amplitude, while TEM and Raman spectroscopy probe the structure in the near surface region. Beginning at 75 and continuing to 87 degrees, a step/terrace morphology forms during sputtering. Microfacets develop at the earliest stages (lowest dose) indicating a role of initial surface topography. Obvious changes in terrace length over this range of angles suggest that morphology is affected by shadowing between neighboring features. In general, a decrease in yield is discovered with increasing dose over this entire range of angles (30-87 deg). The presence of ripples/microfacets and, more specifically, their evolving shape influence the number of sputtered atoms per ion. Dramatic effects on yield (200% decrease) with increasing dose are observed at angles >80 degrees. Additional research investigates the effects of chemical environment on morphology. Experiments involve ion bombardment in the presence of H2O, methanol and H2O2. When sputtering in the presence of these gases, dramatic changes in morphology result as a function of dose and incidence angle. Changes in sputter yield due to the presence of a gas are also quantified as a function of incidence angle from 0-88 degrees.

4:40pm **PN-ThA9 Nanoscale Morphology Control Using Ion Beams**, ***M.J. Aziz***, Harvard University **INVITED**

Low energy ion irradiation of a solid surface can be used to control surface morphology on length scales from 1 micron to 1 nanometer. Focused or unfocused ion irradiation induces a spontaneous self-organization of the surface into nanometer-sized ripples, dots, or holes; it also induces diameter increases and decreases in a pre-existing nanopore by a tradeoff between sputter removal of material and stimulated surface mass transport. Here we report experiments that illuminate the kinetics of evolution of the surface morphological instability; the influence of initial and boundary conditions on guiding the self-organization; and the kinetics governing the fabrication of nanopores for single-molecule detectors.

Plasma Science
Room: C-103 - Session PS-ThA

Dielectric Etch II
Moderator: A.P. Mahorowala, IBM T. J. Watson Research Center

2:00pm **PS-ThA1 Etching Reaction Mechanism of Organic Low-k Dielectric Employing High-Density Plasmas and Multi-Beams**, ***M. Hori***, *H. Nagai*, Nagoya University, Japan, *M. Hiramatsu*, Meijo University, Japan, *T. Goto*, Nagoya University, Japan

An organic film, FLARE, is one of the most prospective candidates for interlayer insulating films with lower dielectric constant (low-k). N_2/H_2 and N_2/NH_3 gas plasmas have been used for etching organic low-k film without degrading the film quality and etch profile. The organic low-k film etching has been studied in ultrahigh frequency (UHF) plasma and inductively coupled plasma (ICP) employing N_2/H_2 and N_2/NH_3 gases. The absolute densities of H and N radicals were measured using the vacuum ultraviolet absorption spectroscopy (VUVAS) employing micro-plasma as a light source. N and H radical densities were estimated on the order of 10^{11} - 10^{12} cm^{-3} and 10^{12} - 10^{13} cm^{-3}, respectively. The behavior of etch rate corresponded to that of H radical density. Therefore, H radicals were found to be important species for organic low-k film etching, while N radicals never etched without ion bombardments. To investigate the roles of radicals and ions from view point of fundamental reactions, the organic low-k film etching reaction was investigated using radical and ion beams. H and N radicals ($\geq 10^{10}$ cm^{-3}) were injected with changing the density under the irradiation of each ion (Ar^+, N_2^+, NH_4^+, H_3^+) with an energy of 500 eV. The etch rate of organic low-k film was linearly increased with increasing H radical density, while suppressed drastically by N radical injection. The etched subsurface reactions of radicals were investigated by in-situ X-ray photoelectron spectroscopy (XPS) and fourier transform-infrared attenuated total reflection (FT-IR ATR). The etching reaction mechanism is discussed on the basis of results in plasma and multi-beam etching.

2:20pm **PS-ThA2 Modeling Dual Inlaid Feature Construction**, ***P.J. Stout***, *S. Rauf, T. Sparks, D. Zhang, P.L.G. Ventzek*, Motorola

A reactor/feature physics based modeling suite has been applied to dual inlaid (DI) via first trench last (VFTL) feature construction. The reactor model is HPEM (developed at the University of Illinois) and the feature model is Papaya (developed at Motorola). Papaya, a 2D/3D Monte Carlo based feature scale model, includes physical effects of transport to surface, specular and diffusive reflection from surface, adsorption, surface diffusion, deposition, sputtering, etching, and crystal structure. Papaya is coupled to the reactor model through "atomic sources". The atomic sources are the identity, flux rate, angular distribution, and energy distribution of specie incident on the feature surface. The atomic sources are used by the feature model to predict feature evolution. The DI feature is used in inlaid copper interconnect construction to define metal lines and their connection to the metal layer below. The advantage of the DI feature is only one metallization step (barrier/seed/plating/CMP) is required to deposit metal into both the metal lines and the via connections to the metal layer below. The DI feature is constructed through a combination of etch, fill, and mask steps. Discussed will be the 3D feature modeling of flurocarbon plasma etching of vias and trenches in SiO_2 to construct a VFTL DI feature. The significant feature effects have been simulated for the interaction of trench etch and etched via profile and the via protect fill material. Effects of feature geometry, via protect material level, and polymerization thickness on the final 3D DI feature profile will be discussed.

2:40pm **PS-ThA3 Profile Evolution During Fluorocarbon Plasma Etching of Low-k Porous Silica[1]**, ***A. Sankaran***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

To achieve shorter RC-delay times in integrated circuits low-k dielectric materials are being investigated for interconnect wiring. Porous silica is a promising candidate. Profile evolution and maintenance of critical dimensions during plasma etching of porous silica are problematic due to the exposure of open pores. To investigate these issues, reaction mechanisms for fluorocarbon plasma etching of porous silicon-dioxide have been developed and incorporated into the Monte-Carlo Feature Profile Model (MCFPM) which was modified to address these two-phase systems. To focus on issues related to the morphology of porous materials, the porous silica in the model was treated as stoichiometric SiO_2. Pores are randomly distributed in the SiO_2 to have a specified average pore radius and volume fraction (porosity). Fluxes to the substrate were obtained from the Hybrid Plasma Equipment Model for inductively coupled plasmas sustained in CHF_3, C_2F_6 and C_4F_8. The surface reaction mechanisms for these chemistries were validated by comparison to experiments.[2] Etch rates and tapering of high aspect ratio features were investigated as a function of bias voltage and diluents (e.g., Ar). We found that etch rates for porous silica materials are generally higher than for SiO_2 even when accounting for the smaller mass density, though etch rates do not necessarily scale linearly pore size or porosity. Scaling parameters (e.g., more tapering with larger polymerizing fluxes) observed for solid SiO_2 are generally applicable to the porous materials. Removal of polymer from exposed pores was also investigated using O_2 plasmas.

[1] Work supported by Semiconductor Research Corp. and National Science Foundation.

[2] Oehrlein et al. JVST A 17, 26 (1999); 18, 2742 (2000)

3:00pm **PS-ThA4 The Effect of Aspect Ratio on the Etching Properties of Porous Low-k Material in Fluorocarbon Plasma**, *S.H. Moon*, ***S.-W. Hwang***, *G.-R. Lee, J.-H. Min*, Seoul National University, Korea

As the critical dimension of integrated circuit devices rapidly shrinks to sub 0.1μm range, micro-structures such as trench, contact and via holes have high aspect ratios and consequently the issue of the aspect-ratio-dependent-etching (ARDE) becomes important. In ARDE study, information about the surface properties of the sidewall and the bottom inside the features is important, but there are few studies about this, especially in low-k interlayer dielectric etching, because the direct analysis of the surface in real features is difficult. In this study, we used a Faraday cage, which allowed us to control the ion incident angle on the substrate, and investigated in macroscopic scale the change in the roughness and chemical composition of porous low-k silsesquioxane with the aspect ratio of trench-shaped structure after etching in CF_4 and CHF_3 plasmas. For the etching experiments, we placed trench structures made of porous silsesquioxane inside the Faraday cage, and the samples were processed at 4mTorr, 600W source power, and -100V bias voltage in TCP etcher. The sidewall height of the samples was fixed at 1cm and the bottom width was varied between 1mm and 1cm such that the aspect ratio of the trench structure was varied between 10 and 1. Etch rates of the bottom and the sidewall of the samples for different aspect ratios were correlated with their surface properties observed by AFM, AES, and FT-IR.

3:20pm **PS-ThA5 Etching of Porous Low-K Dielectric Films in Fluorocarbon Plasmas**, ***S.A. Rasgon***, *B.E. Goodlin, H.H. Sawin*, Massachusetts Institute of Technology

To further reduce interconnect delay and enable higher device speeds (especially as the critical dimensions are lowered below 0.13 µm), it becomes advantageous to reduce the dielectric constant of the interlevel dielectric material between the metal lines. Porous low-k materials are potential candidates to meet this objective. While current research has focused on the material characterization of porous low-k films, little attention has been paid to the etching characteristics, of critical importance for process integration. Our research focuses on the etching characteristics and kinetics of leading candidate porous low-k dielectric films in fluorocarbon chemistries. Etching characteristics of these films are simultaneously compared with OSG, SiO_2, SiC(N), and photoresist films to reveal similarities and differences in etching behavior, and selectivity toward mask and stop layers. Ellipsometric results on porous low-k films indicate a possible competition between diffusion of etching precursors into the porous matrix, and ion-enhanced etching. Specifically, at low DC bias voltages, we note what appears to be a mixed fluorocarbon/porous-low k layer, possibly several hundred Å deep. As DC bias is increased, the mixed layer thins, and disappears around 300 V DC bias. This mixed layer is not present on OSG or SiO_2 samples etched at the same conditions. XPS studies will confirm these results. Understanding these etching behaviors may provide valuable insight into solving the problems of damage to the dielectric constant of porous low-k films, and reverse - selectivity during etching of the stop layer.

3:40pm **PS-ThA6 Plasma Etching Chemistry and Kinetics for Low-k and Porous Low-k Dielectric Films**, ***W. Jin***, Massachusetts Institute of Technology

To further reduce interconnect delay and enable higher device speeds, especially as the critical dimensions are lowered below 0.13µm, the interlevel metal insulator material with dielectric constant as low as 2.0 is desired. Porous materials, which lower the dielectric constant as a result of mixing air with the solid phase, are potential candidates to meet the low dielectric constant objective. Current research is focused on the material characterization, but little attention has been paid to its etching characteristics, although they are critical for process integration. In this research, we have measured etching rates of both porous low-k and low-k (OSG) as functions of ion bombardment energy, ion impinging angle with various fluorocarbon plasma beams, which are necessary for profile evolution modeling of porous low-k etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to the main chamber evacuated by a cryo-pump. Surface reaction is studied by measuring etching rate with an ex-situ spectroscopic ellipsometer. At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. And surface composition is analyzed by an X-ray photoelectron spectroscopy. The possible reasons attributing to the difference of the etching behavior between porous low-k and low-k dielectric films has been studied.

4:00pm **PS-ThA7 In Situ Real Time Monitoring of Evaporation Induced Self-Assembly and Patterned Etching of Low-k Mesoporous SiO_2 in Fluorocarbon Plasmas**, *H. Gerung, C.J. Brinker*, ***S. Han***, University of New Mexico

We have investigated in situ and in real time the sol condensation and the plasma-assisted patterning of mesoporous low-k SiO_2 films, using attenuated total reflection Fourier transform infrared spectroscopy. The porous SiO_2 films are prepared by evaporation induced self-assembly (EISA). The evaporation of ethanol in the sol induces self-assembly of surfactants to form an ordered cubic-phase template. Around this template, tetraethylorthosilicate (TEOS) condenses to create a silica network. The template is subsequently removed by calcination, resulting in a cubic phase mesoporous SiO_2 film. To better understand the condensation sequence, we have monitored the dichroic ratio of Si-O-Si IR absorbance during EISA and examined the propagation of Si-O-Si bond formation for varying film thicknesses. Thus formed porous SiO_2 films, stacked with a patterned photoresist, are etched in an inductively coupled plasma reactor, using CHF_3 and Ar. During etching, the integrated IR absorbance by Si-O-Si asymmetric stretching modes near 1080 cm^{-1} decreases while that of C-F_x ($x = 1, 2$, or 3) stretching modes near 1300 cm^{-1} continues to increase. The rate of decrease in integrated Si-O-Si absorbance translates to the SiO_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 attribute the increasing integrated absorbance to the formation of C-F_x species along the sidewall of patterned SiO_2 trenches. The stretching vibrational modes of carbon-carbon double bonds (C=C) are not observed near 1700 cm^{-1}. The absence of C=C absorbance with the presence of C-F_x absorbance indicates that the sidewall passivation maintains a steady state thickness. We intend to exploit the SiO_2 removal rate and the observed nature of sidewall passivation to predict the etch profile.

4:20pm **PS-ThA8 The Control of the Etching of SiOCH Films using C_4F_8/Ar/N_2 Plasma**, ***T. Tatsumi***, Sony Corporation, Japan, *K. Urata*, Sony Computer Entertainment, Japan, *K. Nagahata*, Sony Corporation, Japan, *S. Iseda*, Sony Computer Entertainment, Japan, *Y. Morita*, Sony Corporation, Japan

The relationship between the etch rates, C-F polymer thickness and the incident fluxes in dual-frequency (60/2MHz) RIE was evaluated by using various in-situ measurements tools, such as IRLAS and OES. To vary the amount of incident CF_x species, the C_4F_8 partial pressures in the C_4F_8/Ar/N_2 (or O_2) was increased under a gas pressure of 75 mTorr and a V_{pp} of 2000 V. The C-F polymer thickness increased when the incident CF_x fluxes were relatively higher than the removal ability of the C-F polymer; that mostly depends on the O and N fluxes (including the O outflux from etched SiOCH). SiOCH films have some methyl groups in the Si-O network and their densities are lower than SiO_2. Comparing to SiO_2 etching, the outflux of O decreased while additional C from the etched surface of SiOCH was supplied to the C-F polymer layer. The difference in outfluxes between SiO_2 and SiOCH drastically changed the process window for the selective etching. We found that the optimum etching condition could be obtained below the "critical point" P_c, where the total C flux became equivalent to O and N total fluxes. We have to carefully control the partial pressure and dissociation degree of C_4F_8 according to the density, composition and aspect ratio of the SiOCH sample and thus find the P_c at witch the maximum etch rate can be obtained. This is because the process window is very narrow and slight change in radical fluxes can induce phenomena such as residues and etch stop that cause serious problems with etching performance.

[1] T.Tatsumi et al., Proceedings of 22nd Symposium on Dry Process (2000) 37.

4:40pm **PS-ThA9 SiO_2 Etch Lag in SiO_2/SiLK^{TM}/SiO_2 Stack Structures**, ***A. Hasegawa***, *K. Ohira, T. Mizutani*, Fujitsu Limited, Japan, *K. Higuchi*, Fujitsu Vlsi Limited, Japan, *M. Okamoto, M. Nakaishi, K. Nakagawa*, Fujitsu Limited, Japan

The etching of stack structure using hard-mask became indispensability by the adoption of the dual damascene process and organic low dielectric constant (k) material for Cu wiring. In this study, SiO_2 etch lag effect depending on existence of SiLK^{TM} layer in stack structure is investigated. SiLK^{TM} is low-k organic dielectrics considered as perspective candidates for the use in microelectronic industry. The sample used in this experiment consists of SiN/upper SiO_2/SiLK^{TM}/lower SiO_2 stacked structure. SiN was used for hard-mask to etch SiO_2. Upper SiO_2 was used for cover layer to protect SiLK^{TM} damage during ashing and/or planarization by chemical mechanical polishing. After SiN trench etch, SiN/upper SiO_2/SiLK^{TM} were etched using hole patterned photoresist mask. Photoresist mask was removed during SiLK^{TM} etch. Then, trench pattern of upper SiO_2 and via pattern of lower SiO_2 were etched at the same time using the patterned SiN/upper SiO_2/SiLK^{TM} layers. The etching of the upper and lower SiO_2 were performed in commercial UHF plasma reactors using a C_5F_8/Ar/O_2 chemistry. The lower SiO_2 etch depth was measured from cross-sectional-scanning-electron-microscopy (SEM) photographs. The etch rate of dense via was 284nm/min. On the other hand, in the isolated via, the etch rate was only 91nm/min. However, in the case of using the stack sample, which was replaced SiLK^{TM} with SiN, etch rate of dense and isolated via were equivalent at 282nm/min. It was found that existence of SiLK^{TM} decreases the SiO_2 etch rate of a particular via pattern remarkably.

5:00pm **PS-ThA10 Etch Process Development of Porous Low-k Dielectrics for Dual Damascene Copper Interconnects**, ***K.D. Brennan***, Texas Instruments, *J.M. Jacobs*, Philips, *P.J. Wolf*, Intel

Advances in plasma etch technology are necessary to integrate low-k dielectrics and low-resistance metal leads to reduce interconnect RC time delay in order to meet the requirements of the International Technology Roadmap for Semiconductors (ITRS). International SEMATECH (ISMT) is currently implementing dual damascene copper interconnects built with porous low-k dielectrics as a means to meet future interconnect requirements. Development and optimization of an etch process for JSR LKD 5109, a porous methyl-silsesquioxane (pMSQ) based dielectric with a k-value of 2.2 is presented. Two level metal interconnects are fabricated, using a dual hard mask approach. The advantages and limitations of this approach for the etch process are discussed.

Surface Science
Room: C-112 - Session SS+EL-ThA

Growth & Etching on Semiconductor Surfaces
Moderator: A.C. Kummel, University of California, San Diego

2:00pm **SS+EL-ThA1 Epitaxial Growth Dynamics of Semiconductor Quantum Dot Structures**, ***S.R. Leone***, University of California and Lawrence Berkeley National Laboratory **INVITED**

The formation of Ge nanodots on Si(100) occurs by strain-induced mechanisms (Ge is 4% larger than Si) and obeys the Stranski-Krastanov (SK) growth mode: a wetting layer (3-5 layers) is followed by the formation of three-dimensional (3D) Ge structures. Quantitative studies of Ge island size distributions and their shape transformations, including huts, pyramids, domes, and superdomes, and shape changes due to annealing of the islands under the influence of surfactants, such as arsenic, are studied by molecular beam epitaxial growth and atomic force microscopy (AFM) post-analysis. For device applications, it is important to attain control over the size and spatial distributions of self-assembled nanostructures. The Ge growth experiments are also carried out on patterned silicon substrates (mesas formed by electron beam lithography followed by etching), for specific positioning of the dots. A 'one island on one mesa' relationship is achieved. The density of islands is higher than can normally be produced on unpatterned silicon, where island coalescence would usually occur well before this density is possible. Preferential growth on the tops of the mesas most likely occurs because the Si mesa tops are deformable, fulfilling a strain relaxation condition. In this work, pyramid-type islands as small as 25 nm are also aligned on the mesa tops, and no limit to the size reduction of the islands is apparent, being controlled mainly by the size of the etched features that can be introduced.

2:40pm **SS+EL-ThA3 Si Deposition on H-terminated Si(100) Surfaces***, ***J.-Y. Ji***, *T.T. Barus, T.-C. Shen,* Utah State University, *G. Qian,* University of Illinois at Urbana-Champaign, *X. Luo,* National Renewable Energy Laboratory, *S. Ren,* Illinois State University, *S. Zhang,* National Renewable Energy Laboratory, *Y.C. Chang*, University of Illinois at Urbana-Champaign

The presence of H has long been considered adverse to Si homoepitaxy. Copel and Tromp[1] reported that while no apparent effect on epitaxy was observed at H coverage <1 ML and H segregates at growth temperature >400 K, a drastic epitaxial temperature increase was required at H coverage >1 ML. We will present the results of our STM, and first principle molecular dynamics studies on Si monohydride and dihydride effect in Si epitaxy. We confirmed that at growth temperatures ~ 500 K, H stays on the growth front on monohydride surfaces and epitaxy can be achieved but the domain sizes are much smaller than those grown on the bare Si. Continuous rebonding apparently is responsible for the epitaxial growth on Si monohydride surfaces. The diffusion barrier for the Si adatom along the Si monohydride dimer rows is calculated to be 1.1 eV which is significantly higher than the corresponding 0.6 eV barrier on the bare Si(100)-2x1 surface. To account for the H segregation, a mechanism to exchange H atoms between a surface Si atom and the incident Si atom is proposed. The experimental and theoretical result on the dihydride effect will be discussed.

*This work is supported by NSF-DMR9875129, ARDA/ARO DAAD 19-00-1-0407 and DARPA-QuIST DAAD 19-01-1-0324.

[1] M. Copel and R. M. Tromp, Phys. Rev. Lett. 72, 1236 (1994).

3:00pm **SS+EL-ThA4 An Atom-Resolved Study of Vacancy Dynamics and Surface Roughening on Bromine-Etched Si(100) Surfaces**, ***C.F. Herrmann****, *J.J. Boland*, University of North Carolina, Chapel Hill

Halogen etching of Si(100) surfaces has long been considered to involve the selective removal of atoms from an essentially static surface. However, our high temperature scanning tunneling microscopy (STM) study reveals that halogen-covered surfaces are highly unstable. This instability stems from the inherent steric repulsions between halogen adatoms on the surface. At high temperatures, repulsive interactions are relieved by vacancy formation, diffusion and surface roughening, each of which is directly observed in real-time by STM. Together, these dynamical processes result in surface features identical to those found after high temperature etching. These results demonstrate that diffusion and roughening must be considered in any model of halogen etching. Moreover, steric repulsions and the instability they create place fundamental limits on the ability to achieve atomically smooth morphologies using halogen etching.

3:20pm **SS+EL-ThA5 Dynamics of Si(100)-(2x1) Surface Modification with Cl**, ***G. Xu***, *E. Graugnard, V. Petrova, K.S. Nakayama, J.H. Weaver,* University of Illinois at Urbana-Champaign

The etching dynamics of Cl-Si(100)-(2x1) at elevated temperature have been studied with variable temperature scanning tunneling microscopy. Clean samples were exposed to Cl_2 at room temperature to near saturation and then heated to 700 K for over 20 hours. By scanning the same area of the sample, we observed pit creation, diffusion, incorporation and annihilation. Pit annihilation has not been reported previously under conditions of steady state etching and surface saturation. We also observed regrowth islands creation, growth and decay. Surface reactions at 700 K produced single Si adatoms, which were bonded to Cl-free Si dimers. Single Si adatoms diffused through these Cl-free Si dimer sites, but adatom diffusion was restricted by the high Cl concentration. The adatoms could form regrowth dimers when they met or they could be accommodated at the ends of regrowth structures. The adatoms could also be released from the regrowth dimer rows with the assistance of bare dimers. We have also observed (3x2) and (5x2) surface structures and, for the first time, the phase transition between (3x2) and (5x2) structures and dimer vacancy lines.

3:40pm **SS+EL-ThA6 Surface Modification without Desorption: Recycling of Cl on Si(100)-(2x1)**, ***K.S. Nakayama***, *E. Graugnard, J.H. Weaver,* University of Illinois at Urbana-Champaign

We demonstrate the structural consequences of thermally activated reactions of Cl on Si(100)-(2x1). We used scanning tunneling microscopy at room temperature to obtain atomic-resolution images of the surface before and after thermal processing. We show surface modification under conditions where Cl is recycled rather than desorbed as $SiCl_2$. In this unexpected reaction, the surface roughens as dimer vacancies are produced. First, a dimer with 2 Cl atoms, 2SiCl, converts to $SiCl_2$ + Si. This allows the destabilized, bare Si atom to escape onto the terrace. At temperatures where the desorption is negligible, the $SiCl_2$ unit decays as the Cl atoms can move to other active sites of the Si surface, allowing the second Si atom to escape. The result is a dimer vacancy, Si atoms on the terrace that can form self-organized regrowth structures, and Cl that is able to participate in another pitting event. Access to this unexpected roughening pathway is controlled by the Cl concentration and temperature. This previously overlooked process represents an important component of Si(100) surface processing.

4:00pm **SS+EL-ThA7 Spontaneous Roughening – Fundamental Limits in Si(100) Halogen Etch Processing**, ***D. Chen***, *J.J. Boland*, University of North Carolina at Chapel Hill

A dynamical Scanning Tunneling Microscopy and Density Functional Theory study of the thermodynamic stability of halogen-terminated Si(100) surfaces is presented. Defects-free halogen-covered Si(100) surfaces are shown to be intrinsically unstable and prone to spontaneous roughening. This instability is the result of steric effects and is observed for all halogens except fluorine (which is already known to yield rough surfaces). These results demonstrate that an atomically smooth Si(100) morphology cannot be realized using halogen etch processing which sets a lower bound on the atomic scale perfection that can be achieved using such processing.

4:20pm **SS+EL-ThA8 Preparation of Atomically Flat Si(100) Surface by Ion Etching**, ***J. Kim***, *J.-Y. Ji, T.-C. Shen,* Utah State University, *J.S. Kline, J.R. Tucker,* University of Illinois

Preparation of atomically flat Si(100) surface under limited thermal budget has been one of the challenging processes in the research of atom-scale electronic device fabrication. While atomically flat monohydride surfaces can be obtained by aqueous NH_4F etching on Si(111) surfaces,[1] wet-chemical process has yet to produce an atomically flat Si(100) hydride surface at a scale of more than a few nanometers. Ion irradiation effects on Si surfaces have been investigated extensively from mid-70s to early 90s as a surface cleaning process prior to Si epitaxy. Recent atomistic studies of ion sputtering on pristine Si and metal surfaces were more focused on the dynamics of ion-induced defects.[2] We are currently using STM to investigate the surface morphologies during ion etching of oxide or wet-chemically prepared Si(100) surfaces by 0.4 - 1.5 keV Ar and Xe ions. We will delineate the effects of ion energy, ion fluence and substrate temperature, and assess the possibility of achieving atomically flat Si(100) surfaces by optimizing these parameters. This work is supported by NSF-DMR9875129, ARDA/ARO DAAD 19-00-1-0407 and DARPA-QuIST DAAD 19-01-1-0324.

[1] G. S. Higashi et al., Appl. Phys. Lett. 56, 656 (1990).

[2] P. Bedrossian, Surf. Sci. 301, 223 (1994) and references therein.

***** Morton S. Traum Award Finalist

4:40pm **SS+EL-ThA9 Probing the Chemistry of Impurities with STM: The Profound Effect of Dissolved Oxygen on Silicon Etching**, ***S.P. Garcia***, *H. Bao, M.A. Hines,* Cornell University

A new technique has been developed to quantify the surface reactivity of impurities, which combines the exquisite defect sensitivity of scanning tunneling microscopy (STM) and the analytical capabilities of atomistic kinetic Monte Carlo (KMC) simulations. This technique exploits kinetic competition between the impurity and a reference etchant to produce impurity-concentration-dependent changes in nanoscale etch morphology. These changes are then quantified using STM measurements and KMC simulations. We used this technique to measure the site-specific reactivity of dissolved O_2 -- a ubiquitous impurity in aqueous solutions – with H-terminated Si(111) surfaces. The site-specific reactivity of O_2(aq) is surprisingly anisotropic. Oxidation of the highly strained dihydride step site is four times faster than oxidation of the relatively unstrained monohydride step site. Both steps are 10^4 times more reactive than terrace sites. FTIR measurements of the Si-H stretch vibration showed that dissolved O_2 inserts O atoms into surface Si-Si backbonds without removing the H-termination. Dissolved O_2 does not attack Si-H bonds, since neither Si-H consumption nor silanol production is observed.

Surface Science
Room: C-110 - Session SS-ThA

Tribology at Surfaces
Moderator: D.W. Brenner, North Carolina State University

2:00pm **SS-ThA1 QCM-STM Studies of the Nanoscale Dynamics of "Model-System" and "Real-World" Lubricants**, ***J. Krim***, North Carolina State University **INVITED**

In order to gain a fundamental understanding of friction, and the closely related phenomenon of lubrication, one must understand, at the molecular level, how the energy associated with the work to overcome friction is converted to heat.[1] Such knowledge is key to understanding the rate at which an interface will heat, and in addition how chemical reactions and other physical processes triggered by heat will be affected by friction. One of the simplest possible geometries in which friction can occur, and thus be studied, is that of a fluid or crystalline monolayer adsorbed on an atomically flat surface. This geometry is experimentally accessible to experiments with a Quartz Crystal Microbalance (QCM), to numerical simulation techniques, and to analytic theory. Measurements of the tribological properties of "model system" and "real world" lubricants have been performed for rare gases, octane and TCP adsorbed on lead, iron and/or copper surfaces in open geometries (with QCM) and also in confined geometries (by bringing a STM tip into tunneling contact with the QCM electrode). Lead substrates are of particular interest on account the recent observation of superconductivity-dependent sliding friction. Iron and copper substrates are of interest for a variety of practical applications. Interaction potentials for adsorbed rare gases are known to a high degree of accuracy, allowing highly reliable comparisons of theory to experiment. TCP is meanwhile a "real-world" lubricant known for its demonstrated anti-wear properties for macroscopic systems. Although this lubricant has been the subject of much research for over 40 years, the atomic-scale details of its lubrication mechanisms are far from being satisfactorily understood.

[1] "Surface science and the atomic-scale origins of friction: what once was old is new again.", J. Krim, Surf. Sci. 500, 741 (2002)

2:40pm **SS-ThA3 A Quantitative Study of the Mechanical and Adhesive Origin of Molecular-Level Friction**, ***J.E. Houston***, Sandia National Laboratories, *H.I. Kim*, Aerospace Corporation

In earlier work, we explored the origins of molecular-level friction using the interfacial force microscope and Au tips and substrates terminated by self-assembled monolayer films having various functional end groups. Here we continue that effort by applying contact-mechanics models to quantitatively analyze the mechanical properties of the films, their interfacial energies and the friction shear-stress values for each functional-group combination. Methyl end-group combinations represent only van der Waals bonding and purely mechanical friction, whereas carboxylic acid groups show significant hydrogen bonding. The results indicate that both the composite elastic modulus and the mechanical portion of the friction shear stress scale inversely with the total molecular length of the tip/substrate films. The adhesive energy shows an odd/even effect changing from inter-film for an even number of methylene units to purely intra-film bonding for odd-numbered films--the intra-film adhesion only appears in the lateral friction force. Very short methyl-terminated combinations indicate a significant non-contact component to the friction force. These results will be discussed in terms of the possible use of these films as molecular-level lubricants. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

3:00pm **SS-ThA4 Frictional Anisotropy at Crystalline Interfaces**, ***C.M. Mancinelli***, *A.J. Gellman,* Carnegie Mellon University, *J.S. Ko,* Merck & Co., Inc.

Fundamental tribological studies in an ultra-high vacuum environment have been performed to probe the effect of anisotropy on the friction between two single crystalline metal surfaces. The study of frictional anisotropy, or the effects of lattice orientation at crystal interfaces, has been conducted to address two main questions: whether slip between sliding surfaces occurs more easily along certain crystallographic directions, and whether the observed orientation effect on friction is a result of surface lattice commensurability. The results of a study of the frictional anisotropy between single crystalline Cu(100) surfaces will be presented. Tribological investigations were conducted on surfaces prepared to be either truly clean or modified by adsorption of molecular ethanol in the boundary lubrication regime. A detailed comparison will be made between these results and those previously obtained for the frictional anisotropy between single crystalline Ni(100) surfaces.

3:20pm **SS-ThA5 Nanopormorphism of C60 and Hydrocarbons on Metal Surfaces**, ***T.S. Coffey***, *M. Abdelmaksoud, J. Krim*, North Carolina State University

We report investigations of the validity of beliefs that nanoscale objects might have the same properties as macroscale objects, termed nanopormorphism. Since C60 molecules to rapidly rotate within their lattice position, tribologists envisioned nano-sized ball bearings. C60 is not an effective lubricant.[1] But differences in interfacial friction between rigid vs. rotating C60 remains an interesting topic. C60 forms close packed hexagonal films on both Ag(111) and Cu(111). However, on Ag(111), C60 spins in its lattice position, while it is rigid on Cu(111).[2] To determine if the spinning of C60 affects interfacial friction, we are employing QCM and AFM to compare the friction of methanol on C60/Ag(111) vs. methanol on C60/Cu(111). We examine whether the rolling nature of the C60 layer impacts the sliding friction as probed by QCM and AFM. Adsorbates at a surface can cause changes in the phonon dispersion curves, creating new modes that can be related to the sliding friction of the adsorbate. Among these new vibrational modes are three Frustrated Translational (FT) modes which probe the curvature of the molecule/surface potential along different spatial directions. For hydrocarbons adsorbed on many metals, the FT modes parallel to the surface (FTx, FTy) have energies much smaller than that perpendicular to the surface (FTz).[3] The stiffness or high "spring constant" of the FTz mode compared to the low "spring constant" of the FTx and FTy modes brings to mind molecular scale shock absorbers. We are using QCM to study octane and acetylene sliding on Cu(111) and Pb(111) to determine how energy and damping of the FTz mode affects sliding friction.

[1] T. Coffey et al., J. Phys. Condensed Matter, 13 (2001) 4991-4999.

[2] T. Sakurai et al., App. Surf. Sci., 87/88 (1995) 405.

[3] B.N.J. Persson and E. Tosatti, Eds, Physics of Sliding Friction, Ch. Woll, Kluwer Academic Publishers, Dorcdrecht, 1996.

4:00pm **SS-ThA7 Tribochemical Wear of Silicon Nitride on Oxide Surfaces Studied by Atomic Force Microscopy**, ***J.T. Dickinson***, *W. Maw, F. Stevens, S.C. Langford*, Washington State University

Nanometer scale tribochemical wear of silicon nitride AFM tips was characterized on a variety of substrates in aquous solutions using atomic force microscopy. Wear at this small scale contrasts markedly with the macroscopic wear of silicon nitride. For aqueous mediated wear, a chemically active substrate (one with the appropriate surface metal-hydroxide bonds) is required. These results are generally consistent with wear due to the formation and breaking of chemical bonds between the tip and the substrate. The wear rates are shown to be nonlinear in the applied normal force. We propose that stress-induced intermediate states involving hydroxyl groups form on both the AFM tip and the substrate. Chemical reactions subsequently form transient bridging chemical bonds that are responsible for tip wear.

4:20pm **SS-ThA8 Adhesion Sensor: Non-Contact AFM for Quantitative Adhesion Measurements**, ***A. Schirmeisen***, *D. Weiner, H. Fuchs*, University of Muenster, Germany

The adhesion characteristics of metal coatings on Polycarbonate are of high technological interest. For example, Aluminum is used to coat plastic surfaces, with a wide range of applications. However, adhesion failure of metal coatings on polycarbonat is often observed. Methods such as flame annealing[1] or plasma treatment[2] are typically employed to improve adhesion characteristics. Yet little is known of the microscopic processes leading to the modified surface properties. We can quantify the adhesion properties of Al on differently treated polymers using dynamic AFM. Conventionally, adhesion tests are performed using a tape puller or similar device. The sample is usually destroyed after the test and no lateral resolution of the adhesion properties is achieved. In a novel approach using NC-AFM we can quantify the adhesion characteristics of the polymer-metal interface with nm-resolution. We measure frequency shift versus distance curves of a functionalised NC-AFM cantilever on the polymer surface. A specially designed UHV apparatus allows the in-situ preparation of tip and sample and the investigation of the interfacial force interactions with a UHV-AFM. The tip is functionalised by evaporation of a thin Al film on the cantilever. The adhesion properties of the polymer are modified by plasma treatment. Measurements of frequency shift versus tip-sample distance reveal the influence of the sample treatment on the adhesion properties. Following the approach of Durig,[3] we calculate force curves from the frequency shift data,[4] and extract quantitative values for the interfacial adhesion energy.

[1] A.P.Pijpers, R.J. Meier, J. Electron Spectr. 121 (2001) 299

[2] C. Seidel, H. Kopf, B.Gotsmann, T. Vieth, H. Fuchs, K. Reihs, Appl. Surf. Sci. 150 (1999) 19

[3] U. Durig, Appl. Phys. Lett. 75 (1999) 433

[4] Calculation based on programm from H. Holscher, CAESAR Institute, Germany.

4:40pm **SS-ThA9 The Frictional Behavior of a Hertzian Contact Analyzed using a New Contact Mechanical Model**, ***U.D. Schwarz***, Lawrence Berkeley National Laboratory, University of California

The study of the friction occurring at a Hertzian contact (i.e., the contact between a sphere and a flat surface or between two spheres) has always been a central issue in nanotribology, since realistic interfaces may be approximated by numerous individual Hertzian contacts that are within certain boundaries statistically distributed in all three dimensions. However, the theoretical description of the mechanical behavior of such contacts under load considering adhesion has been difficult in the past. Generally applicable models (i.e., models covering the "intermediate regime" between small, hard and large, soft contacts, as they might be most frequent in actual interfaces) required always numerical approaches. In this talk, I will present a new theory that covers the full parameter range for an adhesive Hertzian contact, but results in a simple equation describing the effective load acting on the surface that consists of adhesive and external contributions. The theory is based on a model interaction force that includes both short-range and long-range components. Comparison with numerical results obtained from the Maugis-Dugdale model as well as with experimental friction force microscopy data demonstrates the validity of the new approach.

Thin Films
Room: C-101 - Session TF-ThA

Ultra Thin Films
Moderator: T.M. Klein, University of Alabama

2:00pm **TF-ThA1 Oxidation of InP, Si and SiC Surfaces**, ***Y.J. Chabal***, *O. Pluchery, F. Amy, M. Frank, K. Raghavachari*, Agere Systems

Passivation of semiconductor surfaces by thermal oxidation or low temperature oxide deposition is critical for both microelectronics (e.g. gate oxides on Si) and optoelectronics (e.g. epi-growth and wet chemistry of InP-based laser structures). Yet, the amorphous or microcrystalline nature of most oxides has made it difficult to understand and therefore to control oxide growth and composition. We have developed in situ infrared (IR) absorption methods to characterize ultra-thin oxides and to understand their growth in various environments (vacuum, gas ambient, and solution.[1]) In this talk, we contrast the multiphase and layered nature of a variety of oxides (native, wet-chemical, plasma and anodic) grown on InP(100) surfaces to the much simpler stoichiometric SiO_2 films on silicon, and investigate oxide regrowth on acid-etched oxide-free InP surfaces. We also highlight the role of dangling bonds and strain on molecular oxygen dissociation and incorporation into Si(100)-(2x1), 4H-SiC(0001)-(3x3)[2] and 3C-SiC(100)-(3x2) surfaces. Finally, we discuss the role that hydrogen plays during the growth of ultra-thin oxides, and its ability to passivate (or create) interfacial defects.

[1] O. Pluchery, J. Eng Jr., R. L. Opila, Y. J. Chabal, Surf. Sci. (April 2002).

[2] F. Amy et al., Phys. Rev. Lett. 86, 4342 (2001).

2:20pm **TF-ThA2 The Kinetics of Ultrathin Aluminum Oxide Film Growth on Aluminides**, ***J.F. Moore***, *A. Zinoviev, M.J. Pellin*, Argonne National Laboratory

Oxide films grown on metals at high temperature under high vacuum meet the criterion for near-equilibrium growth, since the diffusion rate of atoms in the metal is high enough to prevent kinetically trapped phases from forming. In this study, a number of aluminide single crystal and polycrystalline metals are oxidized at temperatures near their melting point under high vacuum (less than 10^{-5}mBar O_2). The film growth kinetics are measured continuously with x-ray photoelectron spectroscopy (XPS) during oxidation. Phenomena including surface segregation of intermetallic components, diffusion, nucleation, and island formation are elucidated during these experiments. Self-limited growth of aluminum oxide at 3-5nm was observed in some cases, as well as dramatic reduction in cracking due to thermal cycling or lattice mismatch. This last effect is of considerable interest since compounds with a wide range of bulk properties could be used for a given application rather than a more limited set with the appropriate surface structure. The kinetics of the oxidation process in these studies will be discussed, including critical parameters such as temperature, aluminum concentration, and oxygen dose rate (pressure).

2:40pm **TF-ThA3 Stability of Hafnium Oxide and Silicate Ultrathin Films on Si**, ***I.J.R. Baumvol***, Universidade Federal do Rio Grande do Sul, Brazil **INVITED**

Among the potential replacements for SiO_2 or SiO_xN_y as gate dielectric in Si-based advanced MOSFET devices, hafnium oxide (HfO_2) and silicates ($Hf_xSi_yO_z$) seem to be the most promising materials, combining high dielectric permittivity with low leakage current due to a reasonably high barrier height that limits electron tunnelling. In order to be effectively incorporated into ultra-large scale integration (ULSI) fabrication technology, the gate dielectric material must conserve its integrity in further processing steps. In particular, rapid thermal annealing of source and drain dopants, usually performed at and above 1000 °C, has been indicated as the most aggressive step. The main deleterious consequences of post gate dielectric deposition annealing reported so far include thickening of the SiO_2 interlayer and chemical reactions at both gate electrode/dielectric and dielectric/Si interfaces, with the consequent low! ering of the capacitance equivalent thickness, and diffusion of Hf into Si which reduces electron and hole mobilities in the transistor channel. Furthermore, these studies pointed out the need for controlling the effects of annealing in intentionally or unintentionally O_2-containing atmospheres (even at very low O_2 partial pressures), which renders post-deposition annealing even more aggressive to gate dielectric integrity, especially in the near dielectric-semiconductor interface region. The present work describes the results of composition, atomic transport and chemical reaction investigations following rapid thermal annealing in Ar, N_2 and O_2 of ultrathin HfO_2 and $Hf_xSi_yO_z$ films deposited on Si in the temperature range 800 to 1000 °C. Film structures and compositions were established by high-resolution transmission electron microscopy, Rutherford backscattering spectrometry, nuclear reaction analysis, and X-ray photoelectron spectroscopy. Isotopic substitution and sub-nanometric depth resolution profiling using narrow nuclear resonant reaction profiling revealed that O migrates by means of a propagating front from the surface that reacts with the hafnium oxide or silicate networks as it advances, the main reaction channels being O-O and O-N exchanges. O penetration, incorporation in the bulk of the ultrathin film structures, and oxidation of the substrate forming SiO_2 here observed were significantly smalle! r than in previously studied Al, Zr and Gd oxides and silicates. Hf penetration into Si was observed, amounting between 10^{12} and 10^{13} Hf/cm^2, which would degrade electron and hole mobilities in MOSFET transistor channels. Pre-annealing in non-reactive atmospheres like Ar and N_2 increase the stability and resistance to oxidation of the films.

3:20pm **TF-ThA5 Electrical and Physical Properties of Very Thin, Nearly Epitaxial Cu (100) Sputter-deposited at Room Temperature**, *C. Detavernier*, ***S.M. Rossnagel***, *C. Noyan, C. Lavoie*, IBM T.J. Watson Research Center, *T.S. Kuan*, SUNY-Albany, *D. Deduytche, R.L. Van Meirhaeghe*, Universiteit Gent, Belgium

The sputter deposition of high purity Cu onto HF-cleaned Si(100) substrates at room temperature or below results in very highly oriented, nearly epitaxial Cu (100) films with good electrical properties. Using XRD, we could only observe the Si(400) and Cu(200) peaks, indicating that the Cu is strongly textured. The resistivity of these films is found to be much smaller than the typical resistivity values obtained for unannealed polycrystalline PVD Cu films; approximately 1.9 micro-ohm-cm for films > 100 nm thickness, dropping to 1.7 micro-ohm-cm for >200 nm films deposited at 90C. The electrical resistivity increases as the film thickness is decreased, consistent with the non-specular electron-surface scattering. The resistivity increase exceeds the size-effect alone for very thin films which may be indicative of the presence of line defects or low angle grain boundaries. These defects would also explain the broadening of the XRD peaks that we observed for thinner films. The films were stable with time, unlike companion films deposited on silicon dioxide which undergo grain growth on the scale of days resulting in reduced electrical resistivity. TEM analysis shows a high dislocation density in the films, but good evidence of epitaxy. The grain size for 30 nm films is many hundreds of nm. The Cu(100) films are ideal for the study of size effects, specular scattering and any electrical anisotropies due to their near-bulk resistivity, lack of grain boundary effects, and crystalline stability.

3:40pm **TF-ThA6 Epitaxial Growth of Au and Ag Films on Si(111) using Cu Buffer Layers**, ***K. Pedersen***, Aalborg University, Denmark, *P. Morgen,* University of Southern Denmark, *T.G. Pedersen,* Aalborg University, Denmark, *Z.S. Li, S.V. Hoffmann*, Aarhus University, Denmark

Deposition of metals on semiconductor surfaces often lead to films of poor quality due to lattice mismatch or chemical reaction between metal and the substrate. For both Au and Ag growing on Si(111)-7x7 the films are imperfect (111) metal layers. In the case of Au the deposition also creates a disordered, Si-rich layer that floats on top of the Au layer. Furthermore, the surface states usually found on (111) faces of noble metals are absent for these Au and Ag films. Though Cu reacts with Si, growth of a well ordered Cu(111) film starts after a thin reacted phase around the contact layer has been created. The reacted layer thus serves as buffer layer between crystalline Cu and the Si substrate. In synchrotron radiation photoemission experiments we demonstrate how the reacted Cu layer also serves as a buffer layer improving the properties of Au and Ag films on Si(111). Core level spectra show that the buffer layer prevents the reaction between Au and Si. This leads to an ordered surface of the film with a surface state. Thin Ag films grown directly on Si(111)-7x7 form quantum well states that are seen as peaks in valence band spectra. These peaks appear broader and weaker than for Ag grown epitaxially on for instance Fe(001). Furthermore, strains caused by mismatch between Ag and Si lattices shift the surface state above the Fermi level. The thin Cu buffer layer improves on both problems. The sharpness of the quantum well levels increases considerably and the surface state appears just below the Fermi level. From the sharpness of quantum well levels it is concluded that the optimum buffer layer thickness is 6 - 8 atomic layers.

4:00pm **TF-ThA7 Ag Ultra Thin Film Stability on GaAs (110): An ab-initio Study**, ***D.L. Irving***, *S.B. Sinnott,* University of Florida, *R.F. Wood*, Oak Ridge National Laboratory

Metal-semiconductor interfaces are widely utilized in modern device applications. As device sizes are drastically reduced it is essential to have a fundamental understanding of the stability of the ultra thin metallic overlayer on a semiconducting substrate. The Ag(111)/GaAs(110), a system that is known to be non-wetting, has been widely studied in recent years because it has been shown that stable metallic overlayers could be generated by means of a low temperature deposition followed by an anneal to room temperature. The stability of the Ag film was also found to be dependent on the amount of Ag initially deposited onto the GaAs substrate. This research uses density functional theory under the pseudopotential approximation to study the construction of an accurate computational model of this heterogeneous interface. The goal is to determine how strain in the unit cell affects the adhesion of the Ag layer to the GaAs substrate.

4:20pm **TF-ThA8 Synthesis of Ultrasmooth CN_x Overcoats for 1 Tb/in^2 Magnetic Storage Applications**, ***D.-J. Li***, *Y.-W. Chung*, Northwestern University

Nitrogenated carbon (CN_x) is now being used in protective overcoats of commercial hard disk systems, due to its compatibility with existing lubricants as well as desirable tribological and corrosion protection performance. The current goal of the disk drive industry is to increase the areal storage density to 1 Tb/in^2 by reducing the head-disk spacing. Modeling calculations show that the protective overcoat thickness has to reduce from 4-5 nm in current dirves to 1.0 nm. In this case, producing an atomically smooth and dense CN_x coating with low defect density becomes crucial. The purpose of this work is to synthesize smooth and pinhole-free CN_x overcoats over large areas by controlling magnetron sputtering process parameters. Effects of sputter gas composition, target power, substrate bias, substrate tilt and rotation speed on film growth and properties were explored. One important finding from this study is the combined use of substrate tilt and rotation. AFM scans over large sampling areas show that thin CN_x films obtained at -100 V substrate bias with 45 degree substrate tilt and 20 rpm rotation have r.m.s roughness almost four times lower than those prepared without substrate tilt and rotation. These 1-nm thick ultrasmooth coatings reduced corrosion damage by a factor four compared with coatings of the same thickness grown without substrate tilt and rotation. This improved performance is likely a result of more efficient and uniform momentum transfer from energetic species in the plasma to surface atoms parallel to the surface during deposition in this configuration.

4:40pm **TF-ThA9 Ultra-thin Silicon- and Aluminum Oxides on Silicon formed Layer-by-layer**, ***P. Morgen***, *T. Jensen, C. Gundlach,* University of Southern Denmark (SDU), *K. Pedersen, N. Skiversen, P. Kristiansen,* Aalborg University, Denmark, *S.V. Hoffman, Z.S. Li*, Aarhus University, Denmark

At the end of the "road" for silicon based micro- and nano-electronics the gate oxide layers must shrink to their ultimate limits of thickness. We have developed some new layer-by-layer assembly procedures to form the thinnest possible oxides (0.3 - 5nm). These are then subjected to various types of measurements of their structure, chemical-, physical-, and electrical properties. We report details of the different processes to form these oxides, and their nano-chemical composition at - and vertically above - the interface, including a comparison of oxides grown on the Si (111) and Si (001) faces, in studies primarily using synchrotron-induced photoemission. We have established a procedure to monitor the field across ultra-thin layers of silicon oxide, with deposition of Ag on top of the oxide, ranging in coverage from dispersed atoms to above a full layer. Such a field exists for the Si (111)/silicon oxide interface but not for the Si (001)/silicon oxide interface after our processes. In both cases a Schottky barrier is formed under a thicker Ag layer, with the silicon oxide between the metal and semiconductor. Aluminum oxide has recently attracted a lot of interest as a substitute for silicon oxide on silicon, as it has a much higher dielectric strength than for a comparable thickness of silicon oxide. With our method, the layer-by-layer growth of aluminum oxide on silicon is very easy to control and to extend to other substrates than silicon.

5:00pm **TF-ThA10 Characterization of Ultra-Thin Films using Angle Resolved XPS and Maximum Entropy Methods**, ***R. White***, *R. Champaneria, J. Wolstenholme, P. Mack*, Thermo VG Scientific, UK

The Thermo VG Scientific Theta Probe has the unique ability to collect angle resolved XPS (ARXPS) spectra in parallel without the need to tilt the sample. The collection of ARXPS data (free from artifacts associated with sample tilting) is now routine for samples ranging in size from 20 µm to 300 mm. This has made it necessary to implement a consistent method for the generation of depth profiles from ARXPS data. The conversion of ARXPS data into depth profiles is problematic as no single transformation from ARXPS data to depth dependent concentrations exists. As real data contain noise, a weighted sum squares of error between measured and calculated data is not sufficient to determine accurate depth profiles. A usable solution can be found by the inclusion of an entropy term that allows a profile to be generated with the minimum amount of structure. Characterisation of ultrathin high K dielectric overlayers on SiO_2 is one application where ARXPS shows great promise, potentially yielding thickness, distribution, dosage and chemical state information. A maximum entropy approach based on the methods developed by Smith and Livesey has been adopted in order to interpret Theta Probe data. This approach may be thought of as a least squares fitting of the data, with an in-built 'smoothness' parameter to prevent overfitting to noise in the data, for example. Maximum entropy calculations are not restricted to small numbers of chemical state components. This makes this method particularly suitable for ARXPS where low concentration and multi chemical state components need to be profiled. This paper describes the method and results from various systems where this approach has been adopted.

Applied Surface Science
Room: C-106 - Session AS+MM+BI-FrM

BioMEMS and Medical Devices
Moderator: K. Healy, University of California, Berkeley

8:20am **AS+MM+BI-FrM1 Characterization of Implant Surfaces**, ***M. Grunze***, University of Heidelberg, Germany **INVITED**

In this talk I will describe my personal recollection of the development of polymer coating (Polyzene FÂ®) for cardiovascular stents from concept to market. The idea was to develop a "stealth" surface coating for metallic stents which reduces inflammation, thrombosis and restenosis of the blood vessels. My talk discusses the design strategies of the polymer, development of the coating process and the necessary Surface Science characterization, protein, cell and bacteria adhesion experiments, the technical certification process, in vivo experiments in animal models, and the problems and successes in starting a new company to market the product. At this time the story is open-ended, since the results of ongoing long term clinical studies were not available at the time this abstract was written.

9:00am **AS+MM+BI-FrM3 Probing the Orientation of Surface-Immobilized IgG by ToF-SIMS**, ***H. Wang***, *D.G. Castner, B.D. Ratner, S. Jiang*, University of Washington

The orientation of a surface-immobilized IgG is crucial for its ability to detect antigen in biosensors. To probe the orientation of a surface-immobilized IgG, two factors are important. One is a powerful surface analysis technique while the other is a well-controlled surface for specific protein orientation. Static time-of-flight secondary ion mass spectrometry (ToF-SIMS) is well suited for this purpose since the sampling depth of ToF-SIMS (1-1.5 nm) is less than the typical dimension of most proteins (4-10 nm). At the same time, IgG orientation can be controlled by appropriately adjusting microenvironments (e.g., surface charges and solution properties). In this work, we apply ToF-SIMS combined with principle components analysis (PCA) to study the orientation of anti-hCG (human chorionic gonadotropin) on two controlled surfaces using its Fab and Fc fragments as references. The controlled surfaces are achieved using self-assembled monolayers (SAMs) with different terminal groups. Results show that the combined ToF-SIMS and PCA technique is able to probe the difference in orientations for ani-hCG adsorbed on different surfaces. In addition, ToF-SIMS results are compared with those from the protein structure. Consistency of these results indicates the reliability of this method.

9:20am **AS+MM+BI-FrM4 TOF-SIMS Analysis to Monitor Coating Processes in Organic and Biological Surfaces**, ***R. Chatterjee***, *B. Lakshmi, M.J. Pellerite*, 3M

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has proved to be very useful in molecular surface characterization of organic coatings, polymeric systems and biological surfaces. This paper will focus on the application of TOF-SIMS in identifying reaction processes involved in formation of bio-reactive surfaces and organic coatings. In SIMS, absolute quantitative analysis becomes difficult because the ion yield is highly dependent on the morphology and the physical and chemical nature of the surface. Different examples will be used to illustrate how with the use of suitable control experiments, relative quantitative analysis can provide direction in the development of surface modification and surface coating processes. Relative quantitation of TOF-SIMS data was applied to monitor the reaction of aminoacids to different bioreactive surfaces. TOF-SIMS was used to identify presence of different proteins in a multistep sandwich assay. In thin organic coatings, the degree of cure of the silane end group was correlated to the coating durability. Relative quantitation was applied to determine the degree of cure, specify process conditions needed for suitable curing, identify a suitable catalyst to reduce curing times and determine whether lack of cure is the cause of failure. The rate of cure of mono-, bis- and trifunctional silanes, and their effect on the coating durability was investigated.

9:40am **AS+MM+BI-FrM5 Characterization of Protein Interactions with MEMS Devices under Non-Static Conditions**, ***K. Lenghaus***, *J. Dale, D. Henry, J. Hickman,* Clemson University, *J. Jenkins, S. Sundaram,* CFD Research Corporation

The emerging field of micro electromechanical systems (MEMS), when directed to biological applications (environmental monitoring, biosensors etc.), requires an understanding of protein/surface interactions under conditions of flow at low concentrations. Previous protein studies have focussed on adsorption under static conditions and at high concentrations, which can not necessarily be extrapolated to those conditions found in Bio-MEMS under non-static or flow conditions. In an analogous system, the adsorption of proteins to surfaces in in vivo biological systems differs from other adsorption phenomena in that its consequences can be aggressively non-linear, with a biological system's response to minute deviations and changes greatly out of proportion to the magnitude of the change. Thus a relatively small fraction of aggressive sites can induce a response quite out of proportion to their numbers. To study both phenomena we have developed assays to allow enzymes to be quantified at ng/mL levels, and combined with a syringe pump we have created a simple, yet sensitive and robust test bed for protein adsorption under flow conditions. Using this approach, a PEEK capillary was found to have a small number of highly aggressive sites for protein adsorption, corresponding to 5% total surface coverage. These would serve as nucleation sites for further interactions in MEMS devices, and be difficult to detect by other methods. It was further shown that the adsorbed enzymes were in an active state, and this was used to confirm that the rate of desorption from the surface was of the order of 10-4.s-1, corresponding well with values derived from fitting the adsorption isotherm to a computational fluid dynamics model. Thus, studying enzyme adsorption can be used to give several useful insights into the adsorption/desorption behaviour of surfaces at low bulk concentrations of protein as well as generate insights for an in vivo system's protein nucleation behaviour.

10:00am **AS+MM+BI-FrM6 Selective Thermal Patterning of Self-Assembled DNA Monolayers on MEMS-based Microheater Devices**, ***T.H. Huang***, National Institute of Standards and Technology, *N. Ku,* Montgomery Blair High School, *R.E. Cavicchi, M.J. Tarlov*, National Institute of Standards and Technology

We report the selective patterning of self-assembled thiolated DNA probes on gold-coated microheater devices using temperature. The goal of our investigation is to utilize the rapid heating and cooling capabilities of MEMS-based microheaters to prepare biosensing surfaces and to monitor reactions such as DNA hybridization, melting and polymerase chain reaction (PCR). In this study, the self-assembly of thiolated-DNA probes on gold microheater array (four element array) is used as the model system. Modified DNA probes (5' end with disulfide and 3' end with fluorescein) are selectively immobilized onto the gold surface in several steps. First, a passivating layer consists of 1-mercapto-6-hexanol (MCH) is self-assembled onto the gold microheaters. The temperature for one the four heaters is elevated to ca. 200 °C to drive off the MCH. Then the thiolated DNA probes are deposited onto the freshly exposed bare gold surface. Using this method, one can use temperature to selectively deposit different DNA probes on specific heaters. The presence of the DNA probes on the surface is detected using fluorescence microscopy. In order to use the DNA-microheater surface to monitor DNA melting reactions or PCR (which require cycling to high temperatures), it is important for the probe to be thermally stable at the operating temperatures (i.e. 85 °C). We will also present results on the thermal stability of thiolated DNA monolayers on gold.

10:20am **AS+MM+BI-FrM7 Soft and Fuzzy Polymer Coatings for Microfabricated Neural Prosthetic Devices**, ***D.C. Martin,*** The University of Michigan, *X. Cui,* Unilever, *R. Kim, J. Yang, Y. Xiao*, The University of Michigan **INVITED**

Neural prosthetic devices facilitate the functional stimulation of and recording from the peripheral and central nervous systems. It is important that these implantable devices function in vivo for long periods of time. Bioactive and electrically conductive materials are deposited on the surfaces of neural microelectrode arrays through various means to build a stable interface for better biocompatibility and signal transduction. To mediate the mechanical property differences between the brain tissue and silicon device, integrate the device within tissue and minimize the host reaction, bioactive coatings were developed that can be applied over the whole surface of the silicon micro-devices. One approach that has been developed is electrospinning of protein polymers to form a porous film composed of electrospun nano-scale protein fibers with cell-binding sites exposed. Another ongoing approach has been to coat the device with bioactive hydrogel materials which change volume according to their environment, and therefore integrate the device in the tissue with minimal insertion damage. To stabilize the connection between neurons and the electrode sites and facilitate the signal transduction from electrically conductive metal electrode to the ionically conductive tissue, conductive polymers together with bioactive molecules were co-deposited on the electrode site areas by electrochemical deposition. The coatings presented a fuzzy and conductive surface which lowered the impedance of the electrode by 1 to 2 orders of magnitude. The bioactive molecules with cell binding ability in the deposited films on the electrode sites were shown to be able to anchor neurons in both in vitro and in vivo experiments.

11:00am **AS+MM+BI-FrM9 Voltage-Dependent Assembly of the Polysaccharide Chitosan onto an Electrode Surface**, *L.-Q. Wu, A.P. Gadre, H. Yi, M.J. Kastantin, G.W. Rubloff, W.E. Bentley, G.F. Payne,* ***R. Ghodssi***, University of Maryland

We examined the assembly of a basic polysaccharide - chitosan - from solution onto electrode surfaces as a result of voltage bias on the electrode. Chitosan is positively charged and water-soluble under mildly acidic conditions, and is uncharged and insoluble under basic conditions. We observed that chitosan is deposited from acidic solution onto the surface of a negative electrode and that the thickness of the deposited layer is dependent upon the deposition time, the applied voltage, and the chitosan concentration. No deposition occurs on the positive or neutral electrode. Once deposited and neutralized, the chitosan layer can be retained on the electrode surface without the need for an applied voltage. Infrared (FTIR) and electrospray mass spectrometry (ES-MS) confirmed that the deposited material was chitosan. The voltage-controlled deposition of chitosan provides a means for anchoring biopolymer material in specific locations in bioMEMS environments, such as encapsulated microfluidic devices fabricated in our laboratory using MEMS-based polymeric materials (EPON SU-8, Polypyrrole and Polydimethylsiloxane). Furthermore, chitosan's amine functionality should enable standard coupling chemistries to be exploited to anchor additional biomolecules (e.g. DNA and proteins) to the surface of bioMEMS devices.

11:20am **AS+MM+BI-FrM10 Alternative Approaches to Microfluidic Systems Design, Construction and Operation**, ***D.J. Beebe***, University of Wisconsin, Madison **INVITED**

Many approaches to the construction of microfluidic systems have appeared in the last few years including glass and silicon etching and bonding, laser machining, micromolding and others. Here we present an alternative approach to the design, construction and operation of microfluidic systems that we call Âµfluidic tectonics (ÂµFT) that compares to injection molding in cost, but allows for a wide variety of functionality. ÂµFluidic Tectonics utilizes liquid phase photopolymerization, responsive materials and in situ fabrication to achieve elegant yet functional designs. Ultra rapid microchannel fabrication (2 minutes) is demonstrated using off the shelf components (glass microscope slides, polycarbonate top, simple UV lamps and transparency masks). The process eliminates the need for traditional bonding to achieve a closed channel and no master is required (as in elastomeric micromolding). The same basic process has been used to create filtering, flow control, readout (chemical and biological) and mixing components. Thus, the construction platform leads to highly integrated systems by using a single fabrication process and class of materials (photopolymerizable polymers). Closed loop feedback control is demonstrated without the use of electronics. A single structure created in situ from responsive materials performs the sensing and actuation functions. The responsive component senses the local chemical environment and undergoes a volume change in response to changes in the local environment. The volume change is coupled to a valve that regulates the compensating stream providing closed loop regulation. The design flexibility ÂµFT combined with the ease of fabrication and low cost (similar to injection molding) enhances the microfluidic toolbox and broadens the base of potential designers and users by simplifying the construction process and reducing the infrastructure needed to create and use microfluidic systems.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+TF-FrM

Magnetic Thin Films and Surfaces
Moderator: P.A. Dowben, University of Nebraska-Lincoln

8:20am **MI+TF-FrM1 Structure and Magnetism of Ultra Thin Fe Films Grown on CoGa(100)**, ***L.K. Verheij***, *T. Balster, D.A. Kovacs, R. David, R. Franchy*, Forschungszentrum Jülich, Germany

The structure and magnetic properties of thin Fe layers deposited on CoGa(100) (misfit 0.5 %) were investigated by low energy electron diffraction (LEED), by helium scattering (TEAS), and by the magneto optical Kerr effect (MOKE). For room temperature deposition we observe well defined intensity oscillations of the specular helium intensity under anti-phase conditions. Upon increasing the growth temperature to 550 K the amplitude of the oscillations and their number increases substantially. At both growth temperatures a tendency for double layer growth is found up to a film thickness of about 10 ML. The magnetic properties of the Fe films appear to depend on the experimental conditions during growth and on the preparation of the substrate surface. Films with a magnetization with the easy axis parallel to the surface and with the easy axis perpendicular to the surface have been grown. The Curie temperature of the Fe films increases from 240 K to 600 K when the thickness is increased from 1 to 2 ML. Above 650 K, the film is unstable due to intermixing. The relation between the changes of the structure and the magnetic behavior with preparation are discussed.

8:40am **MI+TF-FrM2 Surface Morphology and Magnetization Reversal**, ***R.A. Lukaszew***, *Z. Zhang*, University of Toledo, *R. Clarke*, University of Michigan

We have studied the azimuthal dependence of the magnetization reversal on annealed and non-annealed (001) epitaxial Ni films of the same thickness and deposited under the same conditions on MgO. The coercive field in non-annealed films exhibit 4-fold symmetry as expected from the symmetry of the crystal. The annealed films exhibit an additional uniaxial symmetry superimposed to the four-fold symmetry. STM images of the surface of the annealed films indicate self-assembled periodic stripe nano-patterning, while STM images of the non-annealed films show typical mounded surfaces. Cross sectional TEM studies performed on the annealed films will be correlated with the surface morphology and with the magnetic anisotropy.

9:00am **MI+TF-FrM3 Lande g-factor Variation with Thickness in Ultrathin Permalloy Films**, ***J.P. Nibarger***, *R. Lopusnik, T.J. Silva*, National Institute for Standards and Technology

We have found a variation in the Lande g-factor with thickness in sputtered polycrystalline Permalloy films capped with Cu. The variation of the g-factor is correlated with damping in the absence of an applied bias field. Films were grown on a sapphire substrate with a 5 nm Ta adhesion layer, followed by 10, 25, 50, or 100 nm of NiFe, and finally capped with a 5 nm layer of Cu. Static anisotropy values were obtained using a static inductive magnetometer and the effective saturation magnetization was found using an alternating gradient magnetometer. A pulsed inductive microwave magnetometer (PIMM) was used to extract dynamical information.[1] Using the static values and the Kittel equation for thin films, we extracted the induced uniaxial anisotropy, the Lande g-factor, and the Landau-Lifshitz phenomenological damping parameter, α, from the PIMM measurements. The g-factor increases with decreasing thickness for films below 50 nm, as does also the damping in zero applied field. In addition, the effective saturation magnetization decreases with decreasing thickness, presumably due to surface anisotropy effects. The increase in the g-factor is interpreted as an indicator of enhanced spin-orbit coupling for thinner films: As the films become thinner and thinner, the relative magnitude of the spin-orbit coupling at interfaces becomes dominant. We will discuss the role of spin-orbit in damping by conduction electron scattering, as well as implications for the transport of spin angular momentum in nano-scale magnetic heterostructures.

[1] T. J. Silva, C. S. Lee, T. M. Crawford, C. T. Rogers, J. Appl. Phys. 85, 7849 (1999)

9:20am **MI+TF-FrM4 Determination of the Spin-Spin Coupling Strength in Ultrathin Magnetic Films**, ***N.A.R. Gilman***, *R. Zhang, R.F. Willis*, Penn State University

We present a model of spin-spin coupling in itinerant ferromagnets which provides insight into the observed linear decrease of the Curie temperature with decreasing ultrathin film thickness.[1] The slopes of plots of Tc versus ultrathin film thickness reflect the strength of the spin-spin coupling and the effective range of the spin-spin interactions. Experimental results for alloys of Fe, Co and Ni show this range of spin-spin interactions decreasing with increasing bulk Curie temperature. Measurements of their Fermi surfaces[2] show a direct correlation with the concentration of holes in the d-band.

[1] R. Zhang and R.F. Willis, Phys. Rev. Lett. 86, 2665 (2001).

[2] M. Hochstrasser et al. Phys. Rev. B 60, 17030 (1999).

9:40am **MI+TF-FrM5 Effect of Spatial Confinement on Magnetism: Films, Wires and Dots of Fe**, ***J. Shen***, Oak Ridge National Laboratory **INVITED**

The last decade has witnessed a remarkable transfer of basic science to practical devices in the area of magnetic recording. In less than 10 years, the discovery of a phenomenon that occurs in artificially structured thin films of magnetic and nonmagnetic materials, known as giant magnetoresistance (GMR), had developed into a $100B/yr business in the market of hard disk drive alone. This advance was a result of learning how to grow these films coupled with a basic understanding that allowed optimal tuning of their properties. As efforts to reduce device size scales have continued, it has become increasingly attractive to investigate the magnetic properties of artificial structures with even smaller dimensions and lower dimensionality - nanowires and dots. Using a combination of novel synthesis methods, including laser molecular beam epitaxy, step decoration growth, and buffer layer assisted growth; we have developed a generic way to grow nanometer-sized films, wires and dots on a common template with the same areal density. The ability to grow magnetic nanostructures with differing dimensionalities on the same template means that we can now study the effect of spatial confinement on magnetism and transport. This is crucial to the development of nanometer-scaled spintronic devices, an area in which the next breakthrough in information technology may be anticipated.

10:20am **MI+TF-FrM7 Growth and Magnetic Properties of Artificial $L1_0$ Fe-Co Alloy**

G. Farnan, ***Z. Gai***, *A.P. Baddorf*, *J. Shen*, Oak Ridge National Laboratory

Iron-cobalt alloys are of interest due to their high magnetic moment and Curie temperature, and to the strong magnetic character of both constituents. In bulk, Fe and Co are totally miscible, with B_2 structure being the only ordered alloy phase. In this work, we use modern laser molecular beam epitaxy to artificially grow a new ordered Fe-Co alloy phase, i.e., $[Fe(1ML)/Co(1ML)]_n$ $L1_0$ phase, which consists of alternatively stacked monatomic layers of Fe and Co. By monitoring reflection high energy electron diffraction (RHEED) oscillations during the growth, precise amounts of iron and cobalt were deposited onto a Cu(001) single crystal substrate in ultra high vacuum. In-situ scanning tunneling microscopy images showed almost perfect layer-by-layer morphologies, while low energy electron diffraction (LEED) patterns and Auger electron spectroscopy data collected after each whole layer deposition showed that the fcc phase with layered composition was preserved up to seven monolayers. Ex-situ X-ray diffraction results include new diffraction features confirming the existence of the Fe-Co $L1_0$ alloy. The magneto-optic Kerr effect (MOKE) results showed that the alloy was ferromagnetic with easy axis in plane. After seven monolayers deposition a structural change was observed by LEED and RHEED, and was reflected in a dramatic increase in coercivity and Curie temperature observed in the MOKE study.

[1] Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

10:40am **MI+TF-FrM8 The Effects of Growth Temperature and Composition on the Magnetic Properties of Ni_2MnIn_x Epitaxial Films Grown on InAs (001)**

J.Q. Xie, *J.W. Dong, J. Lu, X.Y. Dong, T.C. Shih, S. McKernan, C.J. Palmstrom*, University of Minnesota

Injecting spin-polarized electrons into a semiconductor from a ferromagnetic material is an emerging concept for novel electronic devices.[1] InAs is the semiconductor of choice because of its high electron mobility and the ease to form an ohmic contact to it. Although no elemental ferromagnet is lattice matched to InAs, the lattice mismatch between the Heusler alloy Ni_2MnIn and InAs is only 0.2%. In bulk, Ni_2MnIn is reported to have a cubic ($L2_1$) crystal structure with a lattice constant a_0 = 6.069 Å and a Curie temperature ~ 314 K. Recent theoretical studies showed that the band structure alignment between Ni_2MnIn and InAs would enhance the injection of the minority spins, suggesting that Ni_2MnIn may be a good choice for spin injection as a ferromagnetic contact.[2] In this presentation, we report on the epitaxial growth of Ni_2MnIn thin films on InAs (001) by molecular beam epitaxy. Determination of the crystal structure of Ni_2MnIn and effects of ordering and composition on magnetic properties of Ni_2MnIn are emphasized. Our transmission electron microscopy studies indicate the pseudomorphic growth of Ni_2MnIn in the B2 structure on InAs (001) with an orientation relationship of $Ni_2MnIn(001)$ || InAs(001) and Ni_2MnIn<100> || InAs<100>. Magnetic measurements show that the Ni_2MnIn films have a Curie temperature ~ 170 K. The lower Curie temperature compared to the bulk value (~ 314 K) is believed to be due to the growth of Ni_2MnIn in the B2 structure. To improve the ordering of Ni_2MnIn thin films, effects of substrate temperature and interfacial layer are investigated. Composition was found to affect the Curie temperature dramatically. For $Ni_2MnIn_{1.7}$, a Curie temperature as high as ~ 290 K was obtained.

[1] S. A. Wolf et al., Science 294, 1488 (2001).

[2] K. A. Kilian and R. H. Victora, J. Appl. Phys. 87, 7064 (2000).

11:00am **MI+TF-FrM9 Structure and Magnetic Properties of Thin Fe Films Grown on InAs(100)**

G. Witte, *L. Ruppel, Ch. Woell, S.F. Fischer, U. Kunze, T. Last*, Ruhr-University Bochum, Germany

On account of its large spin transfer length (i.e. Rashba effect) InAs constitutes a promising material for future spintronic applications. Of particular interest in this context are details of the growth and properties of thin ferromagnetic films on this substrate. Here we report on a combined LEED, XPS and SQUID study of epitaxially grown Fe-films on the indium rich InAs(100)-c(8x2)/(4x2) surface with a particular emphasize on interface alloying and its influence on the magnetic properties. While deposition at room temperature leads to the appearance of a distinct (1x1) LEED pattern for films thicker than 2nm indicating an epitaxial growth of Fe(100) films, the corresponding XPS data reveal the presence of an iron-arsenide species which floates at the surface upon further film growth. Postdeposition annealing causes no improvement of the film quality but enhances the amount of arsenic at the surface. Surprisingly, rapid flash annealing of the films above 700K leads, however, to a thermal dissociation and desorption of the surface arsenic which is accompanied by a change of the film morphology and formation of disconnected islands. This suggests that the epitaxial growth of Fe films on InAs(100) is stabilized by the surface arsenide via a "surfactant effect". Corresponding ex-situ SQUID measurements for 10nm Fe films capped by a 20nm Ag film revealed bulk like magnetic properties over a temperature range of 5-300K. In contrast to that thin Ag films of only 1nm are not sufficient to prevent a partial oxidation of the Fe films as inferred from the XPS data and lead to the appearance of a pronounced exchange bias effect at low temperatures. This observation stress the importance of an appropriate capping.

11:20am **MI+TF-FrM10 Growth and Characterization of Ferromagnetic Fe-Doped Rutile TiO_2 Clusters and Thin Films**

S. Thevuthasan, Pacific Northwest National Laboratory, *Y.J. Kim*, Taejon National University of Technology, *T. Droubay, V. Shutthanandan, A.S. Lea, M.H. Engelhard, S.A. Chambers*, Pacific Northwest National Laboratory, *J. Schneider, R. Sears, B. Sinkovic*, University of Connecticut

There is a growing interest in searching for spin injection materials with high injection efficiencies and room temperature operations. Some of the dilute magnetic semiconductors with the potential for room temperature spintronics applications include Co-doped ZnO, Mn-doped GaN and Co-doped anatase TiO_2. Although there are still some issues associated with the growth of single crystal Co-doped anatase TiO_2, recent experiments show that this material is the most promising candidate because of its room temperature ferromagnetism.[1,2] Recently, we have investigated the growth and characterization of $Fe_xTi_{1-x}O_2$ (x ~ 0.02-0.16) on single crystal $TiO_2(110)$ at the Molecular Beam Epitaxy facility of the Environmental Molecular Sciences Laboratory (EMSL). Some of these films exhibit ferromagnetism at room temperature. The morphology of these films consist of the film proper along with Fe rich clusters containing a mixture of Fe^{2+} and Fe^{3+} valence states. These films were characterized using several surface science techniques including x-ray photoelectron spectroscopy (XPS) atomic force microscopy (AFM), scanning Auger microscopy (SAM), x-ray absorption spectroscopy (XAS), and Rutherford backscattering spectrometry (RBS)/channeling. These results with the magneto-optical Kerr effect (MOKE) measurements from these films will be discussed.

[1] M. Matsumoto et al., Science, 291, (2001) 854.

[2] S.A. Chambers et al., Appl. Phys. Lett. 79 (2001) 3467. Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research and the laboratory directed research and development (LDRD) program.

11:40am **MI+TF-FrM11 MOCVD Growth of $Co_xZn_{1-x}O$ on R-plane Sapphire: Structure, Composition, and Magnetic Properties**

A.C. Tuan, University of Washington, *T. Droubay, J.W. Rogers, S.A. Chambers*, Pacific Northwest National Laboratory

We have grown Al-doped $Co_xZn_{1-x}O$ films by MOCVD for application as a spintronic material. Films were grown at substrate temperatures between 750 and 825 K at a growth rate of ~6 nm/min. XRD and RBS show that up to 35% of the Zn cations can be substituted with Co without disrupting the wurtzite crystal structure of ZnO. Furthermore, XRD pole figures indicate that the films are of near-single crystal quality. Comparison of the Co 2p core-level XPS from our $Co_xZn_{1-x}O$ films with reference spectra for Co metal, Co(II), and Co(III) shows that the Co ions are in the +2 oxidation state. XPS also shows that there is no carbon contamination in the bulk of the film, which suggests that the organometallic precursors are completely oxidized/pyrolyzed. Since the Co distribution in the material strongly affects the magnetic properties, we performed SIMS depth profiling, which confirmed that the Co and Al constituents are uniformly distributed throughout the film and show no segregation at either the interface or the surface. In addition, AFM indicates that the surface is very smooth with an RMS roughness of only 3.7 nm over a 5 x 5 micron area. However, in spite of recent theoretical predictions,[1] we have yet to observe room temperature ferromagnetism in this material. These results differ from those recently obtained by Ueda et al. in which they show weak ferromagnetism that persists to ~300 K from similar PLD-grown films of slightly lower crystalline quality.[2] We are currently performing below-room-temperature magnetic measurements to determine the exact value of the Curie temperature in our material. These results, as well as the effects of post-growth annealing will be presented at the conference.

[1] Sato et al., Japanese Journal of Applied Physics 40, L334-L336 (2001)

[2] Ueda et al., Applied Physics Letters 79(7), 988-990 (2001).

Nanometer Structures
Room: C-207 - Session NS-FrM

Novel Surface Nanoprobes
Moderator: S.A. Smallwood, Wright Patterson Air Force Base

8:20am **NS-FrM1 Correlated Spectroscopic and Scanning Probe Microscopy Approaches to Studying Molecular Assemblies at Interfaces**, ***C. Yip***, University of Toronto, Canada **INVITED**

The rational design of protein-based supramolecular architectures requires careful consideration of not only intramolecular structure but also the intermolecular interactions that control their self-association into higher order structures. We are particularly interested in the role of interfacial structure and chemistry in defining the nucleation and growth of these systems and specifically the synthesis of extended two-dimensional protein arrays. While scanning probe microscopy provides an excellent tool for studying these processes in real-time, there is an obvious need for integrated instrumentation that provides correlated analytical capabilities. We report here on the development and implementation of a multi-modal coaxial instrumentation platform that enabled the simultaneous acquisition of spectral, optical, and probe microscopy data. Examples will be drawn from studies of lipid phase transitions and protein assembly into two and three-dimensional architectures.

9:00am **NS-FrM3 ATR Vibrational Spectroscopy Towards Single Molecule Sensitivity and Molecular Level Spatial Resolution**, ***M. Futamata***, National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

Recent developments in SPM (Scanning Probe Microscopy) or SXS (Surface X-ray Scattering) provide us atomic level information on structural changes at solid/liquid interfaces. However, it is in principle difficult to identify adspecies or to characterize interaction between adspecies and substrates even with these techniques. Vibrational spectroscopy gives valuable information on this point, if inherently low sensitivity is overcome. We have studied highly sensitive ATR (Attenuated Total Reflection)-IR and Raman spectroscopy utilizing surface plasmon polariton (SPP) with higher spatial resolution beyond diffraction limit by combining with SNOM (Scanning Near-field Optical Microscopy). Recently, ATR-IR spectroscopy allowed us to elucidate water molecules at hydrophobic SAM (Self-assembled monolayer)/solution interfaces, whose hydrogen-bond network are completely broken to give a sharp O-H stretching band at quite high-frequency region. In addition, amphiphilic organic nanotubes in solution substituting the water result in multilayer formation of the monomers. On single molecule characterization with micro-SERS (Surface Enhanced Raman Scattering) on Ag nanoparticles, we found the blinking (drastic intensity fluctuation with time) for adenine molecules without using electronic resonance effect. Raman image from aggregated Ag particles shows the parallel polarization to connecting axes gives significantly larger enhancement than perpendicular direction. These results are in good agreement with the theoretical evaluation of the local electric field using FDTD (Finite Difference Time Domain) method. (3) ATR-SNOM Raman spectroscopy utilizing SPP yields the enhancement of Raman signal up to 300 times and enables us to obtain the SNOM-Raman image with ca. 50 nm of spatial resolution.

9:40am **NS-FrM5 Accurate Real-Space Measurements of Surface Lattice Parameters**, ***J.A. Kramar***, *G.M. Witzgall, V.P. Scheuerman*, National Institute of Standards and Technology

At the National Institute of Standards and Technology (NIST), we have built a metrology instrument called the Molecular Measuring Machine (M^3) with the goal of performing nanometer-accuracy two-dimensional feature placement measurements over a 50 mm by 50 mm area. The instrument uses a scanning tunneling microscope to probe the surface topography, and a Michelson interferometer system to measure the lateral probe movement, both having sub-nanometer resolution. The lateral position is servo controlled, based on the interferometer readings, using a digital signal processor. The instrument environment includes temperature control, a vacuum system with a base pressure below 10^{-5} Pa, and seismic and acoustic vibration isolation. Several artifacts have been measured to validate the instrument performance. Initially, an average pitch measurement was made on a grating that was produced by laser-focused atomic deposition of Cr.[1] The average line pitch for this grating was measured to be 212.69 nm, with an estimated fractional standard uncertainty of 25 x 10^{-6}. This estimate was derived from a consideration of the sources of uncertainty for a 1 mm point-to-point measurement, including the effects of interferometer and sample alignments, Abbé errors, motion cross-coupling, and temperature variations. Most recently, M^3 measurements were made of the surface lattice parameters of a conducting organic crystal and compared to the bulk lattice constants as determined by x-ray crystallography. In initial small-area measurements, the lattice constants of nominally 1.02 nm and 750 pm were in agreement to within 70 pm. These data represent a major achievement in performing a direct, real-space measurement of crystal lattice parameters using ultra-high accuracy interferometry.

[1] J.J. McClelland, R.E. Scholten, E.C. Palm, and R.J. Celotta, "Laser Focused Atomic Deposition," Science, Vol. 262, pp. 877-880, 1993.

10:00am **NS-FrM6 Microwave Evanescent Microscope with Coupled Shear-field Topography Measurement**, ***S.W. Robey***, *S.J. Stranick*, National Institute of Standards and Technology

Near-field probes are being developed to combat the diffraction limit in a wide spectral range from the visible through the IR and into the microwave regime. We are developing evanescent capabilities at GHz frequencies for a variety of applications. Two design criteria are broadband capability and the ability to independently measure sample topography. A system based on a coaxial transmission line resonant structure evanescently coupled to the sample via a scanning tunneling microscope tip will be described. Standing wave resonances in the structure provide high sensitivity with quasi-broadband coverage from ~ 1 GHz to 20 GHz. While previous designs have used soft contact or employed the capacitive feedback to provide height control, we have successfully implemented shear-force measurement to provide the necessary independent topographic information on either conducting and insulating materials. A variable single stub mechanism allows tuning to critical coupling at a selected resonance once near-contact is achieved. The design and implementation of the microscope will be discussed, with comparison to other microwave evanescent systems. Measurements on compositionally graded thin films of $Ba_xSr_{1-x}TiO_3$, buried metallic lines on IC's, and investigation of correlations in topographic and dielectric contrast will illustrate capabilities.

10:20am **NS-FrM7 Factors Influencing the Capacitance-Voltage Characteristics Measured by the Scanning Capacitance Microscope**, ***G.H. Buh***, National Institute of Standards and Technology and Seoul Nat'l Univ., Korea, *J.J. Kopanski, J.F. Marchiando, A.G. Birdwell*, National Institute of Standards and Technology, ***Y. Kuk***, Seoul National University, Korea

The scanning capacitance microscope (SCM) can be used to measure two-dimensional dopant profiles in semiconductors with nanometer scale resolution. Dopant concentration information is extracted from the local capacitance-voltage (C-V) characteristics measured between the SCM tip and the semiconductor sample. Two important artifact effects on C-V curves measured via SCM are discussed. It is found that the stray light from the laser of the atomic force microscope (AFM) dramatically affects the measured C-V curve. The difference between the usual SCM C-V curves measured under this high stray light condition and SCM C-V curves measured in a true dark condition will be shown and discussed. The distortion of C-V curves caused by the lock-in modulation voltage will also be discussed. After reducing these effects, SCM C-V curves are obtained that show markedly different behavior from that of conventional one-dimensional C-V curves. These measured C-V curves have a much stretched-out shape and non-zero dC/dV signals in the depletion and inversion region. Measured C-V curves are compared with three-dimensional calculations of the capacitance between the tip and sample. Determination of the dopant density directly from SCM C-V curves will be discussed. Finally, we will discuss optimal SCM imaging conditions, which overcome effects from surface charge and work function variation, and produce more accurate dopant profile measurements.

10:40am **NS-FrM8 Two-Dimensional Dopant Profiling by Novel Scanning Capacitance Force Microscopy**, ***K. Kobayashi***, *K. Kimura, H. Yamada, K. Matsushige*, Kyoto University, Japan

We have newly developed scanning capacitance force microscopy (SCFM), which is capable of mapping local differential capacitance (dC/dV) without external capacitance sensors, based on electrical force detection. 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) is detected using a lock-in amplifier (LIA). Because the magnitude of the induced ESF is proportional to the product of the square of the applied electric field and the capacitance of the sample (C) which can be modulated at f by the applied electric field especially in semiconductors, the amplitude and the phase of the induced ESF alternating at (3f) contain information on the differential capacitance (dC/dV) of the sample. 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. For demonstration of SCFM, a silicon test sample having several microfabricated patterns of p-type, n-type and heavily-doped n-type regions was imaged. Moreover, we demonstrated that SCFM could be also an important analytical tool for high-resolution characterization of ferroelectric domains in ferroelectric material such as a ferroelectric copolymer thin film.

11:00am **NS-FrM9 Imaging Subsurface Reflection Phase with Quantized Electrons**, *I.B. Altfeder, V. Narayanamurti, **D. Chen***, Harvard University

Lead quantum wells (QW) epitaxially grown on annealed Pb/Si(111) interface form a model system for the study of interactions between quantized electrons and adiabatically modulated boundaries. Tunnel spectra of this system reveal a previously unknown adiabatic shift of QW resonances due to lateral variations of the electronic reflection phase at the buried interface. With this effect, lateral distribution of the subsurface reflection phase can be probed, using scanning tunneling microscopy.

I. B. Altfeder, V. Narayanamurti, and D. M. Chen, Phys. Rev. Lett. 88, 206801 (2002).

11:20am **NS-FrM10 Spectroscopic Scanning Tunneling Microscopy Using Semiconductor Tips with Engineered Electronic Structure**, ***P.W. Sutter**, J.S. Palmer, P. Zahl, E.A. Sutter*, Colorado School of Mines

III-V semiconductors and heterostructures are proposed as a new class of materials for use as probe tips for scanning tunneling microscopy (STM). Compared to the metal tips used conventionally, semiconductors with carefully tuned electronic properties have the potential to significantly increase energy resolution and contrast in spectroscopic STM, particularly in emerging applications such as single molecule vibrational microscopy and spectroscopy.[1] We are exploring InAs as a candidate probe material for spectroscopic STM with ultrahigh energy resolution. Using cleaved InAs probes, we demonstrate atomic-resolution STM imaging on highly oriented pyrolithic graphite (HOPG) and on clean semiconductor surfaces, such as Si(111) 7x7. Tunneling spectroscopy with InAs probes on these materials shows clear signatures of the band structure of the semiconductor tips in local conductance spectra. Routes are studied to adjust the Fermi-level in semiconductor tip materials, thus creating a tunneling distribution that is tunable and significantly narrower than that obtainable with a conventional metal tip.

[1] B.C. Stipe, M.A. Rezaei, and W. Ho, Science 280, 1732 (1998).

11:40am **NS-FrM11 First SEM, SAM and Combined SEM/STM Results of a Novel UHV Compatible Electron Column with Sub 3 nm Resolution**, ***J. Westermann**, M. Maier, G. Schaefer,* OMICRON NanoTechnology GmbH, Germany, *J. Bihr,* LEO Elektronenmikroskopie GmbH, Germany, *J. Zach,* CEOS GmbH, Germany, *T. Berghaus*, OMICRON NanoTechnology GmbH, Germany

Scanning Electron Microscopy has been a proven tool for a huge variety of scientific applications for decades. Recently, new challenging applications are emerging from the fields of Semiconductor- and Nanotechnology. A key issue for these applications is the non-destructive imaging of the typically very sensitive, small and thin structures with nanoscale dimensions, as well as the characterisation of their chemical composition and electrical properties. Here, we present electron optical concepts and first results of a true UHV compatible version of an SEM column designed to meet the new requirements of ultra low outgassing, low beam voltages, and high resolution with high beam currents. Performance checks on nanostructured samples prove an ultimate lateral resolution below 3 nm at 15 keV beam energy and still below 5 nm at 3 keV at a working distance being compatible with electron energy analysers, and sample currents being suitable for Auger electron analysis. Beam currents in the nA range can be achieved with spot sizes below 10 nm at 1kV beam energy, thus enabling to use this column as an excitation source for chemical characterisation with ultimate spatial resolution in Scanning Auger Microscopy. First static Auger and SAM results demonstrating the outstanding spatial resolution will be shown. Furthermore, we report on the combination of this SEM column with simultaneous Scanning Probe Microscopy (SPM). This combination allows a continuous zoom from mm scale down to the atomic level on the same sample position, precise positioning of the SPM probe, as well as electrical contacting of nanosized structures (e.g. nanotubes or semiconductor devices).

Plasma Science
Room: C-103 - Session PS-FrM

Plasma Surface Interactions II
Moderator: W.M.M. Kessels, Eindhoven University of Technology

8:20am **PS-FrM1 Study of SiO_2 Etching with Plasma-beam Irradiation**, ***K. Kurihara**, A. Egami, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for Si/SiO_2/SiN etching to achieve high etching performance. A study of the SiO_2 etching mechanism has been still needed to construct a process simulator without experiments of trial and error. A plasma-beam irradiation apparatus, which can control plasma parameters, such as ion energy and radical/ion composition, is very useful to examine the plasma-surface interactions under a real etching environment. We measured Si containing desorbed products from the SiO_2 substrate by quadrupole mass spectrometer during $^{13}CF_4$/Ar gas mixture plasma beam irradiation. Furthermore we analyzed a surface reaction layer by a quasi-in situ X-ray photoelectron spectroscopy analysis after the plasma-beam irradiation. Composition of the desorbed products was almost independent on the ion energy under the condition that the ratio of the radical flux to the ion flux was small (1~2:1). Major desorbed products were SiF_2 and SiF_4. The thickness of the surface reaction layer including Si-F bond increased with increase in the ion energy, but bonding state in the reaction layer did not change. At the relatively high ion energy above 500 eV and ion rich condition, ions play an important role in etching. On the other hand, under the condition that the ion energy was low (~300eV) and the ratio of the radical flux to the ion flux was about 10:1, the relative ratio of highly fluorinated species (SiF_4) increased slightly. Radical species may affect the production of desorbed products at the low ion energy. We will discuss mechanisms of selective etching of SiO_2 to Si or SiN under these conditions, which leads the achievement of the high selectivity for sub-100nm LSI circuit production. This work was funded by NEDO.

8:40am **PS-FrM2 Measurements of Desorbed Products and Etching Yield by CFx+(x=1,2,3) Ion Irradiation**, ***K. Karahashi**, K. Ishikawa, H. Tuboi, K. Yanai, K. Kurihara, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon plasma has been widely used to etch silicon dioxide in the fabrication of semiconductor devices. For further development of integrated semiconductor devices, more precise control of the etching process is required. Thus, we have developed a mass-analyzed ion beam apparatus; Energy controlled single species ions are irradiated to SiO2 surface under ultra-high vacuum condition, and we can study the roles of individual fluorocarbon ion irradiation without gas phase reactions or neutral radicals irradiation. In the present work, we have investigated desorption products and etching yields for silicon or silicon dioxide by CFx+ (x = 1-3) ion bombardments. Desorbed products could detected with a quadrupole mass spectrometer by pulse ion beam method, and estimate the kinetic energy of desorbed products from the time delay of waveform from incident ion pulse. In SiO2 etching by CFx+ ion irradiation, the major desorbed product, which contains silicon, was SiF2. The kinetic energy of SiF2 was less than 0.1 eV. Therefore, products were different from physical sputtering particles such Si and SiF as desorbed from silicon surfaces by CFx+ (x = 1-3) ion bombardments. Etching yields for SiO2 were measured as a function of incident ion energy. The etching yield by F+ ion was smaller than that of Ar+ ion. The effect of chemical reaction of F+ ion did not clearly appeared. Etching yields of CFx+ (x = 1-3) increased with increasing the ion energy and with increasing number of fluorine atom in the ions. Above 1000 eV, etching yields is gradually saturated. Below 500 eV, etching yields abruptly dropped with decreasing ion energy, and fluorocarbon films grew on surfaces. These results suggest that the etching reaction is affected by chemical reactivity of the incident ions, and that the etching reactions are controlled by the incident ion energy and species. This work was supported by NEDO.

9:00am **PS-FrM3 Etch Mechanisms of SiOC and Selectivity to SiO_2 and SiC in Fluorocarbon Based Plasmas**, ***N. Posseme**, T. Chevolleau, L. Vallier, O. Joubert,* CNRS/LTM, France, *P. Mangiagalli*, Applied Materials, France

In CMOS technology, the traditional SiO_2 is being replaced by the so called low k materials in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. Many inorganic materials such as doped oxide and organic materials are being investigated as potential candidates. In this work, the study is focused on the etching of two carbon doped oxide materials: SiOC (k = 2.9) and porous SiOC (k=2.2 with a porosity of 40%).

With these new inorganic materials, fluorocarbon-based etch processes have to be revisited to obtain adequate profile control in high aspect ratio structures, high etch rate and good selectivities to etch stop or hard mask such as SiO_2 (k = 3.9) and SiC (k = 4). This study is dedicated to an analysis of the etch mechanisms of SiOC, SiO_2 and SiC in fluorocarbon plasmas. The etching of these materials is carried out on blanket wafers in a MERIE reactor (Magnetically Enhanced Reactive Ion Etcher) using different fluorocarbon gas (CF_4, C_4F_6, CH_2F_2) mixed with Ar, O_2 and N_2. X-ray Photoelectron Spectroscopy (XPS) analysis of the surface after partial etching shows that the fluorocarbon layer thickness formed at the surface plays a key role in controlling the etch rate and selectivity of SiOC, SiO_2 and SiC. The XPS results indicate that the fluorocarbon layer thickness depends on the plasma chemistry and also on the oxygen and carbon concentration in the etched materials The polymerising gas addition such as CH_2F_2 to $CF_4/N_2/Ar$ gas mixture induces an increase in thickness of the fluorocarbon layer which generates a decrease in etch rate. Similar XPS analysis are also conducted on the SiOC sidewalls using the chemical topography analysis technique.

9:20am **PS-FrM4 Hydrophilic Plasma Surface Modification of Membranes: Surface Analysis, Gas-Phase Diagnostics, and Mechanisms of Energy Transfer**, ***K.R. Kull***, *J. Zhang*, *E.R. Fisher*, Colorado State University

Treatments with nitrogen containing plasma that render asymmetric polyethersulfone (PES) membranes permanently hydrophilic are reported. The modification strategy entails treating these membranes downstream from an inductively coupled rf plasma source. Contact angle measurements confirm that the membranes are wettable as a result of treatment with plasmas containing nitrogen species (Ar/NH_3, O_2/NH_3, N_2). More importantly, the hydrophilic modification is permanent as plasma-treated membranes remain wettable for more than eight months after plasma treatment. The change in wettability is a result of chemical changes in the membrane induced by plasma treatment. FTIR and XPS analysis of treated membranes reveals the incorporation of nitrogen functionalities into the treated membranes. Moreover, there is a concomitant increase in the oxygen to carbon ratio compared to the untreated PES membrane. Mass spectral data reveals gas-phase species are created from plasma-membrane interactions and SEM investigations reveal no visually observable structural damage as a result of the treatment parameters employed. We have also investigated the role of NH and NH_2 radicals in the modification process using laser-induced fluorescence measurements. The velocity of NH radicals in the nitrogen-containing plasmas has been measured and appears to be rf power dependent. Additional data on the surface interactions of NH with PES membranes as well as velocity measurements for scattered NH radicals will be presented and compared to earlier results for NH_2 radicals.[1] Implications for plasma modification mechanisms will also be discussed.

[1] C. I. Butoi, M. L. Steen, J. R. D. Peers, E. R. Fisher, J. Phys. Chem. B 105, 2001, 5957.

9:40am **PS-FrM5 Radical Reactions with Organic/Polymeric Surfaces**, ***J. Torres***, *C.C. Perry*, *S. Bransfield*, *D.H. Fairbrother*, Johns Hopkins University

Plasmas play an important role in polymer surface modification based on their ability to introduce new functionalities at the interface. Atomic or molecular radicals are often cited as the key species responsible for initiating surface reactions during plasma processing. Due to the wide range of reactive species within a plasma, however, surface reactions of individual species are hard to determine. In our work we report the results of the reactions of O and Cl radicals generated by thermal dissociation of O_2 and Cl_2 respectively, with organic thin films and polymers. The present study focuses on the interaction of atomic and molecular oxygen and chlorine with an X-ray modified hexadecane thiols adsorbed on gold using in situ XPS. Oxygen reaction with these hydrocarbon films proceeds in three stages. Initially the reaction dynamics are dominated by the incorporation of new oxygen containing functionalities at the vacuum/film interface. At intermediate O/O_2 exposures, when a steady state concentration of C-O, C=O and O-C=O groups has been established, the production of volatile carbon containing species, including CO_2 is responsible for etching the hydrocarbon film. Upon prolonged O/O_2 exposures, O atoms penetrate to the film/substrate interface, producing Au_2O_3 and sulfonate (RSO_3) species. In contrast, chlorine radicals do not etch the hydrocarbon surface and produce a uniform distribution of CCl and CCl_2 species in the near surface region. The advantages of employing self-assembled monolayers as models for polymeric interfaces as well as the interaction of oxygen and chlorine radicals with polyethylene characterized by XPS, ATR-IR and AFM will also be presented.

10:00am **PS-FrM6 The Interaction Dynamics of Ar/H Plasmas with Silicon Surfaces**, *J. Villette*, *F. Gou*, ***M.A. Gleeson***, *A.W. Kleyn*, Leiden University, The Netherlands

Despite its technological importance the basic reaction dynamics of plasma deposition and etching processes are not known, even though in this case the process takes place almost under vacuum and should be easily accessible to studies at the molecular level. We have developed a new machine for such studies. Samples are placed in the centre of a 70 cm diameter reaction chamber, which can be evacuated up to ultra high vacuum. A cascaded arc plasma source produces an atmospheric plasma, which is collimated and differentially pumped. With a quadrupole mass spectrometer (QMS) we can monitor the particles emitted. An ion beam is produced in an independent source and can be scattered from the crystal that is being modified by the plasma. A time and position sensitive detector (PSD) records the scattered ions and neutrals individually. From their energy and scattering pattern we reconstruct the actual state of the surface. In order to prepare and characterize samples we can remove them from the reaction chamber into the preparation chamber under vacuum. Scattering of protons from clean and hydrogen covered silicon has been studied extensively by Souda et al.[1] The protons reflection is very sensitive to the state of the surface. In our machine we apply this to hydrogen treatment of Si(110). We note that the reflected yield goes up dramatically when switching on the hydrogen discharge. Switching to an Ar discharge we observe the disappearance of the strong hydrogen signal, indicating that even hyperthermal Ar from a cascaded arc recombining plasma is capable of removing hydrogen from silicon.

[1] R. Souda, E. Asari, T. Suzuki, and K. Yamamoto, Surf. Sci. 431, 26 (1999).

10:20am **PS-FrM7 Electron-Stimulated Atomic Scale Recovery of Ion-Induced Damage on Si(100)**, ***T. Narushima***, NRI-AIST, Japan, *M. Kitajima*, NIMS, Japan, *K. Miki*, NRI-AIST and NIMS, Japan

Recently, an importance of process under plasma irradiation is getting higher, because of its high reactivity and reducing process temperature. Surface damages induced by the plasma can be troubles for subsequent processes. But, effects of the plasma irradiation on the damage with atomic level have not been well studied. Previously, we reported that low energy (<40eV) electrons may be used to athermally release the compressive stress in the Si(001) surface layer induced by Ar^+ ions (<100eV) with using the ion and electron accelerated from Ar plasma [Narushima et al., Appl. Phys. Lett. 79, 605 (2001)]. In particular, we have strong evidence that the stress relaxation was found to depend only on the number of irradiated electrons and was independent of the total energy deposition. This indicates that complete relaxation is not promoted by a thermal activation mechanism, but by a non-thermal mechanism. In this paper, we show using scanning tunneling microscope (STM) that the underlying cause of the surface stress relaxation is athermal recrystallization of the surface atoms. Our finding is opposite to the previous report by Nakayama et al. [Phys. Rev. Lett. 82, 980 (1999)] that energetic electrons (>90eV) induce atomic scale damage. This discrepancy may be explained if we delineate 40-90 eV (in the case of Si) as the threshold between thermal and athermal processes for electron-surface atoms interactions. Our STM observation shows chracteristic features to support our hypothesis. The ion-bombarded surface does not have the thermally-generated 2x1 surface reconstruction, but instead a 1x1 reconstruction, which is slightly closer to positions of a 'bulk terminated' surface.

11:00am **PS-FrM9 Reduction of Hole Currents and E' centers in SiO_2 Induced by Vacuum-Ultraviolet-Light Using Pulse-Time-Modulated Plasma**, ***Y. Ishikawa***, *M. Okigawa*, *S. Kumagai*, *S. Samukawa*, Tohoku University, Japan

Plasma processes have been widely used in the fabrication of MOS-LSIs. Some vacuum-ultraviolet lights (VUV) in the plasma generates electron-hole pairs in SiO_2 because of its higher energy than the SiO_2-band-gap. The holes are trapped in SiO_2 and interface states are often formed at the SiO_2-Si boundary.[1] We have reported that pulse-time-modulated (TM) plasma reduce the VUV in the plasma and the hole current in SiO_2.[2] In this study, to understand the relationship between the hole current and damages in SiO_2, the hole current and E' centers (trapped electron at oxygen vacancy in SiO_2) are measured by on-wafer-monitoring and electron-spin-resonance technique (ESR). An aluminum film was deposited on SiO_2 of the on-wafer-monitoring device to eliminate charged particles from the plasma. The more the hole current, the more E' centers were observed in the on-wafer-monitoring device when the TM-He-plasma condition were varied. We also evaluated the time-resolved measurement of the electron density and the VUV intensity in the TM plasma. The VUV light intensity and the hole current decayed just after the plasma-off in TM plasma, whereas the electron density declined with four times longer decay constant. These results indicate that the TM plasma reduce an increase in E' centers as damages due to decrease in the hole current resulting from suppression of the VUV. Additionally, we appraised a depth profile of E' center, resulting in gradually decline and reaching nearly zero at a depth of 15 nm. The relationship between a VUV penetration depth and the E' center profile will be discussed in the meeting.

[1] D. V. McCughan and V. T. Murphy: J. Appl. Phys. 44 (1973) 2008, T. Yunogami, T. Mizutani, K. Suzuki and S. Nishimatsu: Jpn. J. Appl. Phys., 28 (1989) 2172

[2] S. Samukawa, Y. Ishikawa, S. Kumagai and M. Okigawa: Jpn. J. Appl. Phys., 40 (2001) L1346.

11:20am **PS-FrM10 Evolution of Line Edge Roughness During Poly-Si Gate Stack Etching**, ***S. Rauf***, *P.J. Stout, J. Cobb*, Motorola Semiconductor Products Sector

As the transistor dimensions in integrated circuits continue to shrink, the influence of gate surface roughness on transistor electrical characteristics is expected to grow. As a consequence, there is considerable need for gate fabrication processes that minimize or mitigate photoresist and poly-Si gate surface roughness. An integrated 2-dimensional (2D) plasma equipment - feature evolution model has been used to study roughness evolution on photoresist and poly-Si gate surfaces during gate stack etching. The model considers a sequence of typical gate etch processes including resist trimming, anti-reflective coating etching, and poly-Si etching. The plasma equipment simulations of the low-pressure inductively coupled plasmas are based on the Hybrid Plasma Equipment Model (developed at the University of Illinois) and include validated plasma chemical mechanisms for the relevant gas mixtures. The 2D string based feature evolution model (BabyBean) has been developed at Motorola, and it considers reactive ion etching, ion assisted physical sputtering, polymer deposition and sputtering, and isotropic etching by neutral radicals. The feature evolution model has been validated by comparing with process experiments. Simulations show that ions are able to remove "rough" protrusions on the photoresist surface through physical sputtering. This is accompanied by changes in etching or polymer deposition within "rough" cavities due to reduction in local neutral flux. Roughness evolution is sensitive to roughness amplitude and frequency.

11:40am **PS-FrM11 Ar$^+$/XeF$_2$ Beam Etching of Si: What about Doping?**, ***A.A.E. Stevens***, *E. Te Sligte, H.C.W. Beijerinck*, Eindhoven University of Technology, The Netherlands

To circumvent the complexity of plasma etching, well-defined beams of Ar$^+$ ions and XeF$_2$ etch precursor gas are used to study the fundamentals of the etch process of silicon. Ellipsometry has been applied in the beam etching experiment in an attempt to bridge the gap between beam etching and plasma etching. The ellipsometric properties of Si(100) (n-type (P), resistivity = ~ 10 Ω cm) during physical sputtering by Ar$^+$ ions, spontaneous etching by XeF$_2$ and ion-assisted etching have revealed basic information regarding the reaction layer dynamics and composition. Sputtering by Ar$^+$ ions results in an ion damage layer that consists of amorphous silicon (a-Si) with a surface roughness of less than 0.3 nm. The thickness of the a-Si layer can be described well with TRIM simulations. Spontaneous etching by XeF2 is found to cause a rough reaction layer up to 13 nm thick that can be thought of as a rough and (partially) fluorinated silicon (SiF$_x$) surface. Ion-assisted etching is a combination of sputtering by Ar$^+$ions and etching by XeF$_2$, which resembles the actual etch process in plasmas. The reaction layer in this case is a mixture of rough a-Si and SiF$_x$ layer on top of an a-Si layer. In order to obtain a reliable comparison between ellipsometry measurements and simulations the surface roughness has to be known. Atomic force microscopy has been applied to study the surface roughness evolution of Si for various etching conditions, which has been used as input in the ellipsometry simulations. This more detailed description of the reaction layer dynamics and composition has enabled the study of n- and p-doped Si(100) samples with various types of dopants (As, Sb, P, B) and doping concentration (resistivity = 0.001-10 Ω cm). New information regarding the still unanswered question of the effect of doping on the etch mechanism will be presented.

Surface Science
Room: C-110 - Session SS-FrM

Self-Assembly at Surfaces
Moderator: D.H. Fairbrother, The Johns Hopkins University

8:20am **SS-FrM1 Structure of Nitrile-functionalized Alkanethiolate Monolayers on Gold and Silver**, ***A. Shaporenko***, *S. Frey*, Universität Heidelberg, Germany, *Ph. Harder, D.L. Allara*, Pennsylvania State University, *M. Zharnikov, M. Grunze*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) formed from nitrile-functionalized alkanethiols (AT) are perspective candidates for SAM-based lithography and the fabrication of surfaces with low protein affinity. In addition, the polar nitrile group with a relatively large dipole moment is well-suitable to explore to what extent the structure of a non-substituted AT SAM can be affected by strongly interacting tail groups. We used several complementary experimental techniques, such as X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy at the C1s and N1s absorption edges to get an information on the chemical identity, packing density, and orientational order in SAMs formed from CN(CH$_2$)$_{16}$SH (CN-C16) on (111) gold and silver substrates. The results imply that the substitution of the weakly interacting methyl groups by the nitrile entities has a strong influence on the molecular orientation, packing, and the structure of AT SAMs on both gold and silver. A strong dipole-dipole interaction between the polar nitrile groups is assumed to disturb a balance between the headgroup-substrate and interchain interactions, which is responsible for the SAM structure and packing density. In contrast to the methyl-functionalized AT SAMs, only a slight difference in the orientation of the alkyl chains in CN-C16/Au and CN-C16/Ag is observed. The nitrile groups in both CN-C16/Au and CN-C16/Ag are oriented almost parallel to the film surface, which is beneficial to minimize the dipole-dipole interaction between these moieties, but different from the "standard" orientation of the functional groups in ω-functionalized AT SAMs of the same chain length.

8:40am **SS-FrM2 Self-assembled Monolayers on Aluminium: The Role of Oxide Surface Chemistry**, *T.A. Lewington, I. Liakos, G.E. Thompson, R.C. Newman*, UMIST, UK, *E. McAlpine*, Alcan International, UK, ***M.R. Alexander***, UMIST, UK

Application of self-assembling organics molecules on oxide-covered, metal surfaces is of growing interest in areas ranging from medical implants[1] to adhesion promotion pre-treatments.[2] In the latter application area, legislation is driving industry to explore environmentally friendly pre-treatments for aluminium. Corrosion protection has been obtained using di-functional alkyl-phosphonic acids assembled on aluminium as a paint pre-treatment. It has been shown that one of the phosphonic acid head-groups form a phosphonate bond with the hydroxylated oxide film at the surface of the aluminium.[3] In addition to coupling of the resin and surface, it has been proposed that hydration is inhibited at the phosphonate-aluminium interface.[4] In contrast to the stable gold surface utilised in the assembly of alkane-thiols, the oxide at the aluminium surface is readily hydrated on exposure to ambient conditions.[5] It is proposed that this instability causes the inconsistent self-assembly often obtained on the aluminium surface. Thus, the oxide surface chemistry of magnetron sputtered aluminium has been controlled using solution and atmospheric conditioning; the effect on self-assembly of alkane-phosphonic acids is reported. XPS has been used to provide oxide thickness and surface hydroxyl concentration while contact angle and FTIR measurements have been used to probe the SAM coverage and order. Evidence for hydration inhibition by phosphonic acids SAMs is presented.

[1] G. L. KENAUSIS et al. J Phys Chem B 104 (2000) 3298.

[2] I. MAEGE et al Prog Org Coatings 34 (1998) 1.

[3] R. D. RAMSIER et al. Surf Sci 203 (1988) 72.

[4] A. DAVIS et al. J Mater Sci 20 (1985) 975.

[5] M. R. ALEXANDER et al. Surf Int Anal 29 (2000) 468.

9:00am **SS-FrM3 A Thermodynamic Perspective on Self-Assembled Monolayer Growth**, ***D.K. Schwartz***, *J. Mellott*, University of Colorado, *I. Doudevski*, University of California, Santa Barbara, *W. Hayes*, Crompton Corp., *C. Messerschmidt*, Infinion Corp. **INVITED**

Self-assembled monolayers form spontaneously at the solution/solid interface as a consequence of molecular adsorption and two-dimensional self-organization. The self-organization process can be viewed from the perspective of the nucleation and growth of a dense 2D phase (solid) from a less dense phase. In particular, the nucleation and growth kinetics of solid clusters in coexistence with a 2D "vapor" phase agree quantitatively with models of vapor phase epitaxial growth that predict growth regimes and scaling exponents. Other growth mechanisms are found, however, when the adsorbate/substrate interaction is varied. In fact, one can observe a qualitative change in the growth mechanism for a single system as a function of temperature. These mechanisms can be classified into three classes which can be viewed in a 2D thermodynamic context as occurring (1) below the liquid-vapor triple point, (2) above the liquid-vapor triple point, and (3) above the liquid-"solid" critical point, respectively.

9:40am **SS-FrM5 pH-Dependence of the Interaction Between Functionalized Probes and Tri(Ethylene Glycol)-Terminated Self-Assembled Monolayers on Gold Studied with Force Spectroscopy**, ***C. Dicke***, *G. Haehner*, University of St Andrews, UK

The understanding of protein adsorption on ultrathin synthetic surfaces has attracted considerable interest in recent years. In particular, the understanding of non-specific interactions is one of the major concerns. Functionalized self-assembled monolayers (SAMs) represent a class of ultrathin model surfaces that allow it to study the resistance to protein adsorption. Several recent investigations demonstrated the outstanding protein repelling properties of SAMs formed by oligo(ethylene glycol) (OEG) terminated alkanethiols on gold. Different suggestions have been made in order to explain this observation. Due to the strong hydration of the EG units in aqueous solutions an extended net-like structured water layer has been proposed to be responsible for the observed behaviour. The possibility of a specific incorporation of ions from solution into the self-assembled structure has also been suggested. Furthermore, it has been speculated that interactions of hydroxyl and/or hydronium ions with the synthetic interface play a major role. In order to elucidate the nature of the forces underlying the protein resistance in more detail, SAMs of methoxy-tri(ethylene glycol)-terminated undecanethiolates (EG3-OMe) adsorbed on polycrystalline gold were investigated by chemical force spectroscopy under liquids. Measurements with differently functionalised probes were performed under aqueous solutions with various ionic strengths and pH-values.

10:00am **SS-FrM6 Extraordinary Properties of the C 1s Photoemission Line of n-alkanethiolates on Gold and Silver**, ***K. Heister***, *M. Zharnikov*, University Heidelberg, Germany, *L.S.O. Johansson*, University Karlstad, Sweden, *M. Grunze*, University Heidelberg, Germany

The investigation of the C 1s photoemission line for n-alkanethiolate SAMs by synchrotron-based high resolution x-ray photoelectron spectroscopy (HRXPS) shows surprising properties. The energetic position of the C 1s emission line varies significantly by changing the substrate from Au to Ag. The analysis of this effect suggests that the observed shift of about 0.3-0.4 eV is only indirectly related to the substrate. Instead it seems to resemble the details of the film structure which change with the substrate. Besides we have observed that the C 1s peak shape alters with increasing alkyl chain length. The course of the peak shape evolution suggest a deconvolution of the C 1s emission line in several constituents. They can be attributed partly to intrinsic energy losses and partly to the influence of the close SAM-substrate interface on the innermost carbon atoms.

10:20am **SS-FrM7 Temperature-Programmed Desorption and Scanning Tunneling Microscopy Studies of n-Alkane Derivatives on Graphite: Desorption Energetics and the Influence of Functional Groups on Adsorbate Self-Assembly**, ***T. Müller***, *K.T. Rim*, *G.W. Flynn*, Columbia University, *A.V. Teplyakov*, University of Delaware

While carbon materials have found many practical applications ranging from sorption and catalyst support to the protection of magnetic storage media, numerous further uses may follow from the more recently discovered allotropes, fullerenes and carbon nanotubes. Alkane derivatives on the inert support provided by graphite can serve as model systems to study organic thin films and two-dimensional self-assembly. In the present study, Temperature Programmed Desorption (TPD) and Scanning Tunneling Microscopy (STM) are utilized to examine the influence of functionalization on the adsorption energetics and self-assembly of n-alkanes on Highly-Oriented Pyrolytic Graphite (HOPG). For adsorption of 1-bromoalkanes, alkanoic acids, and 2-bromoalkanoic acids, full activation of the substrate surface required annealing temperatures of approximately 700 K. Molecular desorption from physisorbed mono- and multilayers was found to exhibit first and zeroth-order kinetics, respectively. A Redhead analysis of monolayer desorption signals uncovered a profound influence of alkane functional groups. As compared with unfunctionalized n-alkanes, the desorption energies of all derivative species studied here exhibit a reduced chain length dependence in conjunction with an increased adsorption energy in the limit of zero chain length. Both effects reach their maximum for 2-bromoalkanoic acids, where (up to 2-bromooctanoic acid) the adsorption energy is nearly independent of the number of methylene units. The presence of functional groups is seen to introduce additional interactions, causing added configurational constraints and a competition with alkyl chain interactions in determining self-assembly patterns. These trends will be discussed in the context of molecular self-assembly information provided by ambient (liquid/solid) and UHV STM studies.

10:40am **SS-FrM8 Nanomolecular Motion Induced by Molecular Rectificator in the Self-Assembled Monolayers**, ***T. Ishida***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *H. Fukushima*, JRCHMM -JCII and TPRC, SEIKO EPSON Corporation, Japan, *T. Tamaki*, *H. Tokumoto*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Nanoscale molecular motion induced by polarity change of the electric field was observed by scanning tunneling microscopy (STM), when small amounts of asymmetrical disulfides containing terphenyl moieties were embedded into pre-assembled dodecanethiol self-assembled monolayers (SAMs). The class of disulfide was specifically designed to perform the large dielectric anisotropy in the terphenyl moiety. At the positive tip bias, few of protrusions were observed. When the STM tip bias turned to negative, many protrusions appeared on the binary monolayer surface. Scanning tunneling spectroscopy (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. Our observed nanomotion (about 1 min) is much faster than previously observed switching time (at least 20 min).[1] Also, the apparent molecular motion can be observed in the case of nanometer scale domains as well as single molecule.

[1] Z.J. Donhauser et al., Science 292 (2001) 2303-2307.

11:00am **SS-FrM9 Conductance Switching in Single Molecules**, ***Z.J. Donhauser****, *T.P. Pearl*, *P.S. Weiss*, The Pennsylvania State University

We have studied functionalized phenylene ethynylene oligomers as candidate molecular electronic devices using scanning tunneling microscopy (STM). A simple self-assembly strategy has been demonstrated that allows us to control monolayer structure, placement of individual molecules, and switching activity of individual molecules. Alkanethiolate self-assembled monolayers (SAMs) were used as host matrices to isolate and to insulate individual candidate molecular electronic devices. The isolated molecules were individually addressed and electrically probed using STM imaging and spectroscopy. The guest molecules exhibit reversible conductance switching, manifested as a change in the topographic height in STM images. High and low conductance states are visible when the molecules are inserted in dodecanethiolate SAMs, but the low conductance states are of the same height or lower than the host matrix. Using thin alkanethiolate matrices (as low as octanethiolate) reveals that the molecules can occupy at least three discrete conductance states. The amount and rate of active switching can be mediated by the structure of the host matrix. Poorly ordered SAMs were produced using a short deposition time; molecules inserted in these monolayers have a high switching activity. Well-ordered SAMs were produced using a vapor annealing procedure, which has been demonstrated with mixed alkanethiolate monolayers. Guest molecules inserted in vapor annealed SAMs have a low switching activity.

11:20am **SS-FrM10 Metastable Nanopattern Formation during Pb/Cu(111) Self-Assembly**, *R. van Gastel*, *R. Plass*, Sandia National Laboratories, Albuquerque, *N.C. Bartelt*, Sandia National Laboratories, Livermore, ***G.L. Kellogg***, Sandia National Laboratories, Albuquerque

Competing inter-atomic interactions on surfaces can lead to the spontaneous formation of ordered 2-D domain patterns in widely varying systems. The potential use of such patterns as templates for the fabrication of nanostuctures has fostered considerable interest in the underlying self-assembly process. Recently, it has been discovered that two phases of Pb on Cu(111) (a surface alloy and a Pb overlayer) self-assemble into nanoscale domain patters. [1] As the Pb coverage increases, the equilibrium patterns progress from islands of the overlayer (droplets) to stripes to islands of the alloy (inverted droplets). These equilibrium patterns are not the only patterns that can be constructed, however. Here, we use low energy electron microscopy to investigate metastable patterns that can be created by varying the temperature and deposition sequence. These include a stripe phase formed at low Pb coverages, and metastable droplet and inverted droplet phases, in which the island sizes are larger than those of the equilibrium structures. Both the droplet and inverted droplet metastable structures can develop into "froth" patterns -- the 2-D analog of soap bubbles. These patterns evolve in a deterministic manner. If the droplet phase from which a froth phase is created is ordered, a stable array of ordered hexagonal domains results. If the initial droplet phase is not ordered, the froth phase

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* Morton S. Traum Award Finalist

coarsens by a well-defined set of rules.[2] Thus, Pb on Cu(111) provides a model system both to explore the type of metastable patterns that can be formed for nano-template applications and to determine the laws that govern the formation, evolution and stability of nanometer-scale, 2-D patterns. Work supported by the U. S. DOE under Contract DE-AC04-94AL85000.

[1] R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature 412, 875 (2001)

[2] D. Weaire and N. Rivier, Contemp. Phys. 25, 59 (1984)

11:40am **SS-FrM11 Buffer-Layer-Assisted Nanostructure Growth Via Two-Dimensional Cluster-Cluster Aggregation**, *C.L. Haley, **V.N. Antonov**, J.H. Weaver*, University of Illinois at Urbana-Champaign

Physical vapor deposition of metals onto Xe multilayers at 20 K produces three-dimensional clusters. Warming to room temperature desorbs the Xe and causes coalescence. The net motion, and hence the extent of coalescence, depends on the buffer layer thickness. Using transmission electron microscopy, we determined the spatial distribution of these nanostructures as a function of Xe thickness. Using the scaling concepts of cluster-cluster aggregation, we found a fractal dimension ranging from 1.42 to 1.72 for initial fractional coverages of 0.04 to 0.20, consistent with Monte Carlo simulations of two-dimensional diffusion-limited cluster aggregation (DLCA). Both the number density and the weighted average nanostructure size show a power law dependence on the Xe layer thickness, where the latter plays the role of time in DCLA modeling. These relationships facilitate the design of nanostructure arrays generated by desorption-assisted coalescence.

Thin Films
Room: C-101 - Session TF-FrM

Fundamentals of Thin Flm Growth

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

8:20am **TF-FrM1 Supersonic Molecular Beam Studies of Thin Film Nucleation and Growth**, ***J.R. Engstrom***, Cornell University **INVITED**

For over three decades supersonic molecular beams have been used as tools in fields such as rarefied gas dynamics, spectroscopy and chemical reaction dynamics. Over the past several years we have been employing supersonic molecular beam techniques to investigate the fundamental aspects of Si and $Si_{1-x}Ge_x$ thin film growth from gaseous precursors, and more recently to study the nucleation of Cu on SiO_2, TiN and TaN surfaces. These beams prove useful in our case due primarily to two factors- their (kinetic) energy tunability, and their high spatial and temporal resolution. This work using molecular beams has been combined with in situ surface sensitive analytical techniques, such as x-ray photoelectron spectroscopy, low-energy ion scattering and low-energy electron diffraction. We have also made use of independent sources of energetic species, in particular atomic sources, to examine cooperative and synergistic effects in thin film growth. The overall emphasis has been on both developing a better fundamental understanding of existing processes, and potentially developing new processes. We will present a brief overview of our work, focusing on investigations of the effects of strain on gas-surface reactivity in $Si_{1-x}Ge_x$ epitaxial alloys; the growth of thin films at grazing angles of incidence; the exploration of scale-up strategies (experiment and computer simulation) for deposition over large areas, the use of atomic hydrogen to promote the selective area growth of epitaxial Si (and $Si_{1-x}Ge_x$) on patterned Si-SiO_2 substrates, and the nucleation and growth of Cu on TiN and TaN barrier layers, and poly-Si on three-component (Ca-Al-Si)-oxide glasses.

9:00am **TF-FrM3 Mechanism for Epitaxial Breakdown during Low-temperature Ge(001) Molecular Beam Epitaxy**, ***K.A. Bratland**, Y.L. Foo, J.A.N.T. Soares, T. Spila, J. D'Arcy-Gall,* University of Illinois, *P. Desjardins,* École Polytechnique de Montréal, Canada, *J.E. Greene,* University of Illinois

Experiments utilizing in-situ RHEED and post-deposition AFM, XTEM, and high-resolution XTEM, together with kinetic Monte Carlo models were designed to probe surface roughening pathways leading to epitaxial breakdown during low-temperature MBE of group-IV semiconductors. We conclusively demonstrate that epitaxial breakdown is not controlled by background hydrogen adsorption or gradual defect accumulation as previously suggested, but is a fundamental phase transition driven by kinetic surface roughening. Ge(001) layers grown at $T_s > 170$ °C remain fully epitaxial to thicknesses h > 1.6 µm, while deposition at $T_s < 170$ °C leads to a locally abrupt transition from epitaxial to amorphous growth at critical film thicknesses $h_a(T_s)$. Surface morphology during low-temperature Ge(001) MBE evolves via the formation of a periodic array of self-organized round growth mounds which, for deposition at $T_s > 115$ °C, transform to a pyramidal shape with square bases having edges aligned along <100> directions. Surface widths w and in-plane coherence lengths d increase monotonically with film thickness h. As h approaches $h_d(T_s)$, deep cusps bounded by {111} facets form at the base of interisland trenches and we show that epitaxial breakdown is initiated on these facets as the surface roughness reaches a critical T-independent aspect ratio, w/d = 0.02. $h_d(T_s)$ and $h_a(T_s)$ follow relationships $h_{d(a)} = \exp(-E_{d(a)}/kT_s)$, where E_d is 0.61 eV and $E_a = 0.48$ eV. E_d is approximately equal to the Ge adatom diffusion barrier on Ge(001) while $(E_d\text{-}E_a) = 0.13$ eV is the free energy difference between crystalline and amorphous Ge. We summarize our results in a microstructural phase map vs T_s and h, and propose an atomistic growth model to explain the epitaxial to amorphous phase transition.

9:20am **TF-FrM4 $Si_{1-y}C_y$/Si(001) Gas-source Molecular Beam Epitaxy from Si_2H_6 and CH_3SiH_3: Surface Reaction Paths and Growth Kinetics**, ***Y.L. Foo**, K.A. Bratland, B. Cho,* University of Illinois, *P. Desjardins,* École Polytechnique de Montréal, Canada, *J.E. Greene*, University of Illinois

$Si_{1-y}C_y(001)$ alloy layers were grown by gas source molecular-beam epitaxy (GS-MBE) from Si_2H_6/CH_3SiH_3 mixtures as a function of C concentration y (0 to 2.6 at%) and deposition temperature T_s (500-600 °C). High-resolution x-ray diffraction reciprocal lattice maps show that all layers are in tension and fully coherent with their substrates. Film growth rates R decrease with both y and T_s, and the rate of decrease in R as a function of y increases rapidly with T_s. In-situ isotopically-tagged D_2 temperature-programmed desorption (TPD) measurements reveal that C segregates to the second-layer during steady-state $Si_{1-y}C_y(001)$ growth. This, in turn, results in charge-transfer from Si surface dangling bonds to second-layer C atoms, which have a higher electronegativity than Si. From the TPD results, we obtain the $Coverage_{Si*}(y,T_s)$ of Si* surface sites with C backbonds as well as H_2 desorption energies E_d from both Si and Si* surface sites. $Coverage_{Si*}$ increases with increasing y and T_s in the kinetically-limited segregation regime while E_d decreases from 2.52 eV for H_2 desorption from Si surface sites with Si backbonds to 2.22 eV from Si* surface sites. This leads to an increase in the H_2 desorption rate, and hence higher film deposition rates, with increasing y and/or T_s during $Si_{1-y}C_y(001)$ growth. This effect, however, is more than offset by the decrease in Si_2H_6 reactive sticking probabilities at Si* surface sites. Film growth rates $R(T_s,J_{Si\ 2H6},J_{CH3SiH3})$ calculated using a simple transition-state kinetic model, together with measured kinetic parameters, were found to be in good agreement with the experimental data.

9:40am **TF-FrM5 In-Situ Infrared Chemometrics During BPSG Dielectric Thin Film Growth**, ***L.D. Flores**, J.E. Crowell,* University of California, San Diego

Dielectric thin film growth of boron and phosphorus doped silicate glass (BPSG) has been studied using the atmospheric pressure reaction between trimethylborate (TMB), trimethylphosphite (TMPi), tetraethoxysilane (TEOS) and ozone (O_3). In-situ gas-phase transmission FTIR spectroscopy was performed between 400-600°C by probing the variable region between the injector, heated Si wafer and the exhaust zones. Experimental methods for reliable quantitative infrared measurement of gaseous species in the CVD environment will be demonstrated. These studies involve low temperature ozone initiated deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial monoblok vent assembly. We quantify N_2 / O_2 / O_3 reaction products from BPSG precursors while varying the reactant ratios and probing as a function of infrared beam position within the reactor. The products produced during the reaction of TEOS and ozone are compared to those products measured during dopant reaction and incorporation from TMB and/or TMPi addition. Absorbances due to isolated silanol groups (3738 cm^{-1}) are treated using PCA (principle component analysis) techniques as a function of temperature and input reagent concentration to determine formation kinetics. The silanol groups and their reactions with boron and phosphorus dopant sources have been investigated in order to clarify their role in the oxidation process and to determine the reaction mechanism. Pathways involved in the hydrolysis and polycondensation process leading to siloxane formation and network film growth will be presented.

10:00am **TF-FrM6 Surface Chemistry of $TaCl_5$ on Polycrystalline Ta and Cu**, ***A.M. Lemonds**, J.M. White, J.G. Ekerdt*, The University of Texas at Austin

The surface chemistry of $TaCl_5$ on polycrystalline Ta and Cu was studied by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) following adsorption at 130 K. XPS determined that no surface reactions occurred during adsorption at 130 K on Ta, and binding energy shifts in the Ta 4f and Cl 2p XP spectra suggested interactions between $TaCl_5$ molecules in contact with the Ta substrate. TPD analysis from 130 to 900 K showed the desorption of two molecular states between 200 and 300 K from Ta, and the higher temperature state is more structurally ordered than the low temperature state. Chemical reaction between the $TaCl_5$ interfacial layer and O absorbed in the Ta lattice was observed for the 250 K annealing of multilayers adsorbed at 130 K. Surface coverages estimated by XPS were less than coverages estimated by TPD for adsorption on Ta, and the discrepancy is explained by the forward scattering of the substrate Ta 4f metallic photoelectrons through ordered $TaCl_5$ adlayers. A multilayer formed for $TaCl_5$ adsorption on Cu at 130 K, and a single multilayer desorption peak was observed at 275 K. At 300 K, $TaCl_5$ dissociatively adsorbed on Cu, and uptake saturated at less than one monolayer, limited by adsorbed Cl ligands. TPD for this adsorption showed Ta^+ (m/z 181) and Cu^+ (m/z 63) desorption features at 355 and 495 K, respectively. No detectable Ta or Cl was observed by XPS on the Cu surface following TPD, in which the surface temperature reached 900 K.

10:20am **TF-FrM7 Theoretical Design of Thin Film Growth with Functional Properties**, ***K.M.E. Larsson***, Uppsala University, Sweden

INVITED

Advanced surface engineering based on thin films technology is of growing importance in materials sciences today. Techniques to produce materials with tailor-made properties are being developed. Vapor growth processes like CVD (Chemical Vapor Deposition) are especially suited for this purpose. Vapor growth of materials is a very complex and dynamic process. It involves the generation of surface vacancies and adsorption of different gaseous species to various radical surface sites. Other important processes include surface abstraction and migration, as well as nucleation and a continued growth. Quantum mechanical calculations are useful for us to be able to get the atomic-level understanding that is necessary to reach for an understanding of these processes, as well as for making predictions about materials properties. Materials properties can generally be changed in two different ways. Firstly, it is possible to change it by changing the chemical and/or structural composition of the material. Secondly, a change may be obtained by varying the size of nanoparticles, or by varying the film thicknesses. Currently there is a great scientific and technological interest in these types of quantum confinement effects. The underlying reason is that various materials properties can be manipulated in fascinating ways by controlling dimension, rather that by controlling composition alone. Various inorganic compounds, with interatomic bonds that range from covalent to ionic types, will be focused in this presentation. One of the major goals is then to investigate and compare the growth processes for these different materials. Another main goal is to investigate the effect of various parameters (e.g., surface termination, amount and types of defects and dopants, sizes) on materials properties like electrical, optical and mechanical. All of these knowledges are very useful in the development of new experimental designs, as well as in the deposition of more artificial structures.

11:00am **TF-FrM9 Chemical Bonding Requirements for Forming Passive Semiconductor Oxide Interfaces**, *J.Z. Sexton*, ***A.C. Kummel***, University of California, San Diego

The formation of passive, electronically unpinned metal oxide - semiconductor interfaces is a critical part in the development of III / V MOSFET technology. A high quality gate oxide will unpin the Fermi level and will form an interface with low interfacial defect densities. We have done first-principles density functional theory calculations to investigate the chemical bonding requirements for forming a passive gate-oxide / semiconductor interface. Upon MBE deposition onto the GaAs(001)-β2(2x4) surface, Ga_2O inserts into a pair of surface As-dimers. This layer unpins the Fermi level and allows for growth of bulk amorphous oxide. This is in contrast to O_2 chemisorption which displaces surface arsenic atoms and pins the Fermi level. First principles calculations were done to elucidate the mechanism for Fermi level unpinning on this surface. Calculations comparing Ga_2O and O_2 chemisorption on GaAs(001)- β2(2x4) indicate that the requirements for the formation of a passive interface are: 1) charge balance restoration of surface As atoms to near-bulk values, 2) restoration of surface geometry to a bulk-like bonding environment, and 3) sequestering of oxygen atoms near the interface into sites ionically bonded to gallium atoms. These three bonding requirements act synergistically to passivate the interface. The effects are observed in DFT calculations of the local charge densities per atom, interfacial geometry of gallium and arsenic atoms, and local density of states in the band-gap region of the GaAs(001)-β2(2x4) - Ga_2O interface. These calculations provide a roadmap for identifying passivation oxides for other semiconductor surfaces.

11:20am **TF-FrM10 In-situ Observation of the Electron-Current Effect on Mass-Flow in Thin Ag Films on an Insulating Substrate**[1], ***O. Bondarchuk***, *M. Degawa, E.D. Williams*, University of Maryland

As electronic device dimensions become smaller, we can expect surface-induced changes in the electrical properties, including transport phenomena[2] and electromigration phenomena.[3-5] The fluctuations and motion of single-layer steps under the electromigration driving force are the key connection between the atomic scale mechanism and the continuum scale response. This connection can be quantified by using the predictions of Pierre-Louis and Einstein[5] concerning the motion of single-layer deep pits and single-layer height islands under an electromigration force. We have designed an experimental configuration to directly test the theoretically predicted shape distortion and net migration of voids and islands, on thin crystalline Ag films using STM. The Ag films of ~100-200 nm thickness with large (0.5-1 mm in size) features were deposited on mica and studied in-situ under UHV conditions. Growth parameters were tuned to create films with large grains, large atomically flat surface areas, and continuous electrical conductivity while minimizing film thickness. STM imaging was performed with sample carrying up to ~ 1 A, corresponding to a current density of ~ 2.5x105 A/cm2. Voids and islands were created by removing ~0.5 monolayer by 1 keV Ar-ion sputtering at room temperature. Evolution of morphology occurring via thermal activation of metastable structure decay is a competing process with structural evolution via electron current effects.

[1] Work supported by the NSF NIRT and MRSEC programs.

[2] O. Pfennigstorf, A. Petkova, H.L. Guenter, and M. Henzler, Phys. Rev. B 65, 045412(2002).

[3] P.J. Rous, Phys. Rev. B61, 1 (2000).

[4] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov , S.I. Stenin, Surf. Sci. 213, 157 (1989)

[5] O.Pierrre-Louis and T.L. Enstein, Phys.Rev.B62, 13697 (2000).

11:40am **TF-FrM11 Effect of Metal Underlayers on Low Temperature Silicon Growth**, ***K. Xu***, *A. Pradhan, S.I. Shah*, University of Delaware

Previously, we have reported the effect of Kr on the crystallinity of Si films grown at low temperatures on temperature sensitive substrates. An additional contribution to the Si film crystallinity comes from metal underlayers. Silicon films were deposited on glass, metal-coated glass and metal-coated polymer substrates at temperatures between 130-200°C. X-ray diffraction showed that the films deposited on substrates with gold underlayers were polycrystalline while those deposited on bare glass or polymer substrates were x-ray amorphous. Atomic force microscopy (AFM) was used to study the topography and ad-atom diffusion on the surface. AFM micrographs showed that the polycrystalline silicon films had an average grain size of 95nm. The surface diffusion length was calculated from the AFM micrographs. The results showed films deposited on substrates with gold underlayers had larger diffusion lengths which help to increase the grain size. In order to understand the effect of the underlayer grain size, gold films were annealed to temperatures up to 400°C. Silicon films deposited on these annealed substrates showed even higher crystallinity and larger grain size. The results of XRD, AFM and Raman characterizations will be presented. We will correlate the grain size to the diffusion length and present a model for grain growth in silicon films on temperature sensitive substrates.

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