Monday Morning, November 2, 1998

Applied Surface Science Division
Room 307 - Session AS-MoM

Materials Analysis (including Small Dimensions and Synchrotron)

Moderator: F.A. Stevie, Lucent Technologies

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Applied Surface Science Division
Room 307 - Session AS-TuM
Sample Preparation and Tricks of the Trade
Moderator: D.R. Baer, Pacific Northwest National Laboratory

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

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

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

High energy Ag L@sub alpha@ X-rays have several advantages over the more commonly employed Al K@sub alpha@ source. A photon energy of 2984.3 eV means that a Ag source can generate higher core levels, Auger series and has a greater excitation volume. A further advantage over other high energy sources is that the Bragg condition may be satisfied via a second order diffraction within the confines of the conventional Al K@sub alpha@ monochromator body with only minor modifications. Such an approach has previously resulted in a workable source although the sensitivity was reduced in comparison to the Al K@sub alpha @source.@footnote 1@ We have now for the first time implemented a Ag monochromator as a modification to the standard Al mono on a modern magnetic lens based electron spectrometer, the Axis Ultra. The great improvements gained in photoelectron collection efficiency by employing magnetic lens technology improves the sensitivity and ultimate usability of the Ag source making it a viable alternative for the measurement of deep 1s core levels and Auger parameters. The functionality will be demonstrated with examples of Auger parameter and high energy core level spectroscopy. @FootnoteText@ @Footnote 1@K Yates RH West Surface and Interface Analysis Vol 5 No 4 1983 133-138

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Organic Thin Film Interfaces

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Biomaterial Interfaces Group
Room 326 - Session BI+AS+MM+NS+SS-TuA

Nanoscale to Mesocale Biomaterial Structures

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

2:00pm **BI+AS+MM+NS+SS-TuA1 Self-Assembly of a Multidomain Protein: Fibronectin at Lipid Model Interfaces***, **V. Vogel**, G. Baneyx,* University of Washington **INVITED**

Fibronectin, an adhesion protein with multiple recognition sites, mediates cell attachment to synthetic and biological surfaces. In solution, fibronectin exists in a globular state where most of its recognition sites are buried in the protein core. Surface adsorption induces conformational changes in the protein that expose many of these sites. Furthermore, it is known that on the surface of cells fibronectin assembles into detergent insoluble fibers, which are considered to be the main functional form of the protein. Fibronectin is hence a prime example of a protein with multiple recognition sites that can be regulated through environmental control. Unfortunately, the molecular pathways of activation and self-assembly are still poorly understood. We have recently found that fibronectin can self-assemble into fibrillar networks at receptor-free phospholipid monolayer interfaces under physiological conditions. This is a crucial observation since the paradigm in biology is that fibril assembly of fibronectin is mediated by membrane-bound receptor molecules. Availability of a simplified model system allows investigation of the molecular pathways by which appropriate surfaces can activate fibronectin and facilitate self-assembly.

2:40pm **BI+AS+MM+NS+SS-TuA3 Nanofabricated Substrates for Probing Single Biomolecules by Surface Enhanced Raman Scattering***, **S. Petronis**, L.K. Hedberg, H. Xu, M. Käll, B. Kasemo,* Chalmers Univ. of Technology and Univ. of Gothenborg, Sweden

The effect of Raman scattering enhancement when coherent laser light interacts with molecules attached to rough surfaces and microscopic metal domains has been known for more than two decades and is called Surface Enhanced Raman Scattering (SERS). The intensity of the Raman signals for such molecules is frequently enhanced by a factor 10@super 5@-10@super 6@ at best.@footnote 1,2@ However recently much larger enhancement factors, in the range 10@super 14@-10@super 15@, have been observed for molecules adsorbed on colloidal silver particles of specific dimensions.@footnote 3,4@ This giant enhancement allows the recording of vibrational spectra from a single molecule for the first time, instead of the ensemble averaged spectra from many molecules, which are normally obtained in optical spectroscopies. Here we report on an attempt to use nanolithography to fabricate structures of silver in the size range 100 - 200 nm and having different shapes in order to explore the size and geometry dependence of the SERS effect. Microfabricated structures which give the highest enhancement could be used for probing different biomolecules and perhaps designing a biosensor. SERS active substrates were prepared as arrays of silver particles on a Si wafer. Within each array the silver particles had a constant shape, size and separation. Three particle shapes (circular, triangular and square), two particle sizes (100 nm and 200 nm), and five different particle separations (10, 50, 100, 150 and 200 nm) were produced by electron beam lithography with a double-layer resist system and "lift-off" procedure. A reference area of uniformly deposited Ag film mimicked an infinite silver surface. The final structures and the chemical composition of the silver particles were characterized by Scanning Electron Microscopy (SEM) and Auger electron spectroscopy (AES), respectively. Preliminary Raman scattering experiments have been performed on the dye-molecule Rhodamin 6G adsorbed on the nanofabricated substrates. A giant enhancement of the Raman signal was observed on all patterns, but not on the Ag film or the Si surface. @FootnoteText@ @footnote 1@M.Moskovits, Rev. of Mod. Phys., vol. 57, No 3, 1985, pp 783-826 @footnote 2@A.G.Mal'shukov, Phys. Rep., vol 194, Nos 5&6, 1990, pp 343-349 @footnote 3@K.Kneip et al., Phys. Rev. Lett., vol. 78, No 9, 1997, pp1667-1670 @footnote 4@S.Nie, S.R. Emory, Science, vol. 275, No 21, 1997, pp 1102-1106

3:00pm **BI+AS+MM+NS+SS-TuA4 Nanostructured Surfaces for Biorecognition - A Novel Templating Approach***, **H. Shi**, B.D. Ratner,* University of Washington

Materials that specifically recognize proteins may find a variety of applications in separations, sensors and medical materials. Molecular imprinting provides an intriguing approach to plastic antibodies against small molecules, but the use of proteins as templates has been less successful in making protein recognition materials. In this study, nanostructured surfaces with tailored protein-binding cavities are prepared by an imprinting technique based on RF-plasma deposition of organic thin films. A polysaccharide-like surface with protein-imprinted nanopits allows only the template protein to fill the pits, and to bind strongly, because the nanopits are complementary to the template protein in shape and in the distribution of functional groups. The bound protein in its pit is prevented from exchange with protein in the solution due to a strong binding and steric hindrance, while the non-template protein that is weakly adsorbed on the surface is displaceable. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed that nanometer-sized pits, in the shape of imprinted proteins, were created on the surfaces of our protein-imprinted polymer films. Imprinting fidelity was confirmed by AFM analysis of imprints of monodisperse colloidal gold nanoparticles. Electron spectroscopy for chemical analysis (ESCA) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) indicated that template proteins were washed off the surfaces of protein imprints while sugar molecules were covalently incorporated. Radiolabeled -protein adsorption showed that a protein imprint recognized its template protein from a binary mixture with a high specificity. This study illustrates a novel templating strategy for biological molecules that can be exploited for fabrication of biorecognition materials.

3:20pm **BI+AS+MM+NS+SS-TuA5 Sensing and Analyzing Single Molecular Interactions with Microfabricated Devices@footnote 1@***, J.-B.D. Green, **G.U. Lee**,* Naval Research Laboratory **INVITED**

There is an intense effort to create new tools for manipulating and characterizing single macromolecules because of the power that these techniques can bring to the analysis of biological macromolecules. Due to the high force and displacement sensitivity of the atomic force microscope (AFM) it has been used to measure inter- and intramolecular forces between model ligand-receptors, i.e., streptavidin-biotin, complimentary strands of DNA, and biologically relevant supra-molecular structures, i.e. titin. With the success of these measurements, there are efforts to obtain even more detailed force measurements and to establish these techniques in the biotechnology laboratory. Our efforts focus on: 1. Designing force transducers with force (10@super -12@N), time (10@super -5@s) and spatial (10@super -9@m) resolutions that push the thermal noise envelope. 2. Developing immobilization strategies that produce more reliable force measurements. We will discuss two new microfabricated devices under development in our laboratory. The first microfabricated apparatus offers an excellent platform for detailed measurements of intermolecular interactions and possibly even analysis of combinatorial arrays. The second is an ultra-sensitive detector based on piezoresistive force transduction and magnetic microparticles. The future of these and similar devices will be considered. @FootnoteText@ @footnote 1@This work has been conducted in collaboration with Alexey Novoradovsky, Jonah Harley, Mohan Natesan, Steven Metzger, David Baselt, and Richard Colton.

4:00pm **BI+AS+MM+NS+SS-TuA7 Nanomechanical Properties of Cellular Components Determined by Interfacial Force Microscopy***, **P.R. Norton**, K de Jong, J.F. Graham, N.O. Petersen,* University of Western Ontario, Canada

The cell membrane is the contact surface between the cell's internal environment and the outside world. Increasingly it is recognized the there is strong active coupling between mechanical properties and cellular functions in properties such as locomotion and adhesion and in cytoskeletal diseases such as muscular dystrophy.@footnote1@ There is therefore an urgent need to understand the mechanical properties of cells and cellular subcomponents at length scales << 1µm. We will describe our initial experiments to achieve this goal. We have used three different imaging techniques in our investigation of the nanomechanical properties of larynx cells. First, immunofluorescent labelling was used to permit visualization of specific cell components in the confocal microscope, for example to determine whether the cell nucleus was removed in a shearing process. The same cell was then imaged in the atomic force microscope (AFM), permitting identification of components involved in motion such as microspikes. The nanomechanical properties of cells were then studied by nanoindentation using the interfacial force microscope (IFM).@footnote2@ While we have not yet succeeded in imaging and measuring the same cell used in the confocal and atomic force microscopies, we have demonstrated the feasibility of our approach and have obtained quantitative force-distance curves on different regions of a single cell fixed in paraformaldehyde, sodium periodate and lysine, which cross-links the proteins. From these data we can derive the elastic modulus, hardness etc of the specific region of the cell. The modulus of such a cell was ~ 3GPa, comparable to a soft polymer. Similar measurements are planned on unfixed cells. @FootnoteText@

@footnote1@Chen, C.S., et al. Science 276, 1425 (1997) @footnote2@Warren, O.L., et al. Physics in Canada 54, 122 (1998)

4:20pm **BI+AS+MM+NS+SS-TuA8 Unbinding Force of NTA-M@super 2+@--Histidine Complexes. The His-Tag Immobilization Force***, J.G. Forbes, P. Yim,* University of Maryland, College Park

A sequence of six or more histidines will bind tightly to a Cu, Ni, or Co complex. The compound typically used to immobilized the metal is N-(5-amino-1-carboxypentyl)iminodiacetic acid (NTA). Most proteins will not bind to the complex unless there is a sequence of histidines, which is readily added using recombinant DNA techniques. The histidine tag may be removed from the metal complex with a high concentration of imidazole or by protonating the histidines at a pH below 6. We have studied the the unbinding strength of this interaction with the atomic force microscope (AFM). To perform this measurement, we have functionalized silicon nitride AFM tips with NTA-M@super 2+@. A glass slide was coated with recombinant DNAse I with a his-tag on the C-terminus. Unbinding force measurements were made in phosphate buffered saline (PBS) to reduce electrostatic interactions. We find that the unbinding force for the NTA-M@super 2+@/His-tag interaction to be ca. 85~pN for each of the metal complexes. Interestingly, 0.5~M imidazole does not remove the interaction, but only changes the distribution of the measured forces. This is a result of the non-equilibrium condition of the tip being forced into the protein coated surface. The interaction is almost completely removed by lowering the pH to 5.0 where the histidines are protonated and can no longer coordinate with the nickel. The remaining interaction forces are due to the histidines which are exposed when the tip presses into the surface. These results provide a quantitative measurement of mechanical strength of binding of proteins to surfaces functionalized with NTA-M@super 2+@.

4:40pm **BI+AS+MM+NS+SS-TuA9 Sieving of DNA Molecules in Nanofluidic Channel***, **J. Han**, H.G. Craighead,* Cornell University

Entropic trapping and sieving effect of long DNA molecules was studied in variable thickness nanofluidic channels. We used photolithography and etching techniques to define fluid channels on Si wafers, and anodic bonding method to seal the channel with a thin pyrex glass coverslip. The channel consists of alternating regions with two different channel thicknesses(~100nm and 1.6µm). We studied electrophoretic motion of lambda phage DNA in this channel by epi-fluorescence microscopy. Since the radius of gyration of a typical long DNA molecule is larger than the smaller gap of the channel, the shallow part of the channel can be an entropic barrier for DNA motion.Therefore, DNA molecules were retarded when they entered into the thin region from the thick region. We measured the mobility of DNA molecules in these channels and observed that below a certain electric field, mobility of DNA molecule decreased to near zero drastically, showing that DNA molecules be entropically trapped and sieved. The threshold electric field was mainly dependent on the geometry of channel(e.g. gap size) and the length of DNA driven. This suggests a new type of separation device for DNA and other polymers.

5:00pm **BI+AS+MM+NS+SS-TuA10 Detection of Molecular Ion and Quantification of Pentapeptide on Plasma Hydroxylated Fluoropolymer by Time of Flight Secondary Ion Mass Spectrometry***, J.A. Gardella, **L.M. Sun**,* State University of New York, Buffalo

Abstract: Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) was modified by a hydrogen/methanol radio frequency glow discharge plasma. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was employed to characterize the modified FEP surface and three pentapetides (YGGFM, YGGFL, YIGSR) which were microsyringe deposited on the modified FEP film. New fragments of OH (CF@sub 2@)n in negative ion SIMS of the modified FEP film indicated that -OH functional group had been incorporated on the FEP surface after plasma treatment. In the positive ion SIMS of three pentapeptides on the hydroxylated FEP film, protonated molecular ions were dominant signals from the peptides whereas not many fragments were observed either from the peptides or the impurity. Sodium and potassium adduct molecular ions were detected as well as oxidized protonated molecular ion of YGGFM in the positive ion SIMS spectrum. Negative ion SIMS of YGGFL yielded a deprotonated molecular ion. The mixture of these three pentapetides was also studied by TOF-SIMS. The relative intensity of protonated molecular ions of YGGFL, YGGFM and YIGSR showed the possibility of quantification on the hydroxylated fluoropolymer by TOF-SIMS. As a study of substrate effects, TOF-SIMS spectra of these peptides on oxidized Ag substrate were recorded. Comparing SIMS results of pentapetides on Ag and on modified FEP film, fewer fragments occurred from the FEP film than that from the Ag substrate. A substrate like the FEP fluoropolymer might be beneficial for the quantification of peptides because of the intensity of parentlike species in SIMS measurement.

Applied Surface Science Division
Room 307 - Session AS+BI+SS-WeM

Organized Molecular Monolayers

Moderator: H.G. Tompkins, Motorola, Inc.

8:20am **AS+BI+SS-WeM1 Structural Characterization of the Outermost Surface Monolayers of CH@sub 3@ and CF@sub 3@ Terminated n-Alkanethiol Monolayers Self-Assembled on Au(111)**, *L. Houssiau, **J.W. Rabalais**,* University of Houston

Time-of-flight scattering and recoiling spectrometry (TOF-SARS) was used for surface elemental and structural characterization of hexa- and hepta-decanethiols (C@sub 16@ and C@sub 17@ for short) and of 16,16,16-trifluorohexadecanethiol (FC@sub 16@) self-assembled monolayers (SAMs) on a Au(111) surface. The substrate was also characterized after in-situ sputtering and annealing by TOF-SARS and LEED in order to identify its crystalline orientation. The azimuthal angle scans performed on the C@sub 16@ samples displayed unique features, indicating well-ordered structures. The recoiling intensities of the H and C atoms exhibited a clear 60° periodicity, with H recoil maxima and C recoil minima displayed at 30° from the substrate nearest-neighbor directions. Several models were tested by means of classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC). The molecular length, tilt angle, and twist angle were varied in the simulations. Good agreement between the experiments and simulations for both C and H signals was obtained for a (@sr@3x@sr@3)R30 structure of SAM lattice, with the molecules tilted along the substrate nearest-neighbor directions by 35° from the surface normal. Moreover, a twisting of the molecular plane by 55° from the plane normal to the surface had to be considered in order to reproduce the H angular variations. Similar measurements on the C@sub 17@ samples showed much weaker variations for the H and C recoil intensities. This is believed to be due to the high tilt angle of the end methyl group. The FC@sub 16@ samples showed the presence of C and F atoms in the surface layer. No evidence for H and C recoil azimuthal variation was observed on the FC@sub 16@ samples, although a weak azimuthal periodicity was noticed for the F recoils.

8:40am **AS+BI+SS-WeM2 Fundamental Studies of Phase Transitions in Functionalized Amphiphile Monolayers**, ***G.E. Poirier**,* National Institute of Standards and Technology

Alkanethiol molecules chemisorb strongly to noble metal surfaces. Intermolecular dispersion forces compress the molecules into a dense, commensurate, crystalline film that spontaneously terminates growth at one molecular monolayer. The thickness of the film, its dielectric constant, and the physical properties of the exposed surface can be controlled by changing the length of the alkyl chain, its degree of saturation, and its terminal functional group, respectively. These systems are therefore desirable in any application requiring control of the adhesive, tribological, or electron transfer properties of metal surfaces. This talk will outline experiments in which methyl-terminated alkanethiol monolayers were prepared by vapor deposition onto clean Au(111) in ultra-high vacuum and characterized in-situ using molecular-resolution scanning tunneling microscopy.

9:00am **AS+BI+SS-WeM3 Characterization of Fluorinated Monolayers**, ***D.G. Castner**,* University of Washington **INVITED**

Self assembly processes have made it possible to prepare organic monolayers with well-defined surface structures and chemistries. The ability to systematically vary the surface structure and chemistry of these self-assembled monolayers (SAMs) provide an excellent method for examining the relationship between the surface properties of a film and its performance in a given application (e.g., cell culture). To develop these relationships requires detailed characterization of the surface composition, molecular structure, orientation, and topography of the films with techniques such as XPS, ToF SIMS, NEXAFS, and STM. How the methods and molecules used to form fluorinated films affect the resulting film structure will be discussed. The degree of ordering and relative orientation in SAMs prepared with perfluoroalkyl thiols depend on the length of the fluorinated tail. Although SAMs prepared from thiols with long perfluoroalkyl tails are highly ordered, their stability is limited by the single point attachment of the Au-S bond. This stability can be increased by using grafted copolymers containing both perfluorinated and alkanethiol side chains to generate multipoint attachment of each polymer chain. However, this method of increasing film stability also results in a decreased degree of film orientation. Typically films prepared using polymers with perfluorinated side chains are highly disordered. Only at high concentrations of perfluoroalkyl side chains (>50%) is any ordering detected in polymeric monolayers. Other methods, such as trifluoroacetic anhydride derivatization of hydroxyl-terminated alkanethiols can also be used to produce fluorinated surfaces. Depending on the derivatization system, the high degree of ordering in the starting SAM can be retained after derivatization.

9:40am **AS+BI+SS-WeM5 Controlling Defects in Self-Assembled Monolayers**, ***J.J. Jackiw**, J.J. Arnold, J.A. Johnson, T.D. Dunbar, T.L. Spiva, D.L. Allara, P.S. Weiss,* The Pennsylvania State University

Much is known about the formation, structure, stability, and properties of alkanethiolate monolayers on Au (111). We have begun to explore the effects of changing the molecule-surface linkage. In the cases of alkanethiolates and alkaneselenolates, monolayers can be made respectively from: thiols and selenols, disulfides and diselenides, and by deprotecting alkanethioacetates and alkaneselenoacetates, which are less prone to oxidation. Our experiments probe monolayer structures and defects resulting from the deposition of dodecanethiol, didodecane disulfide, didodecane diselenide, dodecaneselenol, and in situ deprotected dodecanethioacetate and dodecaneselenoacetate. We compare the structures and defects in the resulting monolayers. The defect identities and densities are important in determining the properties of the films, especially our ability to manipulate their structures and compositions.

10:00am **AS+BI+SS-WeM6 New Preparation Methods for Self Assembly of Alkanethiolates on III-V Semiconductor Surfaces**, ***C.K. Mars**, D.L. Allara,* Pennsylvania State University

The ability to control the chemical composition of III-V surfaces is vital in semiconductor technology. Alkanethiolate monolayers prepared from thiol melts at temperatures near 100°C have been shown to mimic the improved electronic passivation properties seen on III-V semiconductors with Na@sub 2@S and NH@sub 4@S@sub x@ treatments. We have developed a new process by which these films can be grown reliably in a highly organized state from millimolar ethanol solutions near 50°C. In addition, by adding controlled amounts of base to these solutions, the degree of organization as determined by IR spectroscopy and contact angle measurements, can further be improved. This new process has allowed us to deposit a wide variety of films including aromatic and functionalized molecules as well as layers anchored by other chalcogenide elements.

10:20am **AS+BI+SS-WeM7 The Effect of Solvents and Electrical Fields on the Molecular Conformation in Organic Monolayers**, ***M. Grunze**, M. Buck, F. Eisert, M. Zolk, P. Harder,* University of Heidelberg, Germany*; A. Pertsin,* Russian Academy of Sciences, Russia*; H.J. Kreuzer,* Dalhousie University, Canada **INVITED**

The molecular conformation in self-assembled monolayers (SAMs) of functionalized alkanethiols is affected by the presence of solvents. The polarity and ability of the solvent molecules to form hydrogen bridge bonds, and the lateral density in the SAMs determines the orientation of the terminal functional moiety at the organic film/solvent interface. We will discuss our in situ Sum Frequency Generation (SFG) and protein adsorption experiments on methyl- and oligo(ethylene glycol)-terminated self-assembled alkanethiolate monolayers, and present atomistic force field calculations to explain our data. These results show that spectroscopic measurements taken in vacuum or ambient atmosphere are not necessarily representative for the molecular structure and chemical nature of organic surfaces immersed in a liquid.

11:00am **AS+BI+SS-WeM9 Nanometer-Scale Design and Fabrication of Polymer Interfaces using Polydiacetylene Monolayers**, ***M.D. Mowery**[1], M. Cai,* University of Michigan*; H. Menzel,* University of Hannover, Germany*; C.E. Evans,* University of Michigan

The selective control of polymer interfacial characteristics such as viscoelasticity and electronic properties is crucial for numerous important applications from sensor design to device fabrication. In this work, robust interfacial polymer films are successfully fabricated within a single molecular layer with nanometer-scale control of the polymer physical structure. The formation of these unique polymer films is accomplished by the spontaneous assembly of alkyl disulfide precursors containing conjugated diacetylene groups at the gold-solution interface. The resultant well-defined monomer assembly is covalently linked through UV photopolymerization, forming a highly conjugated polymer backbone parallel to the surface. Nanometer-scale control of the interfacial structure is accomplished by manipulating the vertical position of the polymer

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backbone within the single layer assembly. Additionally, photo-templating affords lateral control over the formation of polymer domains. These subtle variations in physical structure have a profound impact on the global electronic and viscoelastic properties of the polymer interface. The impact of these structural variations is demonstrated by surface infrared and Raman spectroscopy as well as electrochemical capacitance, heterogeneous electron transfer, and reductive desorption measurements. Furthermore, AFM is utilized to physically image the interfacial structure and evaluate the polymer viscoelastic properties. Finally, the application of these monolayer polymers for lithographic applications and the implications for interfacial design are discussed.

11:20am **AS+BI+SS-WeM10 Bias-dependent Contrast in STM Images of Phenyloctadecylethers***, **I.H. Musselman**, H.S. Lee, S. Iyengar,* University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images were acquired from monolayers of the ethers physisorbed onto highly oriented pyrolytic graphite. The contrast exhibited by the X-POE molecules in these images varied as a function of tip-sample bias. For example, STM images acquired at biases of approximately -0.5 to -0.6 V (sample negative) exhibited a dim alkyl tail and a series of bright spots corresponding to functionalities in the head group (e.g. halogen, phenyl group, oxygen). However, at biases more negative than -1.2 V, the largest contribution to contrast was observed for the alkyl tail (e.g. octadecyl group). A comparison of STM images of the adsorbed X-POE molecules with electron density contours calculated using HyperChem suggested a bias-dependent participation of individual bonding molecular orbitals to tunneling. A resonance tunneling mechanism between the tip and molecular orbitals adjacent to and including the highest occupied molecular orbital (HOMO) is proposed.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

11:40am **AS+BI+SS-WeM11 Self-Assembling Trichloro- and Trimethoxy-silanes on TiO@sub 2@(100) Crystal***, **R. Magnée**, J.-J. Pireaux,* LISE - Facultés Universitaires Notre-Dame de la Paix, Belgium

Trichlorosilanes (CH@sub 3@(CH@sub 2@)@sub n@SiCl@sub 3@, n = 1, 7, 17) and trimethoxysilanes (CH@sub 3@(CH@sub 2@)@sub n@Si(OCH@sub 3@)@sub 3@ , n = 2, 7, 17) SAM's were deposited by dipping a TiO@sub 2@ (100) crystal in a 10@super -3@M toluene solution for 4 hours. The titanium dioxide surface was prepared by Ar@super +@ sputtering, annealing in UHV to get a clear LEED (1x3) pattern, then exposed to atmosphere before dipping. Silane molecules need H@sub 2@O or a hydroxylated surface to react but it was not necessary to hydroxylate the TiO@sub 2@ because of the air exposure. Hydroxylation was confirmed by FT-IR and XPS. X-Ray and Ultra-violet Photoelectrons Spectroscopy (XPS, UPS) were then used for the SAM's charaterization. We expect a siloxane network to appear at the interface in addition to the Ti-O-Si bonds. XPS results show that the silane groups do indeed bind to the TiO@sub 2@ surface but that some defects are also present at the interface: for n=17 the amount of OH groups is 4 % of the total oxygen signal while this value is doubled for n=7. Probably due to the higher reactivity of chlorine atoms, trichlorosilanes present less defects than trimethoxysilanes. By comparison with theoretical calculations,@footnote 1@ UPS provides information on the alkane chain conformation: we show that longer silane molecules (n=17) are grafted in a zigzag planar conformation, while n=7 molecules seem to present chain defects. This is consistent with the self-assembling process that depends on long-range interchain interactions. For the smallest chains (n=1,2), the XPS C/Si ratios are always too high, suggesting some contamination: this is probably due to solvent incorporation in the layer. HREELS analysis (not yet performed at the date of abstract submission) may help to get more information on the order of the layers. @FootnoteText@ @footnote 1@ A.-S. Duwez, S. Di Paolo, J. Ghijsen, J. Riga, M. Deleuze, J. Delhalle, J. Phys. Chem. B, 101 (1997) 884.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+AS-WeM

Innovative Force, Near-Field Optics, and Tunneling Measurements

Moderator: H.G. Craighead, Cornell University

8:20am **NS+AS-WeM1 Recent Progress in the Functionalisation of AFM Probes using Electron-Beam Nanolithography***, H. Zhou, G.M. Mills, B.K. Chong, L. Donaldson, **J.M.R. Weaver**,* Glasgow University, Scotland **INVITED**

Scanned probe microscopy has greatly expanded the range of contrast mechanisms available to microscopists. Until recently, however, the only techniquees available to the non-specialist user have been those which involve either the modification of the SPM instrumentation (for example Scanning Capacitance Microscopy) or relatively simple functionalisation of the probe (for example Magnetic Force Microscopy). More complex techniques, based on the fabrication of advanced probes, have largely remained confined to a relatively small number of groups. These include the Hall Probe Microscope,@footnote 1@ The scanning Single Electron Transistor@footnote 2@ and others. Recently progress has been made towards methods whereby probes may be modified using batch fabrication techniques such as focussed ion beam deposition,@footnote 3@ controlled etching processes@footnote 4@ or direct-write electron-beam lithography.@footnote 5@ This talk describes recent work in which the last named method has been used to fabricate Near-Field Optical (SNOM), Thermal (SThM) and Magnetic sensors. Results will be presented from SNOM and SThM sensors and progress in sensor technology will also be discussed. @FootnoteText@ @footnote 1@A. Oral et. al. J. Vac. Sci. Technol. B14 (2) p.1202-5 (1996) @footnote 2@M.J. Yoo et. al. Science 276 (5312) p.579-82 (1997) @footnote 3@K. Luo et. al. Appl. Phys. Lett. 71 (12) p.1604-6 (1997) @footnote 4@E. Oesterschulze Appl. Phys. A66, S3-9 (1998) @footnote 5@H. Zhou et. al. J. Vac. Sci. Technol B16 (1) p.54-58 (1998)

9:00am **NS+AS-WeM3 Surface Derivatization of Nanoscale Tungsten Tips for Interfacial Force Microscopy***, **K. Griffiths**, P.R. Norton, J.F. Graham, M. Kovar, F. Ogini, O.L. Warren,* University of Western Ontario, Canada

Interfacial force microscopy (IFM) is a novel technique not only for imaging surfaces at resolutions approaching those obtainable with atomic force microscopy, but also for the quantitative determination of the mechanical properties of a material such as elastic modulus, hardness etc., with lateral resolutions of ~nm and depth resolutions ~0.1 nm. The IFM force-compensated sensor permits the acquisition of quantitative force (f) versus distance (d) curves, which through appropriate analysis yield the mechanical properties. Because of the extreme pressures that can be attained in tip-surface contact (many GPa), it is essential to passivate the chemical interactions between the probe tip and the substrate under investigation to prevent strong adhesion effects such as metal-metal bond formation. Studies on Au surfaces are feasible because of the efficacy of self-assembled thiol monolayers on Au. However, convenient and effective protective monolayers are not generally available for many substrates, and it is best to develop a general procedure of passivating the probe tip. Our present studies involve parabaloidal tungsten tips of radii 25<r<200 nm. We have shown that it is possible to use silyl coupling agents (octadecyltrichlorosilane; OTS) to derivatize tungsten surfaces. Using the same techniques we have shown that the nm-scale W-tips can also be derivatized. Measurements were made of the f-d curves for the following tip-substrate couples: underivatized W-tip against underivatized Au(111) surface, underivatized W-tip against derivatized Au(111) surface (C-18 thiol SAM) and derivatized W-tip (OTS) against underivatized Au(111). The data clearly show that the OTS derivatized tips were passivated against adhesive contact even at pressures of many GPa, demonstrating the necessary stability for use in nanoindentation experiments.

9:20am **NS+AS-WeM4 Silicon Cantilevers for Ultrahigh-Density Data Storage***, **A. Kikukawa**, H. Koyanagi, K. Etoh, S. Hosaka,* Hitachi Ltd., Japan

In the past few years we have been working on applying atomic force microscopy (AFM) technologies in data storage. One of the most important issues is to increase the data transfer rate (DTR). Thus, it is required to increase the cantilever resonance frequency but keeping the spring constant sufficiently small. Also, an integrated sharp tip is required for reading the small recorded marks. The smallest one we have made so far is an equilateral-triangle cantilever 7 µm long and 0.1 µm thick. Its measured resonance frequency is 6.1 MHz, which is about two magnitudes higher than most of the cantilevers used in AFM, and the calculated spring constant is 0.75 N/m. It was fabricated from a SOI (silicon on insulator) wafer using anisotropic reactive ion etching (RIE) for cantilever shape etching, isotropic RIE for the tip etching, and KOH anisotropic etching for removing excess bulk silicon on the back side and making it a freestanding cantilever. The most difficult part in making such small cantilevers was to control the variation of their dimensions. They are caused mostly by the lateral variation of the wafer thickness and the alignment error (±4 µm at maximum) between the cantilever pattern defined on the active layer and the handling piece pattern defined on the bulk side. We reduced the variation to a sufficient level not by connecting the cantilever directly to the handling piece but by connecting the cantilever via a supporting region sufficiently thicker than the cantilever and whose shape was defined from the cantilever side. We also developed new type of optical lever that can focus the incident beam spot diameter as small as 5 µm and that can be operated with a bandwidth as wide as 10 MHz. From a noise characteristic analysis, the sensitivity of the system was obtained as 4.84 µrad at 10 MHz bandwidth which corresponds to 0.48 Å when a 10 µm long cantilever is used. That is, we now have basic technologies for demonstrating a DTR of 10 Mbps.

9:40am **NS+AS-WeM5 Capacitative Force Modulation Technique in Nanoindentation***, **S. Asif**, K.J. Wahl, R.J. Colton,* Naval Research Laboratory*; S.G. Corcoran,* Hysitron, Inc.

The sinusoidal force modulation technique for nanoindentation has been implemented using a three-plate capacitative force/displacement transducer developed by Hysitron, Inc. The force modulation technique can be used to detect the surface of the specimen very accurately with the stiffness sensitivity of 1N/m or less. The low spring mass (243mg), spring stiffness (120N/m) and the low damping coefficient (0.007 Ns/m) of the transducer allows one to measure the damping losses in most of the materials including metals. The experimental results on indium at room temperature indicate that the damping of the material influences the modulus measurement. The technique can be used to measure the loss and storage modulus of polymer materials (e.g. poly(vinylethylene)) and thin film systems. The experimental technique will be described together with the importance of system calibration and specimen mounting.

10:00am **NS+AS-WeM6 Nanoindentation as a Probe of Stress State***, **K.F. Jarausch**,* North Carolina State University*; J.D. Kiely, J.E. Houston,* Sandia National Laboratories*; P.E. Russell,* North Carolina State University

A dependence of elastic response on the local stress-state of a material has been demonstrated using the interfacial force microscope (IFM). This investigation was prompted by a previous IFM survey in which the mechanical response of Au thin films was found to correlate with the films' residual stress state and not with morphology or substrate adhesion. In order to better establish the details of this relationship a concentric ring bending device was built to investigate the dependence of IFM nanoindentation measurements on applied tensile and compressive stresses. The measured elastic modulus was shown to increase to 65 +-6MPa with applied compressive stress (50 +-10MPa) and decrease to 32 +-9MPa with applied tensile stress (-50 +-10MPa). The response of the unstressed film was 47 +-6MPa throughout the measurement sequence demonstrating that this change in response is not due to any permanent change in the film. Elastic response was also found to vary as a function of work hardening, indentation position relative to morphological defects, and ion implantation dose. Results from these five experiments will be discussed in terms of possible mechanisms, in an effort to identify how stress alters the measurement process and causes the variation of Au's nano-mechanical properties. These experiments suggest that the IFM has the potential for being able to measure stress state on a very local level. The portion of this work done at Sandia, which is a multiprogram laboratory operated by Sandia Corporation--a Lockheed Martin Company, was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

10:20am **NS+AS-WeM7 Nano-scale Observations of Stress-Enhanced Dissolution in Monoclinic CaHPO@sub4@ 2H@sub 2@O: Chemical vs. Mechanical Effects***, **S.C. Langford**, L. Scudiero, J.T. Dickinson,* Washington State University

In several mechanical wear situations, e.g., biomaterials in hip replacements and mechanochemical polishing (used extensively in the microlectronics industry), a surface experiences simultaneous tribological loading and corrosive chemical exposure. The combination can greatly increase wear rates. We examine single crystal brushite [CaHPO@sub 4@ 2H@sub 2@O] (a model biomaterial) in buffered aqueous solutions mechanically stimulated by the tip of a Scanning Force Microscope (SFM). Quantitative data on nanometer-scale wear of single atomic layer steps are readily obtained. The (010) faces of this material are strongly anisotropic, forming trianglular etch pits bounded by three crystallographically distinct steps in aqueous solution. Stress-enhanced dissolution is readily observed along all three steps. On each step, the wear rate is a highly nonlinear (essentially exponential) function of contact force; this function dependence is modeled in terms of stress-enhanced double kink nucleation. At low contact forces, etch pit growth principally involves dissolution along [210] steps; in contrast, the [101] steps are far more vulnerable to wear at high contact forces than the other steps. Damaged regions along [101] steps are especially vulnerable to subsequent chemical dissolution. We exploit this effect to produce atomically flat surfaces many microns in dimension. We also describe the influence of tip velocity and solution chemistry on the rates of corrosive wear. This highly anisotropic material provides a useful system for isolating aspects of the crystal structure which render it vulnerable to chemical etching from those which make it vulnerable to mechanical damage. This work is supported in part by a grant from the National Science Foundation, Grant CMS-9414405.

10:40am **NS+AS-WeM8 Conductance and Force at an Atomically Defined Junction***, **G. Cross**, A. Schirmeisen, A. Stalder, P. Grütter,* McGill University, Canada*; U. Dürig,* IBM Research Division, Switzerland

We have simultaneously measured conductivity and force between an atomically defined tip and atomically flat sample in UHV. The sharp metal tips are manipulated and characterized on an atomic scale both before and after the sample approach by field ion microscopy (FIM). Conductivity over a large range is obtained by a multidecade nonlinear current amplifier,@footnote 1@ while simultaneously forces between the tip and sample are measured by an in-situ differential interferometer with sub-nN force sensitivity. We report on the conductivity and force vs. tip-sample separation relationships for specific atomic tip geometry. In particular, we have examined the precontact regime characterized by short-ranged attractive forces. In this regime, we find that for a trimer W tip approaching an Au(111) surface, the square of the force depends linearly on conductivity. This can be understood if one assumes that both tunneling and adhesion quantum mechanical exchange interactions are due to overlap of tip and sample wavefunctions.@footnote 2@ @FootnoteText@ @footnote 1@U. Dürig, L. Novotny, B. Michel, A. Stalder , Rev. Sci. Instr. 68, 3814 (1997) @footnote 2@C. Chen, J. Phys. Cond. Matter 3, 1227 (1991)

11:00am **NS+AS-WeM9 Chemical Imaging with Scanning Near Field Infrared Microscopy***, **C.A. Michaels**,* National Institute of Standards and Technology, US*; R.R. Cavanagh, S.J. Stranick, L.J. Richter,* National Institute of Standards and Technology

The development of a scanning near field microscope that utilizes infrared absorption as the optical contrast mechanism will be discussed. This instrument couples the nanoscale spatial resolution of a scanned probe with the chemical specificity of vibrational spectroscopy. This combination allows the in situ mapping of chemical functional groups with subwavelength spatial resolution. Key elements of the microscope include; an ultrafast IR light source producing pulses with a FWHM bandwidth of 150 cm@super -1@, an infrared focal plane array based spectrometer allowing parallel detection of the entire pulse bandwidth with 4 cm@super -1@ resolution, and a near field probe fabricated from fluoride glass fiber allowing single mode transmission over the range 2.2 to 4.5 µm. Factors influencing the optical and topographic resolution characteristics of this microscope will be presented. Additionally, the performance of the microscope in discriminating chemical species based on their IR optical properties will also be described.

11:20am **NS+AS-WeM10 Tapping-Mode and Nonoptical Force Sensing Near-Field Scanning Optical Microscopy***, **D.P. Tsai**, Y.Y. Lu,* National Chung Cheng University, Taiwan

We present a tapping-mode and nonoptical force sensing near-field scanning optical microscopy system. A high Q quartz tuning fork with resonance frequency of 32.768 kHz is used as a force sensing transducer. The piezoeletric current of the tuning fork is lock-in amplified and served as a signal for distance control. Excellent quality of tapping-mode sensing and imaging was obtained. The sensitivity of image is comparable to optical force sensing technique. Results show low background signal and high signal to noise (S/N)ratio for near-field optical contrast, and the elimination of possible optical excitations arising from the force sensing laser light source. Applications on the near-field optical writing and reading on the light sensitive samples show the advantages of this novel method.

11:40am **NS+AS-WeM11 Development and Application of a Dual-Probe Scanning Tunneling Microscope for Nanoscale Investigations of Materials***, **H. Grube**, M. Allgeier, J.J. Boland,* University of North Carolina, Chapel Hill

Scanning tunneling microscopy has evolved into a valuable tool for the study of the structural and electronic properties of semiconductor and metal surfaces, as well as enabling fabrication of novel nanoscopic electronic devices. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states (LDOS).@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within 100nm of the first is expected to enable measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ To this end our lab has completed construction of one of the first dual probe STMs in which tips can be placed 10-100nm apart. Each tip is mounted on an independent tube scanner with independent piezo drivers, current preamplifiers and feedback controllers. The scanners have two and three degrees of freedom for coarse motion, achieved through the use of modified commercial inertial sliders. These five degrees of freedom allow for the precise positioning of the two probes into overlapping scanning ranges of the tubes. In this DP-STM configuration it is possible to inject a current into the sample at an arbitrary location with one tip and detecting a change of the electrical environment of the sample with the other probe arbitrarily positioned close by. Therefore it is possible to probe the transport properties of the medium or three terminal nanoscale device. Our DP-STM has been characterized by using each tip to scan its local surface environment and then overlaying the images obtained to determine the inter-tip separation. @FootnoteText@ @footnote 1@G. Binnig et al., Phys. Rev. Lett., 49 (1), 57 (1982) @footnote 2@Q. Niu, M.C. Chang and C.K. Shih, Phys. Rev., B 51 (8), 5502 (1995) @footnote 3@J.M. Beyers and M.E. Flatte, Phys. Rev. Lett., 74 (2), 306 (1995) @footnote 4@J.M. Beyers and M.E. Flatte, J. Phys. Chem. Solids., 56 (12), 1701 (1995)

Applied Surface Science Division
Room 307 - Session AS-WeA

Polymer Surfaces, Films and Interfaces

Moderator: D.G. Castner, University of Washington

2:00pm **AS-WeA1 Changes in the Band Structure Across the Surface Ferroelectric Phase Transition in the Crystalline Ferroelectric Copolymer P(VDF-TrFE)***, **J. Choi**, P.A. Dowben, A.V. Bune, S. Ducharme,* University of Nebraska, Lincoln*; V.M. Fridkin, S.P. Palto, N. Petukhova,* The Russian Academy of Sciences, Russia

Recently, the ferroelectric copolymer poly(VDF-TrFE, 70:30) LB films have been attracted because of the new surface ferroelectric phase transition and correlation of the surface ferroelectric transition with the electronic structure.@Footnote 1,2@ The relationship between the electronic structural and the conformational structural change of the crystalline 5 ML films of poly(VDF-TrFE, 70:30) has been studied in detail using several methods angle resolved inverse photoemission spectroscopy, low energy electron diffraction, angle resolved X-ray photoemission, and work function across the surface ferroelectric transition. Their results indicate that the Brillouin zone size is doubled across the surface ferroelectric transition. These is a C-F bond reorientation across the ferroelectric phase transition. Most profound are the change in the unoccupied (conduction band) band structure. @FootnoteText@ @footnote 1@A. V. Bune, V. M. Fridkin, Stephen Ducharme, L. M. Blinov, S. P. Palto, A. Sorokin, S. G. Yudin, and A. Zlatkin, Nature (London) (to be published) @footnote 2@Jaewu Choi, P. A. Dowben, Shawn Pebley, A. V. Bune, Stephen Ducharme, V. M. Fridkin, S. P. Palto, and N. Petukhova, Phys. Rev. Lett. 80, 1328(1998)

2:20pm **AS-WeA2 UV Photopolymerization of Methyl Methacrylate and Acrylic Acid on Pt(110) Using Time-Resolved FT-IRAS***, J. Yan, K. Green, T. Jachimowski, **J. Lauterbach**,* Purdue University

The adsorption and polymerization characteristics of methyl methacrylate (MMA) and acrylic acid on platinum were studied under varying conditions using time-resolved Fourier-transform IR reflection-absorption spectroscopy (FT-IRAS). Methyl methacrylate adsorbs physically on Pt(110) at 100 K, while acrylic acid likely chemically adsorbs. Adsorption of these monomers results in broadening of features, peak shifts, and changes in the intensity ratios of different peaks in the vibrational spectra, as compared to their liquid phase values. The most significant observation in the FT-IRAS spectrum of adsorbed MMA is the absence of the vibrational bending mode of the @alpha@-CH3 group of the monomer in the adsorbed films. The FT-IRAS spectrum of acrylic acid shows that it adsorbs in both the cis and trans forms showing a relative increase in the cis form with coverage. The UV-initiated photopolymerization of MMA and acrylic acid were examined by monitoring the disappearance/appearance of characteristic absorption bands as the monomer was converted to polymer. MMA polymerization results in the expected decrease in intensity of the C=C bond of the monomer and also a decrease in the intensity of the carbonyl group of the monomer. Associated with the decrease in intensity of the carbonyl group is the observation of surface bonded CO. The most significant result of the photopolymerization of acrylic acid is the appearance of CO@sub 2@ on the surface as the polymerization proceeds. In contrast with MMA we did not observe large changes in the intensities of the carbonyl and C=C peaks indicating that although polymerization was occurring, decarboxylation was more likely.

2:40pm **AS-WeA3 Correlations of the Structure and Mechanical Properties of Polymer Surfaces: Combined Sum Frequency Generation-Surface Vibrational Spectroscopy and Atomic Force Microscopy Studies***, **G.A. Somorjai**, D. Gracias, D. Zhang,* University of California, Berkeley **INVITED**

Vibrational spectroscopy by sum frequency generation (SFG) is a non-linear optical technique that is totally monolayer sensitive and can be employed for studies of solid-liquid, solid-solid, and solid-gas interfaces. It provides information about the surface structure and orientation of molecules at the interface. Atomic force microscopy permits measurements of the elastic moduli and the friction coefficient of interfaces with excellent spatial resolution. We utilized both techniques to investigate polyethylene (low and high density), polypropylene (atactic, isotactic) surfaces, and a polymer blend, Biospan-S, in air and in liquids and as a function of temperature. The structure and orientation of CH@sub 2@ and CH@sub 3@ groups at the interface readily identify polyethylene and polypropylene types. Structural changes that occur near and at the glass transition temperatures are detectable. The friction coefficients and elastic moduli correlate well with changes of surface structure. Biospan-S undergoes structural changes when placed in an aqueous solution from air resulting in the migration of the hydrophilic polymer components to the surface. Good correlations of these changes with variations of contact angle were found. AFM detects phase segregation as the composition of the polymer blend is altered.

3:20pm **AS-WeA5 Hydrolysis Degradation of Biodegradable Polymers A Time-of-Flight Secondary Ion Mass Spectrometry Study***, J.A. Gardella, Jr., **J. Chen**[1],* State University of New York, Buffalo

Biodegradable polymers have found many applications such as controlled release for drug delivery and as wound healing devices. The characteristics of surface hydrolysis as a degradation mechanism for biodegradable polymers are crucial to the application. Time-of-flight secondary ion mass spectrometry (ToF SIMS) makes it possible to observe the in-vitro hydrolysis products directly as intact low molecular weight oligomers. In this study, we have investigated the hydrolysis degradation of important biodegradable polymers, in particular, polyesters such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA), the copolymer poly(lactic-co-glycolic acid) (PLG) and various polyanhydrides. The in-vitro hydrolysis reaction is conducted on polymer disc samples at 37 @super 0@C in a physiological buffer for a range of hydrolysis periods from one to twelve hours. The hydrolysis products are observed in ToF SIMS spectra as peaks assigned to intact molecular ions. The molecular weight distribution of hydrolysis products is then obtained. The capability of using ToF SIMS in direct characterization of surface degradation kinetics of biodegradable polymers is demonstrated.

3:40pm **AS-WeA6 Effect of PDMS Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion***, J. Zhao,* State University of New York, Buffalo*; S.R. Rojstaczer,* Occidental Chemical Corporation*; J.A. Gardella, **J. Chen**,* State University of New York, Buffalo

Polyimidesiloxane (SIM) copolymers are becoming increasingly important materials in the microelectronics industry in applications, such as die attach adhesives, due to their attractive properties, such as good adhesion, low dielectric constant and low stress. In this study, a series of SIM copolymers, based on @alpha@,@omega@-aminopropylpoly(dimethylsiloxane)(PDMS), 2,2-bis(4-[4-aminophenoxyl]phenyl)propane(BAPP) and 4,4'-oxydiphthalic-anhydride(ODPA) was synthesized in our laboratories. We investigated the effect of siloxane segment length on the surface composition of the SIM copolymers and its role in adhesion. The aim is to elucidate the correlation between polymer structure, surface composition, and the adhesion strength, as evaluated by peel tests. In-depth compositional profiles of the near surface region to approximately 100Å depth were simulated from the results of angle-dependent Electron Spectroscopy for Chemical Analysis (ESCA) experiments by using a deconvolution computer program. The simulated in-depth compositional profiles show that the topmost surface of the air (free) surface of the 75µm thick SIM copolymer film consists of a siloxane-rich layer, even with the shortest siloxane segment. For a given siloxane bulk content, a longer siloxane segment gives a surface richer in siloxane. The adhesion strength was determined by peel testing of SIM copolymers-Fe/Ni Alloy-42 laminates. The peel strength decreases exponentially with increasing thickness of the surface siloxane-rich layer, which corresponds to a longer siloxane segment length. However, all values of adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results that both siloxane and polyimide are essential components to rendering the high adhesion strength. The siloxane component provides a good diffusive ability, while the polyimide component interacts with the substrate to give rise to adhesion strength. Longer siloxane segments in the SIM copolymers are found to be detrimental to adhesion strength by way of interference with the polyimide-metal interaction.

4:00pm **AS-WeA7 Interface Characterization with Combined XPS and TOF-SIMS An Application to the Metallization of Plasma Modified Polymer Surfaces***, **D. Wolany**, T. Fladung, Th. Gantenfort, L. Wiedmann, A. Benninghoven,* Universität Münster, Germany

In recent years, the combination of time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) has gained considerable importance for the analysis of technologically relevant surfaces and interfaces, e. g. for device technology or for surface modification of organic substances. The polymer-metal interface is of particular interest, because such compound materials are used e. g. for compact disks or flexible electronic circuit boards. The polymer-metal

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

interface itself, however, is not accessible by surface analytical techniques except in the case of adhesion failure. The combination of TOF-SIMS and XPS can help in this situation by characterization of the original polymer substrate, the surface of the plasma modified polymer, and the initial stages of metal deposition. In this way, one can obtain valuable insights into the interaction mechanisms between the metal and the substrate. We present results for Cu on polyimide modified in an oxygen plasma, and Al on polycarbonate modified in oxygen, argon and SF@sub 6@ plasmas, respectively. In both cases, XPS shows, after plasma modification, the occurrence of additional binding states within the polymer. In the initial stages of metallization, metal-substrate bonds can be identified which are characteristic for adhesion of the metal. The TOF-SIMS fragmentation patterns both after plasma treatment and after metallization allow the identification of specific interaction mechanisms between the polymer and the metal. In addition, standard technical adhesion tests (peel test, twist-off test) were applied to similar samples with thick metallic overlayers.@footnote 1@ In this way we established correlations between the plasma parameters used for substrate modification, the chemical and physical properties of the modified substrate and the polymer-metal interface, and the adhesion strength of the compound material. @FootnoteText@ @footnote 1@Federal Institute for Materials Research and Testing (BAM), Berlin, 12200, Germany

4:20pm **AS-WeA8 XPS Evidence of Redox Chemistry Between Cold Rolled Steel and Polyaniline***, **B.C. Beard**, P. Spellane,* Akzo Nobel Chemicals, Inc.

The electrochemical response of polyaniline (PANI) in its undoped intermediate (emeraldine base, EB) oxidation state coated on cold rolled steel (CRS) or glass substrates has been evaluated by xray photoelectron spectroscopy (XPS). The oxidation state of the polymer was determined from the ratio of amine to imine nitrogen chemical states observed in the N(1s) photoelectron spectrum. A room temperture air dried PANI coating cast from NMP solution onto CRS was found to be reduced relative to its as-synthesized, air stable state. Heating the PANI coated on CRS in the absence of air (165°C, in ultra high vacuum) produced an even deeper reduction, resulting from the transfer of electronic charge to the polymer from the metal substrate. Subsequent brief exposure of this reduced PANI coating to air at elevated temperature (165°C) reoxidized the PANI to the EB state. Analogous treatment of a PANI coating on glass caused no such change in oxidation state of the polymer. Unlike steel which provides a redox couple with PANI, glass is electro-inactive.

4:40pm **AS-WeA9 Evaluation of the Degradation Mechanism(s) Associated with Acid Rain Exposure of Acrylic Melamine Based Automotive Clearcoats***, **P.J. Schmitz**, J.W. Holubka, L.F. Xu,* Ford Motor Company

Environmental exposure of clearcoats to ambient conditions of low pH can result in visible surface pitting. The degradation phenomenon associated with this localized loss of material is thought to occur primarily through crosslink hydrolysis as a result of acid rain exposure. Although this phenomenon has been studied quite extensively, limited chemical data has been presented that confirms the mechanism(s) of the degradation process. Most conclusions that have been made are largely based on empirical considerations involving observations that degradation is most prevalent in areas having low pH rain, and the results of field exposure studies that indicate the sensitivity of a particular coating to environmental degradation is directly associated with the ease of hydrolysis of the crosslink. In this study, we have used XPS to monitor changes occurring at the clearcoat surface as a result of field exposure, to attempt to more clearly define degradation products, and therefore the mechanism(s) associated with the degradation phenomenon. Changes were observed in the N, C, and O core level spectra after field exposure, and were found to be consistent with the modification of melamine crosslinkers following laboratory acid treatment. Bulk elemental analysis and XPS core level results, obtained from sulfuric acid treated crosslinkers, were found to be consistent with melamine salt (sulfate) formation. The confirmation of residual melamine sulfate on the clear coat surface following field exposure, strongly suggests that the prominent degradation pathway is acid rain induced crosslink hydrolysis. The identification of degradation products associated with environmental exposure could prove useful in the development of laboratory testing for the evaluation of clearcoat hydrolysis resistance, to verify that exposure conditions reproduce field degradation pathways.

5:00pm **AS-WeA10 Optical Characterization of FEP Teflon: Pristine and from Hubble Space Telescope@footnote 1@***, **C.L. Bungay**,* Univeristy of Nebraska, Lincoln*; J.N. Hilfiker,* J. A. Woollam Co., Inc.*; J.A. Woollam,* University of Nebraska, Lincoln

Polymers used on spacecraft are often susceptible to environmental degradation in Low Earth Orbit (LEO). Therefore, the behavior of materials used on spacecraft such as the International Space Station and Hubble Space Telescope (Hubble) must be well characterized to ensure long term survivability of the spacecraft. Optical methods are favorable to study space application materials because they are non-contact and non-destructive. However, polymer films are often biaxially anisotropic and this anisotropy is usually not accounted for when optical measurements are acquired. In this work FEP Teflon (pristine and exposed to the LEO environment on Hubble) are studied using various optical measurements, including transmission ellipsometry, reflection ellipsometry and transmission intensity. By acquiring a series of different optical measurements the optical constants in three orthogonal directions and their optical axis orientations were determined. The optical data were also studied to help determine the extent of degradation of aluminized FEP returned from the first and second Hubble servicing missions. @FootnoteText@ @footnote 1@Research funded by NASA Lewis contract #NAG3-2086 and NASA Epscor contract #NCC5-169

Thursday Morning, November 5, 1998

Applied Surface Science Division
Room 307 - Session AS-ThM

Gaede-Langmuir Award Address and Quantitative Surface Analysis

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

9:00am **AS-ThM3 Resolution Enhancement of XPS Spectra by Maximum Entropy Deconvolution***, S.J. Splinter,* B.C. Research Inc., Canada*;* ***N.S. McIntyre,*** The University of Western Ontario, Canada **INVITED**

Detailed Analysis of XPS spectra is often limited by the resolution available in the measurements. Energy resolution improvement can be achieved in practice by monochromatization of the exciting x-rays and/or by very high energy resolution analysis of the emitted photoelectrons through improved instrumentation. Both of these approaches, however, require expensive high-intensity photon sources. This added cost therefore provides an acute motivation for the development of a reliable computational means for resolution enhancement. In this talk, I will describe a method for enhancing the energy resolution of photoelectron spectra by deconvolution based on the maximum entropy method (MEM). I will first review the theory of deconvolution as applied to XPS and briefly discuss previous work in this area. I will then present the mathematical description of MEM, explaining why this represents a better approach to take, and describe the algorithmic and computational details used to solve the large-scale non-linear constrained optimization problem. Several representative examples of simulated and experimental spectra will be presented.

9:40am **AS-ThM5 Evaluation of Calculated and Measured Electron Inelastic Mean Free Paths***, A. Jablonski,* Polish Academy of Sciences, Poland*;* ***C.J. Powell,*** National Institute of Standards and Technology

NIST will release a database in 1998 that provides values of electron inelastic mean free paths (IMFPs) for use in surface analysis by AES and XPS. The database includes IMFPs calculated from optical data and measured by elastic-peak electron spectroscopy. IMFPs can also be obtained from the predictive formulae proposed by Seah and Dench, Tanuma et al., and Gries. We present here an evaluation of calculated and measured IMFPs for seven elemental solids (Al, Si, Ni, Cu, Ge, Ag, and Au); these solids were selected because, for each, there were two or more independent IMFP calculations and two or more independent IMFP measurements. For each element, calculated IMFPs have been compared, measured IMFPs have been compared, and calculated and measured IMFPs have been compared. Our preliminary results indicate that the best agreement among the calculated IMFPs (as determined from mean relative deviations with respect to a common fitted curve) is found for Al, Ni, and Ag. Similarly, the best agreement among the experimental values is found for Si, Cu, and Ge, and the best agreement between calculated and measured values is found for Cu, Ag, and Au. We will discuss reasons for the differences found in our comparisons.

10:00am **AS-ThM6 Development of Well Defined Reference Samples for ARXPS Depth Profiling Studies***,* ***B.J. Tyler****, S.J. Hunt,* Montana State University

Quantifying the changes in material composition in the near surface region is important for a wide range of research problems. With inorganic and metallic samples, this information can often be obtained by sputter depth profiling. However, for organic samples, ion sputtering typically destroys the chemical structures of interest before they can be measured. As a result, angle resolve XPS is the preferred method for studying concentration depth profiles (CDP) for polymeric materials and organic thin films. As the interest in organic surfaces has grown, demand for quantitative measures of CPDs for these surfaces has also grown. While qualitative interpretation of ARXPS results is routine, there are many barriers to quantitative calculation of concentration depth profiles (CDPs) from ARXPS results. Many algorithms have been developed for this purpose but determining accurate confidence limits for CDPs, which are calculated with these algorithms, is currently the most significant challenge for quantitative depth profiling with ADESCA. One barrier to assessing the accuracy of CDPs is lack of adequate reference samples. We have evaluated the use of self-assembling monolayers, spin cast polymers, and plasma deposited films for their potential as standards for ARXPS work. The thin films were made on ultra smooth gold and silca substrate. Surface roughness and film thickness have been measured with AFM. ARXPS data for the samples was measured on both a PHI 5600 XPS system and a SSI s-probe. Resulting depth profiles calculated with several algorithms will be presented.

10:20am **AS-ThM7 Trajectory Projection Factor Analysis***,* ***D.J. Pocker****, B.R. York,* IBM SSD

Linear least squares (LLS) analyses of arrays of Auger or ESCA spectra (as from depth profiles, line scans or maps) run into problems when the data does not contain regions with pure spectra for one or more of the compounds. In addition, target factor analysis (TFA) encounters problems when there is not prior knowledege of the profiles for each compound. We present here an eigenanalysis and coordinate transformation method which straightforwardly extracts spectra for the pure compounds along with their associated profiles from arrays with overlapping spectra of up to 4 compounds. In the method, the profiles for the mathematically distinct eigenspectra are plotted against each other, yielding a TRAJECTORY through the orthogonal eigenspace. PROJECTION of this trajectory onto/into a well chosen plane or volume then allows a simple transformation of coordinates to define a non-orthogonal, chemically interesting space. From this, the pure compound spectra and profiles are easily computed. (The limit of 4 is from the graphical nature of the analysis. The concept extends to an arbitrary number of compounds. Also, for favorable 4 compound cases, overlaps as bad as "never fewer than 3" can be treated.)

10:40am **AS-ThM8 Quantitative High-Resolution Imaging with Sputter-Initiated Resonance Ionization Spectroscopy***,* ***K.F. Willey,*** Atom Sciences, Inc.*; H.F. Arlinghaus,* Westfälische Wilhelms-Universität Münster, Germany*; T.J. Whitaker,* Atom Sciences, Inc.

The demand for sub-micron lateral analysis, as a result of decreasing material size, has been met by the development of liquid metal ion gun (LMIG) sources capable of achieving spot sizes less than 50 nm. The trade-off however, is the reduction in ion beam current at the sample. Therefore, highly sensitive detection techniques are required. Our technique, Sputter-Initiated Resonance Ionization Spectroscopy (SIRIS), incorporates resonant ionization of sputtered neutral particles with time-of-flight mass detection. The two major advantages this approach has over conventional SIMS are that analysis of neutrals generally increases the detection efficiency by at least two orders of magnitude, and that resonance ionization nearly eliminates mass interferences. Additionally, analysis of neutrals substantially removes matrix effects, which is crucial for quantitative surface analysis. Sputtering is achieved with a gallium LMIG, a mass-filtered microbeam ion gun, and a mass-filtered low-energy sputtering ion gun. Sub-micron lateral resolution and few nanometer depth resolution have been obtained by eroding the sample with the low-energy ion gun while analyzing with the LMIG. In our presentation, we will describe the SIRIS technique and its dynamic range for quantitative analysis and imaging capabilities as they pertain to semiconductor research. In particular, Ge and B depth profiles on near one µm spot size and Cu trace element images obtained from Cd precipitates in CdZnTe films will be presented.

11:00am **AS-ThM9 Quantitative Detection of Metals in Organic Matrices by Laser-SNMS***,* ***A. Schnieders,*** *H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany

TOF-SIMS and Laser-SNMS have been established as powerful tools for high sensitive trace analysis of elements in inorganic materials, like alloys and semiconductors. Detection limits for almost all elements are in the range of 10@super 8@ - 10@super 9@ particles/cm@super 2@ of a single monolayer. For many analytical applications comparable sensitivities for the detection of metals in organic matrices are required, e. g. in life sciences. Unfortunately, TOF-SIMS is limited by the low secondary ion yields for metals in these matrices. The sensitivity is several decades lower than for the same metals on semiconductor surfaces. Because of the decoupling of the desorption and ionization processes, the use of Laser-SNMS is a promising approach to get rid of this limitation. Laser-SNMS combines the advantages of ion beam induced desorption with the possibility to optimize the ionization efficiency. For our investigations we applied nonresonant multiphoton ionization allowing a nonselective and highly efficient postionization of sputtered neutrals. As a model system for metals in organic matrices we prepared submonolayer coverages of several metals (Be, Cr, Mn, Fe, Co, Ni, Mo, W) on different polymer foils (polycarbonate, polyimide, and polyvinylidenechloride) by sputter deposition. We used these standards for quantification. Relative sensitivity factors of the respective elements are found to be similar to those for material sputtered from alloys or semiconductors within a factor of 3. The detection limits are in the range of 10@super 8@ to 10@super 9@ particles/cm@super 2@. We also used Laser-SNMS for the identification of the active center of a purple acid phosphatase. Our results demonstrate the detection and identification of single metal atoms in organic macromolecules with an atom concentration down to < 100 ppm. The use of resonant photoionization lowers the detection limits for similar systems by further decades.

Applied Surface Science Division
Room 307 - Session AS-ThA

SIMS - Depth Profiling and Molecular Surface Analysis

Moderator: D. Simons, National Institute of Standards and Technology

2:00pm **AS-ThA1 Sputtering Rate Change and Surface Roughening in SIMS Measurements Using Oblique and Normal Incidence Oxygen Bombardment, With and Without Oxygen Flooding***, **C.W. Magee,*** Evans East*; S.P. Smith, G.R. Mount,* Charles Evans and Associates*; H.-J. Gossmann, B. Herner,* Bell Laboratories, Lucent Technologies

Measuring depth profiles for ultra-low energy ion implants in Si requires accurate analyses within the top 1 to 10 nanometers of the sample surface where the "surface transient" affects secondary ion yields. Flooding the Si surface with oxygen during analysis is an accepted method for reducing the magnitude of the surface transient effect. However, a recent study by Wittmaack and Corcoran@footnote 1@ suggests that flooding with oxygen when using 2 keV oblique incidence O2 bombardment will result in an unavoidable change in the sputtering rate for the first 20-40 nanometers of the depth profile. Another recent study, this one by Jiang and Alkemade@footnote 2@, substantiated the claims of Wittmaack and Corcoran. Jiang and Alkemade used 1keV O2 bombardment instead of 2 keV, and they found that the depth of sputter rate change extended less than 11.7 nanometers. The study of Jiang and Alkemade used a Si sample in which contained internal Ge delta layers which were grown by MBE at intervals of 11.9 nanometers. This sample allowed them to compare unambiguously the apparent depth of the Ge layers to the known depths, thus exposing any changes in sputtering rate throughout the structure of 10 equally spaced Ge delta layers. The weakness of the Jiang and Alkemade experiment lay in the rather wide spacing of the delta layers (11.9 nanometers) as well as the fact that different energies and angles of primary ion incidence were not tried. This present study is an extension of the Jiang and Alkemade work. It involves using a similar MBE sample with internal marker layers to also determine, unambiguously, enhancements in initial sputter rates and the depths to which the enhanced initial sputter rates extend. Most importantly, we have investigated a large portion of the energy-angle of incidence parameter space and have found several sets of conditions of oblique incidence with oxygen bombardment which show virtually no enhanced sputter rate at the beginning of the analysis. Data will also be shown which duplicates the sputtering conditions of the experiments shown in reference 1. We will show that some of the conclusions drawn by the authors of reference 1 are not supported by our data. @FootnoteText@ @footnote 1@K. Wittmaack and S.F. Corcoran, J.V.S.T. B 16(1), 272 (1998). @footnote 2@ Z.X. Jiang and P.F.A. Alkemade, Proc. 11th Annn. Conf. On SIMS, edited by G. Gillen, R. Lareau, J. Bennett and F. Stevie, John Wiley & Sons, (1998).

2:20pm **AS-ThA2 Secondary Ion Mass Spectrometry of Deep Trench Capacitors in Dynamic Random Access Memory***, **C.C. Parks,*** IBM Analytical Services*; H. Glawischnig,* Siemens AG, Germany*; M. Levy,* IBM Burlington*; Chr. Dieseldorff,* Siemens at International Sematech

Secondary Ion Mass Spectrometry (SIMS) supported the development of deep trench capacitors in Dynamic Random Access Memory (DRAM). SIMS is done efficiently by analyzing thousands of cells in parallel and the approach described in this paper is scalable to the multi-Gbit generation. By projecting out fundamental values using geometrical formalisms, the behavior of contaminants and dopants in sub-micrometer geometries is understood without the need for small-area measurements. Contamination aspects are addressed: quantifying and partitioning of halogen, alkali, and transition-metal residues among deep trench and other processing sectors. The deposition of self-limiting layers of arsenic during polysilicon fill of the deep trench is explored in detail. The doping of the trench side-walls, either through angle ion implants or by drive-in of doped-glass deposition, is quantified.

2:40pm **AS-ThA3 TOF-SIMS Depth Profiling of Novel Si Devices***, **J.G.M. van Berkum,** P.C. Zalm,* Philips CFT - Materials Analysis, The Netherlands **INVITED**

Since about two years, concentration depth profiles of dopants in e.g. Si are not only measured with magnetic-sector SIMS or quadrupole SIMS, but also with time-of-flight (TOF) SIMS. In this technique, two ion sources are operated alternatingly: (i) a short-pulsed high-energy ‘analysis’ beam (typically 800 ps 11 keV Ar@super +@) produces secondary ion mass spectra and (ii) in between the pulses a low-energy ‘sputter’ beam (typically <1 keV O@sub 2@@super +@ or Cs@super +@) erodes the surface. The ion beam mixing is (almost) completely determined by the energy of the sputter beam. Therefore, a very good depth resolution can be obtained without concessions to the analysis beam. High mass resolution (up to M/@DELTA@M=10.000) can be maintained due to the short pulse length and imaging during the depth profile with a lateral resolution down to 100 nm is possible. Thanks to the simultaneous mass detection, TOF-SIMS is particularly useful for devices with ultra-steep dopant profiles in the presence of other dopants or in devices with oxide layers or SiGe hetero-epitaxial layers. For example, for understanding the electrical behaviour of Schottky diodes or tunnel diodes with a high concentration of one or two dopants in an ultra-thin SiGe layer, it is essential to measure the dopant and the Ge concentrations at exactly the same depth. The same holds for CMOS devices with SiGe channel (typically a few nm’s of SiGe at a few nm’s distance from the gate oxide) or bipolar transistors with hetero-epitaxial base. The optimum condition for such measurements may differ from the optimum conditions for the elements separately. For B, P, As and Ge in Si, we often use O@sub 2@@super +@ primary ions, positive secondary ions and oxygen flooding to enhance the ion yields and suppress the pre-equilibrium effects. The segregation of Ge due to oxygen flooding is quantified by comparative measurements using different measurement conditions.

3:40pm **AS-ThA6 Nitrogen Incorporation and Trace Element Analysis of Nanocrystalline Diamond Thin Films by SIMS***, **D. Zhou,*** University of Central Florida*; F.A. Stevie, J. Mckinley,* Cirent Semiconductor*; H. Gnaser,* University of Kaiserslautern, Germany

Nitrogen has been recognized as an important impurity in diamond, and the nature of its electronic states has been a central concern in elucidating the electronic and the optical properties of both natural and synthetically grown diamond. Although substitutional nitrogen in diamond is a deep donor impurity, it can affect that optical transparency, thermal conductivity, and electron field emission characteristics of diamond. We report that nitrogen has been successfully incorporated into nanodiamond films produced from a N@sub 2@/CH@sub 4@ microwave plasma enhanced CVD. High mass resolution SIMS (with a Cs@super +@ source) characterization shows that the concentration of the incorporated nitrogen, monitored via CN@super -@ (26.0031 amu), can be as high as 10@super 21@ atoms/cm@super 3@ depending on the ratio of N@sub 2@ to CH@sub 4@ in the reactant gas and on the substrate temperature used for the film preparation. The SIMS depth profile demonstrates that the incorporated nitrogen is uniform through the diamond films (about 1 micron thick) except for the surface and the interface between the film and substrate. Furthermore, SIMS (with an O@sub 2@@super +@ source) analysis reveals that alkali elements such as Na, K and Li appear to be the major trace metallic impurities and/or contamination for the diamond thin films produced from CH@sub 4@/N@sub 2@, CH@sub 4@/Ar, or CH@sub 4@/H@sub 2@ discharge, but they are the bulk impurities only for the thin films prepared from CH@sub 4@/N@sub 2@ plasma. These alkali impurities could also play important roles in electronic properties such as electron field emission of nanodiamond thin films. The authors would like to acknowledge the support from the Advanced Materials Processing and Analysis Center and UCF/Cirent Materials Characterization Facility at University of Central Florida. D. Zhou also specially acknowledge valuable discussion with D. M. Gruen and A. R. Krauss at Argonne National Laboratory.

4:00pm **AS-ThA7 Quantitative ToF-SIMS Analysis of Industrial Polymers***, **A.A. Galuska,** D.W. Abmayr,* Exxon Chemical Co. **INVITED**

In recent years, ToF-SIMS has been developed as a tool for surface (top 10 Å) and microscopic (= 60 µm) polymer analysis. The technique is most commonly used to qualitatively identify chemical species on polymer surfaces. However, quantitative methods can also be routinely performed on polymer articles. In fact, much of the real power of the technique for industrial polymer analysis is associated with the quantitative information that can be obtained from the ToF-SIMS mass spectra. In this presentation, we will discuss quantitative ToF-SIMS methods for the analysis of comonomers, sequence distributions, MWs, and trace elements in various polymers. Issues associated with microscopic bulk analysis will also be discussed. When possible, quantitative methods will be demonstrated using industrially meaningful analyses.

4:40pm **AS-ThA9 Secondary Ion Emission from Molecular Surfaces and Overlayers under Noble Gas and Molecular Primary Ion Bombardment***, **D. Stapel,** A. Benninghoven,* Universität Münster, Germany

By changing from atomic to molecular primary ions, considerable increases in secondary ion yields Y(X@sub i@@super q@) are achieved, in particular for molecular surfaces and overlayers. In an earlier paper@footnote 1@ we report on yield increases up to a factor of 1000 for polymer surfaces under 10 keV SF@sub 5@@super +@ bombardment. The corresponding increase of damage cross sections @sigma@(X@sub i@@super q@) is relatively small, so that the increase in ionization efficiencies E(X@sub i@@super q@) = Y(X@sub i@@super q@)/@sigma@(X@sub i@@super q@) remains high. This has important consequences for the analytical application of molecular SIMS - for spectroscopy as well as for imaging and microarea analysis. For further yield optimization and for a better understanding of this yield enhancement by the use of molecular primary ions, we carried out systematic investigations for different polymers, metals and semiconductor materials, covered by a variety of molecular overlayers as biomolecules, additives, LB- and SA-layers, etc. Comparing molecular (SF@sub 5@@super +@ , C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 10@@super +@, ...) and atomic (Ar@super +@, Kr@super +@, Xe@super +@) primary ion bombardment we found for nearly all of the investigated molecular surfaces and overlayers a strong increase in molecular ion yields, a much smaller increase in the corresponding damage cross sections, and smaller secondary ion emission depths. Experimental results will be presented and will be compared with model calculations. @FootnoteText@ @footnote 1@ F. Kötter, A. Benninghoven, Appl. Surf. Sci., in press

5:00pm **AS-ThA10 Coincidence Counting in Highly Charged Ion Based Time-of-Flight Secondary Ion Mass Spectrometry***, **A.V. Hamza**, T. Schenkel, A.V. Barnes, D.H. Schneider,* Lawrence Livermore National Laboratory

The high (>1) secondary ion yield per incident primary ion, which is produced when slow, highly charged ions impinge on a surface, affords the collection of time-of-flight secondary ion mass spectra in coincidence mode. In coincidence mode a spectrum may be acquired in which a particular secondary ion is required for each recorded primary ion event. Primary ion events that do not exhibit the required secondary ion are discarded. Since the primary highly charged ion induces the emission of secondary ions from a localized area of ~20 nm, the coincidence measurement insures that secondary ion emission be from within 20 nm of the coincident secondary ion emission. Hence localized (20nm scale) chemical information is obtained. An example of the power of this technique with highly charged ions is presented for a tungsten/SiO@sub 2@ patterned silicon sample wafer. Details of the wafer processing steps can be discerned from the coincidence spectra. By this coincidence method trace impurities can be associated with tungsten features. This work was performed under the auspices of the U. S. Department of Energy at Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

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

AS-ThP1 Mass Spectral Frequency Plots: A New Tool For Static SIMS Data Interpretation*, **A.M. Spool,*** IBM Corporation

The experienced Static SIMS Analyst will examine common peak mass differences in addition to common peak positions in attempting to interpret a spectrum of a new or unknown sample. Mass differences of 44 amu, for example, suggest polymers with an ethylene oxide monomer, common to many surfactants. Many species with biological origins will display peaks differing by 2 methylene groups (28 amu). Fluorinated polymers will often have peaks with mass differences of 50 amu corresponding to a perfluorinated methylene. Spectra of many polymers will have common peak differences that correspond to the mass of their monomers. In this paper I propose a simple algorithm that converts spectra with unit mass resolution to a plot of the "frequency" of peaks in the mass spectrum. The resulting "pseudo-power spectra" or "mass spectral frequency plots" are more indicative of the type of species on the sample than the exact identity of these species. The algorithm proposed simply involves multiplying the intensity of the peak at each mass by the peak intensity at every other mass, and adding each result to the bin corresponding to the difference between the masses. The intensities of the resulting peaks at each "delta" are a function of the number of peaks with those mass differences, and the intensities of the original peaks. Examples of these plots will be shown and their utility demonstrated.

AS-ThP2 The Münster High Mass Resolution Static SIMS Library*, **B.C. Schwede,*** University of Münster, Germany*; T. Heller, D. Rading, E. Niehuis,* ION-TOF GmbH, Germany*; B. Hagenhoff,* TASCON GmbH, Germany*; L. Wiedmann, A. Benninghoven,* University of Münster, Germany

Despite the high mass resolution and accurate mass determination available with high-performance TOF-SIMS instruments, the interpretation of a TOF-SIMS spectrum is a tedious process. This paper describes the "Münster High Mass Resolution Static SIMS Library" which can support the user in this situation. The reference spectra were collected with various state-of-the-art TOF-SIMS instruments at the University of Münster, at ION-TOF and at TASCON. The library contains positive and negative spectra from a large variety of substances, with special emphasis on polymers, additives and semiconductor materials. It is structured in a hierarchical, easily extendable manner. All reference spectra are included in the library as interpreted lists of peaks. This library is embedded in the TOF-SIMS IV software package which offers tools like a reference browser or a facility to list all reference spectra which include specified peaks. The evaluation tools are based on a search algorithm specifically designed for the identification of compounds in mixtures. In order to evaluate the similarity of spectra, a version of the PBM algorithm@footnote 1@ was adapted to the specific needs of TOF-SIMS. The performance of the search algorithm was tested by analyzing mixtures of two substances with known composition. The results will be presented and compared to those achieved using principal component analysis (PCA) and neural networks. @FootnoteText@ @footnote 1@ F.W. McLafferty, R.H. Hertel, R.D. Villwock, Organic Mass Spectrometry 1974, Vol. 9, pp. 690-702

AS-ThP3 Formation of Alkanethiol Self-Assembled Monolayers on Oxidized Gold Surfaces*, **C. Yan,** A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany*; C. Wöll,* Ruhr-Universität-Bochum, Germany

The formation of alkanethiol self-assembled monolayers (SAM) on oxidized gold was studied by x-ray photoelectron (XPS), near edge x-ray absorption fine structure (NEXAFS) and infrared spectroscopy. Different oxidation procedures, exposure of gold to atomic oxygen in vacuum and to UV/ozone in air, lead to different types of surface gold oxides, distinguishable by their oxygen XP spectra. On the gold oxide formed by exposure to atomic oxygen stable SAMs were formed from ethanolic solution as well as via vapor deposition. Two sulfur species were distinguished by XPS, gold thiolate and a species related to the reaction of the thiol with the oxide that was found encapsulated under the self-assembled monolayer. The monolayers adsorbed from ethanolic solution were denser packed and less tilted than the layers formed by vapor deposition and SAMs on clean gold surfaces. The gold oxide produced by exposure to UV/ozone in air was removed during thiol adsorption from ethanolic solution and a monolayer assembled on the bare gold. Chemical vapor deposition on this oxide did not lead to well defined monolayers.

AS-ThP4 XPS and ISS Study of X-ray Damage of Alkanethiol Self-Assembled Monolayers on Gold and Silver*, **D.E. King,** L.S. Dake, A.W. Czanderna,* National Renewable Energy Laboratory

X-ray photoelectron spectroscopy (XPS) has been extensively used to study the chemistry of self-assembled monolayers (SAMs). While XPS is often considered the most non-destructive surface analysis technique, it is known that X-ray exposure and the resulting secondary electron emission can alter the reactivity of many materials. Organic materials can be particularly susceptible to damage resulting from X-ray bombardment during XPS. We have studied the effects of both Mg and Al K-alpha X-ray exposure on acid and methyl functionalized alkanethiol SAMs on gold and silver substrates. In the methyl terminated SAMs, a 20 percent reduction in C 1s peak area results after a 3 hour X-ray exposure. In the acid-terminated SAMs, both carbon and oxygen XPS signals decrease rapidly, with a relatively greater loss in the oxygen signal. Ion scattering spectroscopy (ISS) depth profiles indicate that it takes longer to sputter the irradiated SAMs than non-irradiated SAMs. We conclude that chemical changes in the monolayers result from the X-ray exposure. Although these changes are not detectable with XPS, the increased resistance to sputtering by the ISS beam indicates changes in bonding that are consistent with C-C crosslinking between the chains in the SAMs. XPS and ISS data will be presented for methyl and acid terminated alkanethiols after subjecting the SAMs to increasing times of X-ray exposure. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selinsgrove, PA 17870-1001

AS-ThP5 Identification of Halogen Atoms in STM Images of Substituted Phenyloctadecylethers*, **H.S. Lee,** S. Iyengar, I.H. Musselman,* University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images acquired from these ethers have revealed a bias-dependent contrast which corresponds to calculated electron density contours of various X-POE molecular orbitals. STM images of the X-POEs reflecting the electron density contour of the highest occupied molecular orbital (HOMO) exhibited four bright spots - one for the halogen atom, two representing the pair of lobes of the phenyl ring, and one for the oxygen/alpha-carbon atoms. For each X-POE, a minimum of three sets of four submolecular resolution HOMO images were acquired. The intensities of the spots for the halogen atom and the lobe of the phenyl ring closest to the halogen were measured and their ratio was calculated. The ratios for Cl-POE, Br-POE and I-POE were 0.48 ± 0.05, 0.58 ± 0.05 and 0.75 ± 0.07, respectively. An analysis of variance revealed that the intensity ratios of the X-POEs could be clearly distinguished among all data sets.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

AS-ThP6 Identification of Surface Nitrogen Functionalities Using Gas Phase Derivatization and XPS Analysis*, **Y. Liu,** L.J. Gerenser, P.M. Thompson, J.M. Grace,* Eastman Kodak Company

X-ray photoelectron spectroscopy (XPS) has been widely used as a primary surface analytical technique to determine the surface atomic compositions of polymeric materials. It provides quantitative elemental composition with excellent surface sensitivity. However, quite often, it is very difficult to identify the functional groups when the core-level binding energy shifts of these species are small. We have developed an approach using gas phase derivatization reactions in combination with XPS surface analysis for semi-quantitative determination of nitrogen functional groups. This poster will focus on the studies of two derivatization reagents, trifluoroacetic anhydride and trifluorotolualdehyde, and their applications in the identification of nitrogen functionalities including primary and secondary amines, amides and nitriles.

AS-ThP7 In-situ Characterization of Plasma Polymerized Films Using External Reflection Infrared Spectroscopy*, F.J. Boerio,* ***R.H. Turner,*** University of Cincinnati

External reflection infrared spectroscopy was used for the in-situ characterization of plasma polymerized films of acetylene, hexamethyldisilazane (HMDSZ), and hexamethyldisiloxane (HMDSO) as a function of thickness. The films were deposited onto polished iron and aluminum substrates in an inductively coupled RF reactor interfaced to an FTIR spectrometer. In-situ characterization of the films enabled the effects of oxidation during atmospheric exposure of the films to be reduced or eliminated. Conducting the investigations as a function of film thickness enabled spectral features associated with the bulk of the films and with the film/substrate interface to be identified. Infrared spectra of plasma polymerized acetylene films on iron substrates were characterized by a band near 3325 cm@super -1@ that was tentatively assigned to CH stretching in an acetylide species at the interface and by a band near 3300 cm@super -1@ that was assigned to the CH stretching vibration in mono-substituted acetylene groups in the bulk of the films. In a few cases, infrared spectroscopy was used to investigate adsorption of the neat monomers onto the substrates. Thus, infrared spectra of HMDSZ monomer adsorbed onto iron substrates were characterized by bands assigned to siloxane bonds, indicating some polymerization of the monomer.

AS-ThP8 X-Ray Microanalysis Inverse Modeling@footnote 1@*, **H.W. Wagner**, W.S.M. Werner, H. Störi,* Technische Universität Wien, Austria

The typical electron interaction volume in electron microprobe analysis (EPMA) is in the order of several cubic microns. For a single spot measurement of a sample with complex geometry, the source distribution of characteristic x-ray signals within this volume cannot be determined, therefore making it impossible to gain information on the sample structure. A set of measurements performed under different conditions (e.g. beam energies, incidence angles) does contain structural information, however not in a readily available form. The present work describes an approach for the extraction of structural information from EPMA measurements. The inverse modeling method relies on an efficient way to compute the forward transformation, i.e. the calculation of a generated x-ray signal of a known structure and experimental setup, and the application of appropriate mathematical optimization techniques. The use of simulated annealing as optimization method turned out to be advantageous in this context. The presented approach can be applied to arbitrary 2-D structures and accounts for possible a priori information on the sample structure. @FootnoteText@ @footnote 1@ The authors wish to thank Digital Equipment Corp. for support of this work.

AS-ThP9 Analysis of X-ray Growth Oscillations During Heteroepitaxy*, **J. Baker**,* Risoe National Laboratory, Japan*; F. Berg Rasmussen, M. Nielsen, R. Feidenhans'l,* Risoe National Laboratory, Denmark

Despite recent progress,@footnote 1@ x-ray intensity oscillations recorded during heteroepitaxial growth are an under-exploited source of information on buried interface roughness, growth-front roughness, and inter-layer spacings. We explore some fundamental aspects of growth curve shape and their dependence on the x-ray scattering vector and film properties. In particular, the super-periodic modulation of oscillation amplitudes is demonstrated. Oscillations during the growth KCl/NaCl(001) are shown as a typical example of the phenomenon. @FootnoteText@ @footnote 1@E. Weschke, C. Schüssler-Langeheine, R. Meier, and G. Kaindl, Phys. Rev. Lett. 79, 3954 (1997).

AS-ThP10 Surface X-ray Diffractometer for MOVPE growth at SPring-8*, **T. Kawamura**, Y. Utsumi, M. Sugiyama, Y. Watanabe,* NTT Basic Research Laboratories, Japan*; J. Matsui, Y. Kagoshima, Y. Tsusaka,* Himeji Institute of Technology, Japan

We developed a grazing incidence x-ray diffractometer, installed at the SPring-8 synchrotron facility, to enable the analysis of the initial stage of III-V compound semiconductor homoepitaxial growth in gas-phase. To maintain growth conditions, the z-axis arrangement is used instead of the conventional 4-axes arrangement. The detection range of x-rays is from -5.0 degrees to 135 degrees in 2@theta@, and the incident and the take-off angle ranges from 0 degrees to 15 degrees. To align the goniometer system, additional stages were attached for horizontal and vertical translation, and rotation around the z-axis. The material gases are delivered with a conventional MOVPE gas handling system, consisting of carrier gas supply, material gas handling, and exhaust subsystems. Hydrogen and nitrogen are used for carrier gases, and organometallic vapor sources are selected for material gases. For safety, to avoid the leaks, the whole system, including the goniometer, were installed in an isolated and the cabinet is maintained at lower than atmospheric prresure.

AS-ThP11 Quantitative Wafer Surface Trace Metal Analysis by TXRF and Surface SIMS*, J.M. Metz, S.P. Smith, **M.J. Edgell**, V.K.F. Chia,* Charles Evans & Associates

Ultra-clean Si wafer surfaces are critical to the fabrication of ULSI devices. This is reflected by the stringent contamination limits for polished and epitaxial substrates, and surface preparation (i.e. before gate oxide growth) suggested by the National Technology Roadmap for Semiconductors (NTRS). Today's requirement for surface metals is typically in the range of 10@super 10@ atoms/cm@super 2@. Future needs in the year 2003 are anticipated to be 1x10@super 10@ atoms/cm@super 2@ for Al, Ca, and Zn, and 2x10@super 10@ atoms/cm@super 2@ for Fe, Ni, Cu, and Na. The transition metals Fe, Ni, Cu, and Na are considered to be very damaging at the gate oxide level, and therefore requirements for these are becoming more stringent. It is even considered that surface metals on epi substrates before gate oxidation may have to be as tight as for polished substrates, because the low temperature processing at small design rules leads to less effective gettering in the p+ substrate of p/p+ epi. Al is important to monitor because at concentrations below 10@super 11@ atoms/cm@super 2@ it can increase the oxide growth rate in the very thin gate oxide regime. This is a different effect compared to higher levels of Al (e.g. >10@super 12@ atoms/cm@super 2@) decreasing gate oxide thickness for thicker gate oxides. TXRF and SurfaceSIMS are two of the most powerful analytical techniques available for substrate and interface engineering. Both these techniques provide quantitative trace metal information at the surface of wafers. TXRF is an excellent survey tool capable of analyzing 300 mm wafers to a depth of about 50 Å. Quantification at the Si/SiO@sub 2@ interface is very important and may be performed accurately using SurfaceSIMS. The information provided by these two techniques allows pre-clean technologies used on silicon substrates to be evaluated. This presentation reviews the two techniques and illustrates with examples how they compliment each other.

AS-ThP12 AFM Explanation of the Improved Resolution in Auger Depth Profiles by Using the Zalar Rotation*, **L. Lozzi**, S. Santucci, D. Pacifico, P. Picozzi,* Università dell'Aquila, Italy*; R. Alfonsetti,* Texas Instruments ITALIA, Italy

Auger Microscopy, as a consequence of its high lateral resolution (around 10 nm) and its sensitivity to the surface, is a powerful tool to investigate elemental and chemical composition of surfaces, interfaces and thin films, particularly in microelectronics artifacts with dimensions lower than 200 nm. In this paper we studied the TiN/AlSiCu interface, with interfacial oxygen, of a 500 nm wide metal line of a 64 Mbit DRAM device. The sharpness of this interface and the presence of interdiffused interfacial contaminants may affect the device behaviour. The elemental depth profile of the investigated system has been performed by using the Auger Spectroscopy assisted by Ar ion sputtering. The profiles have been performed using two different methods of sample sputtering: the first one maintaining the sample in a fixed position respect to the ion beam and the second one by rotating the sample with a Zalar rotation accessory. The profiles have been interrupted when the TiN/AlSiCu interface had slightly overcome. The sputtering crater has been observed by using an AFM microscope. For identical samples we observed, in the case of the fixed sputtered sample, a particularly rough TiN/AlSiCu interface with evident finger prints of preferential sputtering which produces a sensibly enlarged interface depth profile. In the case of the rotated sample, we obtained a sharp interface profile which corresponds to a flat surface of the bottom of the crater with a roughness comparable to that of the not sputtered surface. In this case the presence of interfacial oxygen bonded to Al has been carefully localised.

AS-ThP13 Structure of Plasma Polymerized SiO@sub2@Films: Corrosion Protection of Steel and Aluminum Substrates*, **R.G. Dillingham**,* Brighton Technologies Group, Inc.*; F.J. Boerio,* University of Cincinnati

Plasma polymerized organosiloxanes made using excess oxygen as a carrier gas have a silica-like structure, and function as excellent corrosion inhibiting coatings and primers for adhesive bonding and painting. Similar structures can be obtained using a variety of reactor configurations and polymerization conditions, but details of film structure and performance can vary. Infrared spectra of these films show non-bridging Si-O and -OH species. The relative amount of structural imperfection is a strong function of deposition conditions. These structural features provide reactivity necessary for adhesion of paints and adhesives, but limit corrosion protection, probably by increasing electrolyte diffusion. Structures that provide optimum corrosion protection do not necessarily provide optimum overlayer adhesion. This work relates film deposition conditions to structural defects, and shows how these defects affect the electrical impedance spectra and corrosion inhibiting capabilities of plasma polymerized SiO@sub2@.

Friday Morning, November 6, 1998

Applied Surface Science Division
Room 307 - Session AS+VT-FrM

Application of Surface Analysis Techniques to Semiconductor Technology

Moderator: F.A. Stevie, Cirent Semiconductor

8:20am **AS+VT-FrM1 An Overview of the Applications of Surface Analysis Techniques in Semiconductor Technology***, **B.R. Rogers**, R. Gregory, G. Harris, D. Werho, W. Chen,* Motorola, Inc. **INVITED**

Over the years the role of surfaces and interfaces has become increasingly important in determining the performance of semiconductor based microelectronic circuits. Consequently, the use of both new and traditional surface analysis techniques in the development of materials and processes as well as in manufacturing metrology and trouble shooting has become more and more popular. This presentation will review the strengths and weaknesses of the more common surface analysis techniques, such as Auger electron spectroscopy, Rutherford backscattering spectrometry, secondary ion mass spectrometry, total reflection x-ray fluorescence, and atomic force microscopy. Some of the newer scanning probe based techniques, such as scanning thermal microscopy and scanning capacitance microscopy, will be introduced. Several application examples will be presented to highlight the strengths and complimentary nature of these techniques. These examples will include: analysis of barrier metal composition as a function of depth into device features, two dimensional dopant profiling, measurement of ion implantation damage in SiC, analysis of fluorinated silicon dioxide film stability, development of wafer cleaning techniques, and the optimization of chemical mechanical polishing processes.

9:00am **AS+VT-FrM3 An Evaluation of SIMS Analytical Capabilities For Sub-0.25 Micron Implant Technology***, **V.K.F. Chia**,* Charles Evans & Associates

The applications of SIMS (secondary ion mass spectrometry) to the microelectronics industry are very diverse. In the ion implantation sector SIMS is perhaps the most widely used analytical technique. This is not too surprising because SIMS can detect all elements, produce high precision profiles, and provide elemental surface and bulk information with excellent detection sensitivity. As the design rule continues to shrink the question that arises is, "Can SIMS still be a valuable tool?". This paper addresses this question and reviews advances made in protocol development. For example, SIMS can perform high precision implant characterization (HPIC) to match the dose delivered by two different implanters to within <1% (67% confidence interval) during process replication or transfer, and for initial implanter qualification during fab start-ups. A better understanding of near-surface profiling phenomena has led to more accurate depth profiling of ultra-low energy ion implants (e.g. <1 keV B). SurfaceSIMS was developed to monitor and accurately quantify unintentional contamination that occurs during ion implantation, for example dopant cross-contamination in multi-purpose implanters, and to monitor inadvertent contamination related to sputter erosion or outgassing of implanter construction materials. As device dimensions shrink in size the need to perform ion implant characterization in small areas with high sensitivity becomes increasingly important. One solution is to interleave reactive primary ion species with high current density probes. This procedure enables 12 µm x 12 µm areas to be depth profiled with a sensitivity similar to analyzing a 180 µm x 180 µm area using Cs primary ions alone. In view of these advancements, SIMS appears to be well positioned to continue its primary role in ion implant characterization beyond the year 2000.

9:20am **AS+VT-FrM4 Accurate Dynamic Secondary Ion Mass Spectrometry (SIMS) and Auger Electron Spectroscopy (AES) Characterization of SiGe Stoichiometry and Hetero-Junction Bipolar Transistor (HBT) Dopant Levels***, **T.H. Büyüklimanli**, J.T. Mayer, M.S. Denker, R.L. Moore, C.W. Magee,* Evans East

The recent growth of the consumer microwave electronics market has spurred the development of SiGe HBTs. There are several physical and chemical properties of the device that affect performance and most importantly bandwidth. This has prompted us to take a fresh look at the acquisition and quantification of the SIMS and AES data. This paper investigates the characterization of two parameters of device fabrication: first the stoichiometry of the Ge-doped base layer, second the dopant (typically B) and impurity (typically O) concentration and distribution in the base layer. SIMS and AES were used to characterize a sample set ranging from 5-45 atomic percent Ge. Each sample was ion implanted with B, P, C and O. Differences in sputter rates, recommended analytical protocols (SIMS), data post-processing and changes in relative sensitivity factors will be addressed.

9:40am **AS+VT-FrM5 A Comparison Auger and TOF-SIMS Depth Profiling of Silicon Oxide Nitride Multilayers Using Low Incident Ion Energy***, **S.E. Molis**, R.E. Davis,* IBM Corporation, East Fishkill Facility*; D.W. Kisker,* IBM Research Division*; D. Paul,* Physical Electronics

The ever-shrinking dimensions of semiconductor devices have placed steadily more difficult challenges in front of analytical instruments and methods as well as fabrication tools and processing. In the future, this shrinkage will have a proportionally greater impact on the vertical dimensions. The SIA Technology Roadmap lists for example a gate oxide thickness equivalent of 2-3 nm by the year 2001, and a phasing out of SiO2 in favor of alternative dielectric materials. The difficulty of this analytical challenge makes it likely that no single technique will be able to tackle any type of complex process problem alone. Rather, a synergistic approach involving the strengths of each will be called for. New techniques are needed, and the current limits of current techniques must be extended. This paper describes one approach, teaming TOF-SIMS and Auger electron spectroscopy, with sputter ion gun designs which can provide adequate sputter rates at impact energies of less than 500 eV, to improve depth resolution. A Ni-Cr multilayer standard of thicker dimensions was used to measure and optimize experimental conditions. A set of various thin oxide and nitride single films and multilayers wa examined by both techniques, to mutual advantage. The TOF-SIMS approach generally gave superior depth resolution compared to Auger, although not as good as the structural view of X-TEM. The SIMS matrix effect was interpreted by comparison to the Auger profiles. TOF-SIMS was able to give some insight into the question of hydrogen content of the films. The propensity for thermal damage was also studied.

10:00am **AS+VT-FrM6 A New High Performance TOF-SIMS Instrument for 300 mm Wafer Inspection***, **E. Niehuis**, C. Bendel, D. Rading,* ION-TOF GmbH, Germany

We have developed a high performance TOF-SIMS instrument for the analysis of wafers up to 300 mm diameter. It includes a new sample stage with 5 axis and interferometric x,y position control for ultimate navigation accuracy. The instrument is equipped with a Ga liquid metal ion gun for surface analysis and imaging, and a flexible dual source gun with electron impact and Cs source for dual beam depth profiling. In a production environment high sample throughput, high reproducibility and ease of use are most important. To meet these requirements, we implemented complete instrument automation to setup the instrument for a specific task, to find a specific area on a wafer and to acquire and analyze the data. The navigation part includes the import of coordinates from other inspection tools, an auto-heigth-adjustment and optical pattern recognition. For the interpretation of the spectra we make use of a high mass resolution SIMS database for automated compound identification. In this paper we will describe the instrument performance and discuss the various applications of this tool in IC production. TOF-SIMS can be used for the screening of various surface contaminants like trace metals (alkali, transition metals), small inorganic molecules (e.g. sulfates) as well as organic contaminants (e.g. photoresist residues, cleaning agents, plasticizers from storage containers). The technique also offers depth profiling with excellent depth resolution for the characterization of gate oxides and ultra-shallow implants. In defect review TOF-SIMS provides high lateral resolution and detailed chemical information on sub-micron particles.

10:20am **AS+VT-FrM7 Automated Process Monitoring Using ESCA and Numerical Methods***, **D.J. Hook**, J.F. Moulder, J.S. Hammond,* Physical Electronics, Inc.

There currently exists a need in the electronics industry for automated process control to increase product yield and reliability. An example of this is the hard disk industries' push to higher media storage density that has placed increasingly stringent requirements on the lubrication media needed for disk surfaces. Similarly, uniformity of oxide thickness on silicon wafers is an important property that can affect the finished device and in turn overall production capability of a semi-conductor facility. The ability to obtain quantitative ESCA results over large areas and present information in an easy to understand visual format can provide feedback for the production environment. The combination of totally automated process monitoring with Graphical User Interface (GUI) driven film thickness calculations and large area mapping software is a new development in ESCA which can address this need. Examples of automatically collected lube thickness measurements on new and used hard disks and oxide thickness maps on cleaned 200 mm silicon wafers will be presented.

10:40am **AS+VT-FrM8 Measurement of Carrier Concentration and Lattice Absorption in Bulk and Epitaxial Silicon Carbide Using Infrared Ellipsometry***, **T.E. Tiwald,*** University of Nebraska, Lincoln*; S. Zollner,* Motorola Semiconductor Products Sector*; J.A. Woollam,* University of Nebraska, Lincoln*; J. Christiansen,* Motorola Semiconductor Products Sector*; P.G. Snyder,* University of Nebraska, Lincoln

We have measured the dielectric function of bulk nitrogen-doped 4H and 6H SiC substrates from 700 to 4000 cm@super -1@ using Fourier-transform infrared spectroscopic ellipsometry. We observe a strong reststrahlen band between 800 and 1000 cm@super -1@ due to photon absorption by transverse optical phonons. The shape of this band is influenced by plasma oscillations of free electrons, which can be described with the Drude model. A detailed analysis of the data allows the determination of the free electron concentration, which is between 10@super 18@ and 10@super 19@ cm@super -3@, in good agreement with electrical measurements. We were also able to determine the surface layer thickness for epitaxial 4H SiC (with an electron concentration of 10@super 16@ cm@super -3@) on heavily-doped bulk 4H SiC. Finally, we observe Berreman peaks near the longitudinal optical phonon energy in all samples. These interference effects are the result of carrier depletion and accumulation near the surface. The effect is strongest in the epitaxial sample and the more lightly doped substrates.

11:00am **AS+VT-FrM9 Si Dopant Site Within Ion Implanted GaN Lattice***, **H. Kobayashi,** W.M. Gibson,* State University of New York, Albany

There has been considerable interest in GaN for the fabrication of blue light emitting devices. In addition, this material is attractive for use in high temperature or high power electronic devices. Therefore, ion implantation for selective area doping is becoming more important for future Ga N device technology. It has been demonstrated that Si and Mg ion implantation and post-implant annealing are useful to obtain n-type and p-type GaN, respectively. However, there is still little information on actual lattice lo cation of impurities. We have investigated the Si dopant site in the GaN la ttice using ion channeling technique in combination with Rutherford backscattering spectrometry (RBS), particle induced X-ray emission (PIXE) and nuclear reaction analysis (NRA). Metalorganic chemical vapor deposition (MOCVD) grown GaN on a c-plane sapphire substrate implanted with @super 28@Si at a do se of 7x10@super 14@cm@super -2@ with post-implant annealing was investigated. Channeling measurements were performed by taking angular scans around the and axes and recording RBS, PIXE and NRA yields for Ga, Si and N, respectively. The channeling results indicate that almost 100 % of Si goes into the Ga site when the samples are annealed at 1100°C for 30 minutes while for annealing at 1050°C and below, Si is distributed almost randomly. This suggests that a drastic change of Si substitutionality takes place in a narrow temperature region near 1100°C. Our results directly indicate that the electrical activation of Si implanted GaN with post-implant annealing is due to the formation of substitutional Si at this temperature.

11:20am **AS+VT-FrM10 Laser Assisted Etching of InP Studied with XPS***, **D.M. Wieliczka,** J.M. Wrobel, C.E. Moffitt,* University of Missouri, Kansas City*; J.J. Dubowski,* National Research Council of Canada, Canada

X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) have been used to study the surface chemistry and morphology of InP wafers after photo-chemical etching of the surface. The etching process employed 308 nm illumination from a XeCl excimer laser in conjunction with a low pressure atmosphere of 10%/90% Cl@sub 2@/ He mixture. The samples were exposed to laser radiation with fluences ranging from 73 mJ/cm@super 2@ to 210 mJ/cm@super 2@. The lower fluence is well below the ablation threshold for InP under vacuum conditions. The use of a Kratos AXIS-HS photoelectron spectrometer allowed for mapping the surface chemical composition within the illuminated region and in the vicinity with a 60 µm spot size. Photoelecron spectral lines from In, P, Cl, C, and O were monitored for determining the surface chemical composition and for creating surface maps of the illuminated regions. The results showed a distinct correlation between surface chemical composition and laser fluence. At high fluence levels, the surface composition changed dramatically between the illuminated region and the exterior. Evidence for In-Cl compounds was found within the crater with thermal processes occurring in the region near the crater. At low laser fluence, the etching process showed no thermal effects in the near crater region and produced a crater with minimal Cl incorporation. In addition to the chemical changes with fluence, the surface morphology is dramatically altered. At high fluence levels, SEM images indicate the etched surface was rough and deposits of ablated material were left in the vicinity of the crater. At low fluence the images indicate a better surface morphology. This work was supported by the University of Missouri Research Board.

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS+AS-FrM

Innovative Nanoscale Measurements

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am **NS+AS-FrM1 Nanoscale Variations in Surface Potentials at Interfaces***, **B.D. Huey,** D.A. Bonnell,* University of Pennsylvania, US

Nanoscale variations in the electronic properties of individual oxide grain boundaries have been directly measured. In-situ application of atomic force microscopy used as a Kelvin probe maps local field variations in the presence of lateral applied bias and current flow within an oxide grain boundary device, providing measurements while the device is in operation. The in-situ experiment involves: 1) applying a lateral bias across microfabricated contacts on varistor and SrTiO@sub 3@ bicrystals, and 2) simultaneously mapping the surface potential in the vicinity of grain boundaries. Voltage dependent properties of both multiple boundaries as well as carefully characterized individual interfaces are thus measured. The non-linear voltage dependence of potential barriers at the grain boundaries is additionally obtained at the nanoscale as a function of local orientation, chemical content, and position.

8:40am **NS+AS-FrM2 Noncontact Measurement of Electrical Dissipation using Ultrasensitive Cantilevers***, **T.D. Stowe,*** Stanford University*; D. Rugar,* IBM Almaden Research Center*; D.J. Thomson,* University of Manitoba, Canada*; T.W. Kenny,* Stanford University

We have used ultralow loss 0.17 µmm thick silicon cantilevers to measure electrical dissipation in insulators and doped silicon samples using a technique similar to the one originally developed by Denk and Pohl.@footnote 1@ Images were taken by recording the mechanical Q of a self-oscillating cantilever as it was scanned 10-100 nm above the sample surface in a perpendicular orientation. All experiments were performed at room temperature in vacuum with cantilevers having 10@super -4@-10@super-3@ N/m spring constants and 10-100 kHz resonant frequencies. Electrical dissipation was measured as function of applied voltage, tip-sample distance, and resistivity. We were able to measure electrical dissipation as small as 10@super -14@ N-s/m and ohmic losses as small as 10@super -18@ Watts. Using tips with 50 nm radii, we were able to simultaneously image permanent charge in the surface oxide and doping levels between 10@super 15@-10@super 19@ /cm@super 3@ in silicon with 200 nm spatial resolution. Possibilities for improving the spatial resolution and doping sensitivity of this technique will be discussed. @FootnoteText@ @footnote 1@W. Denk and D. W. Pohl, Appl. Phys. Lett. 59, 2171 (1991).

9:00am **NS+AS-FrM3 Nanocalorimetry for Thermodynamic Measurements of Nanostructures***, **L.H. Allen,*** University of Illinois, Urbana-Champaign **INVITED**

This talk will focus on a novel calorimetry technique@footnote 1,2,3@ for measuring the thermodynamic properties of nanometer size material. The thermodynamic properties of material having small nanometer dimensions can be considerably different as compared to material in bulk form (e.g., the reduction of melting point). This occurs because of the tremendous influence of the surface energy. Conventional differential scanning calorimetry (DSC) techniques are extremely difficult to apply to the study of small structures because the total amount of heat generated during the transformation is too small as compared with the background heat capacity of the calorimeter. The new nanocalorimeter is fabricated using standard MEMS thin film techniques and it has the capability of measuring the dynamics of the energy exchange at the level of 0.2 nanojoule. This technique is so sensitive that it can easily measure the melting process of 1 Angstrom of Sn, which has been deposited on a Si-N surface. Results of specific materials studies will be discussed including the size-dependent melting point depression of small particles of Sn and Al and preliminary work on the coalescence of small clusters. @FootnoteText@ @footnote 1@S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath and L.H. Allen, "Size-Dependent Melting Properties of Small Tin Particles: Nanocalorimetric Measurements", Phys. Rev. Lett. 77, 99-103 (1996) @footnote 2@S.-L. Lai, P. Infante and L. H. Allen, "Heat capacity of Sn nanostructures via Thin Film Differential Scanning Calorimetry," Appl. Phys. Lett., 70, 43-46(1997).

@footnote 3@S. L. Lai, J. Carlsson and L. H. Allen, "Melting Point Depression of Al Clusters Generated During the Early Stages of Film Growth: Nanocalorimetry Measurements," Appl. Phys. Lett., Appl. Phys. Lett. 72, 1098 (1998)

9:40am **NS+AS-FrM5 Recent Advances in Scanning Capacitance Microscopy*, C.C. Williams*,** *J.S. McMurray, V.V. Zavyalov, J. Kim,* University of Utah **INVITED**

Scanning Capacitance Microscopy is a rapidly developing technique for the characterization of the electronic properties of semiconductor materials on a 10 nanometer scale. Oxide, semiconductor interface and near surface "bulk" properties can be studied by this technique. Recently, new capabilities have been developed to extract quantitative dopant/carrier profiles near electrical junctions in cross-sectioned devices. Built-in internal electric fields have been measured and compared with electrical models. Random distributions of nanometer scale "defects" have been observed at the surface of uniformly doped and oxidized silicon samples. Two-dimensional diffusion of dopant impurities has been measured by SCM and directly compared with predictions of TSUPREM4. These new developments and capabilities of the Scanning Capacitance Microscope will be described and presented.

10:20am **NS+AS-FrM7 Nanometer-scale Electrical Characterization of Semiconductor with a Scanning Capacitance Microscope*, H. Tomiye*,** *Y. Takafumi,* Tohoku University, Japan

Recently, nanometer-scale material characterization has become a necessity in Si technology. The scanning probe microscope is one of the most powerful characterization techniques at this scale. A variety of information can be obtained by this technique which is of importance in the assessment of material and device aspects of silicon. Scanning capacitance microscope (SCaM) can clearly show local variation of capacitance, which reflects the electrical properties of a Si substrate, SiO@sub 2@/Si interface and SiO@sub 2@ layer. We have developed a SCaM/AFM consisting of a W wire cantilever and a capacitance sensor. The unique features of our microscope are as follows: (1) Our SCaM can directly detect a sample capacitance with / without using lock-in amplifier. It means we can measure capacitance (C) of the sample in addition to the capacitance derivative (dC/dV). (2) We can simultaneously obtain a SCaM image and C-V characteristics. It means we can achieve quantitative measurements of the capacitance at a nanometer-scale. (3) The spatial resolution for the capacitance measurements is estimated to be less than 20 nm. It is demonstrated that the local impurity concentration profiling of lateral p-n junction is achieved by the C-V measurements. We have injected electrical charge into a SiO2 layer and investigated the nature of charge storage at the SiO@sub 2@/Si system by the SCaM and C-V characterization. A shift of the flat-band voltage due to the trapped charges is observed, which enables one to estimate the density of trapped charge. This paper will report on the development of a SCaM and its applications to the characterization of SiO@sub 2@/Si and fabrication of a charge storage device.

10:40am **NS+AS-FrM8 A Study on the Post-stress Charges in SiO@sub2@ Films on Si by Scanning Capacitance Microscope*, K. Mang*,** Samsung Electronics, Korea*; C.J. Kang, G.H. Buh, C.K. Kim, S. Lee, C. Im, Y. Kuk,* Seoul National University, Korea

Using scanning capacitance microscope, The induced traps on SiO@sub2@ were imaged with @<=@20nm spatial resolution. The static and dynamic behaviors of the electronic charges were evaluated. After a voltage stress, an anomalous post-stress charge generation and relaxation effect were found. Depending on the polarity of stress voltage, post-stress tip voltage and stressed time, different relaxation trend exists at the stressed area. The induced charge density in the stressed SiO@sub2@ film was higher with the stressed time The trap dynamics is also a function of initial stress field. With the high field applied to the SiO@sub2@ film, the larger and faster generation(or relaxtion) was observed. After the trapped charges are formed, the amount and polarity of the charge vary dynamically. It is believed that thermal excitation or tunneling of one or two electrons, can cause the turn around effect, which has been poorly understood so far.

11:00am **NS+AS-FrM9 Imaging Buried Interfacial Lattices with Quantized Electrons*, I.B. Altfeder*,** *D.M. Chen,* The Rowland Institute for Science

We demonstrate that interfacial lattices buried under as much as 100 Å of a metal can be directly imaged by low temperature scanning tunneling microscopy with an unexpectedly high lateral resolution.@footnote 1@ To achive such a remarkable resolving power we expolite the presence of the quantum-size sigularities in the electron energy spectrum in the metal as well as its high sensitivity to the defects at the boundaries. Our theoretical model shows that this unique phenomena can be atrributed to the nondifractive scattering of the quantized electron waves at the interface as a result of their highly anisotropic motions in a two dimensional nano-structure. @FootnoteText@ @footnote 1@I. B. Altfeder, D. M. Chen, K. A. Matveev, Phys. Rev. Lett. (in press). @footnote 2@I. B. Altfeder, K. A. Matveev, D. M. Chen, Phys. Rev. Lett. 78, 2815 (1997).

11:20am **NS+AS-FrM10 Nanoparticle Near-Field Spectroscopy by a Microscopically Narrow (Subnanometer) Electron-Beam*, H. Cohen*,** Weizmann Institute of Science, Israel*; T. Maniv,* Technion, Israel*; Y. Rosenfeld Hacohen, R. Tenne,* Weizmann Institute of Science, Israel*; O. Stephan, C. Colliex,* University of Paris-Sud, France

Single nanoparticle near-field spectroscopy is performed in a scanning transmission electron microscope at non-intersecting beam-particle configuration. Separating the surface collective modes from the entire excitations spectrum, the energy loss signal is quantitatively accounted for, using a relatively simple theoretical model. Advantaged by the sub nanometer size of the e-probe, the highly controlled beam-surface distance introduces an effective window in momentum space, exposed to a long wavelength relativistic dispersion, which provides an enhanced sensitivity to beam and particle size effects. The spatial dispersion of the particle dielectric function, associated with the electronic band structure, is practically filtered out. "Particle spectroscopy", namely the selective excitation of modes which characterize the particle geometry and size, is available at selected beam-particle distances.

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