**Applied Surface Science Division** 

Room 4C - Session AS-TuP

#### **Poster Session**

AS-TuP1 Pattern Measurements of Reticles with Optical Proximity Correction Assist Features Using the Atomic Force Microscope, K.-J. Chao, *R.J. Plano, J.R. Kingsley,* Charles Evans & Associates; *F. Chen, R. Caldwell,* MicroUnity Systems Engineering, Inc.

A 4X, 6-inch reticle with optical proximity correction (OPC) assist features intended for deep ultraviolet (DUV) exposure was investigated. A set of chrome lines with designed CD (linewidths in this case) from 0.24 to 2.00 microns was profiled by AFM. The goal of this work is to present a method to ensure consistent measurement of chrome lines widths on the reticle. This is done by consistently measuring the line width at the half-height position on the line cross-section, i.e., full width at half maximum (FWHM). defining the boundaries of the line width at the half height locations of the edge steps. Using this method, the CD linearity is found to be within ±20nm over a range of line widths from 2.00 um to 0.4 um. Additionally, the CD uniformity is found to be worse when the widths of the lines are nominally less than 0.4 um.

#### AS-TuP2 Changes in the Performance of a Cylindrical Mirror Analyzer Induced by Sputter Depth Profiling, *M. Kottke*, Motorola, Inc

Optimum performance of a cylindrical mirror analyzer (CMA) is dependent upon proper fringe field correction at both ends of the concentric cylinders. In many CMAs this fringe field correction is accomplished with concentric metal rings deposited on the surfaces of solid ceramics which completely seal off the ends of the analyzer. This paper describes the degradation in performance of the analyzer caused by the redeposition of sputtered secondary ions onto the surface of the conical ceramic at the input of the CMA. It will be shown that the time frame of this degradation varies widely from days to months (or even years) depending on the materials being analyzed and the mode of operation of the CMA. It will also be shown that the loss in integrity of the fringe field correction causes large changes in the energy transmission function of the analyzer. Errors in quantitative calculations based on the use of elemental sensitivity factors determined from standards run on a specific instrument at a fixed point in time can therefore be proportionately large. Alternate modes of operation which minimize degradation are presented along with a discussion of alternate fringe field correction schemes.

#### AS-TuP3 Formation of Dioptase-like Structures in Silica Xerogeles Doped with Copper, F. Ruiz, J.R. Martinez-Mendoza, Universidad Autonoma de San Luis Potosi, Mexico; J. Gonzalez-Hernandez, CINVESTAV-IPN, Mexico

Using IR absorption and Raman spectroscopy we have analyzed the incorporation of Cu in SiO@sub 2@ matrix in samples prepared by the solgel method. Samples contain Cu at 30 %wt and were studied as a function of annealing temperature. It is found that the heat treatments have a remarkable influence on the structure. With this analysis we inferred that the final structure of the sample contain dioptase-like structures (Cu@sub 6@[Si@sub 6@O@sub 18@]\*6H@sub 2@O).

#### AS-TuP4 Reaction of Fluorocarbon Contaminants with Aluminum Oxides: Inadvertant Fluoride Formation during Low Temperature Plasma Cleaning of Aluminum Alloy Surfaces, C.E. Moffitt<sup>1</sup>, D.M. Wieliczka, University of Missouri, Kansas City; C.M. Reddy, Q. Yu, H.K. Yasuda, University of Missouri, Columbia

Plasma deposited films have shown promise as intermediate adhesion and barrier layers for use in the interface engineering of corrosion protection systems on various materials. The surface treatment of plasma deposited trimethylsilane (TMS) films with fluorocarbon plasmas has been seen to significantly improve the adhesion of certain paints to these films, which are strongly adhered to underlying aluminum alloy substrates. Oxygen plasma cleaning of the alloy surfaces, prior to deposition of the TMS film, is normally employed to remove organic contaminants. During testing, one batch of aluminum panels was processed without the oxygen plasma treatment and exhibited extensive adhesion failures. An investigation of these results shows that low levels of fluorocarbon contaminants readily react with the alloy surface and deposit a carbonaceous layer, which dramatically interferes with the adhesion of the plasma polymer to the alloys. XPS studies show that the presence of even low levels of these contaminants in the chamber, during the oxygen cleaning process, is sufficient to induce the conversion of the surface from oxide to a mixture

of oxide and fluoride. When present, this fluoride layer is found to reduce the corrosion resistance of test panels. Support for this work was provided by DARPA under U.S. Air Force contract F33615-96-C-5055.

#### AS-TuP5 Photodegradation and Direct Patterning of PVDF and P(VDF-TrFE) using Sychrotron-based X-rays, *P.T. Sprunger*, *J. Choi*, *E. Morikawa*, *H. Manohara*, Louisiana State University

Upon hard and soft X-ray exposure from a synchrotron storage ring, the photodegradation and direct patterning of PVDF and copolymer P(VDF-TrFE) thick and thin films have been studied with ultraviolet photoemission and mass spectroscopy. After exposure of soft white light X-rays (<1 keV) on crystalline, 5 ML P(VDF-TrFE) films, ultraviolet photoelectron spectroscopy reveals that the photodegradation mechanism involves both an increase in the carbon conjugation (single to double bond formation). With increasing illumination amount of white light, new valence band features emerge near and cross the Fermi level. Furthermore, there is an attenuation of the fluorine 2s core-level intensity due to photodetachment. The photodetached components of the copolymer, as detected with mass spectroscopy, are hydrogen, fluorine, and HF. This photodegradation mechanism affords the ability to direct patterning of PVDF and P(VDF-TrFE) using X-rays. Without the use of any reactive chemical gas, a maximum etched depth in excess of 9 mm is achieved using hard X-rays (2 keV to 16 keV) in thick, amorphous films of PVDF. The ability to pattern PVDF, a piezoelectric, pyroelectric and ferroelectric polymer, has potential applications in the areas of micro-sensors, actuators and non-volatile ferroelectric random access memory (NVFRAMS) technology.

AS-TuP6 An Ellipsometric Study of Plasma Deposited Thin Films, T. El-Agez, C.E. Moffitt, University of Missouri, Kansas City; H.K. Yasuda, University of Missouri, Columbia; D.M. Wieliczka, University of Missouri, Kansas City

Spectroscopic ellipsometry was used to study films produced from a plasma of trimethyl silane gas deposited on silicon substrates. In addition to the as formed plasma film, the film surfaces were treated with either an oxygen or nitrogen plasma. Ellipsometric measurements were made on the films within 1 day after deposition and as a function of time, to determine the influence of atmospheric conditions. Additionally, the films were exposed to ultra-violet light and the changes were again tracked as a function of time. Several models were used to analyze the ellipsometry results with all of them taking into account the silicon substrate and oxide layer. One kept the overall film thickness constant, i.e. the oxide grew into the deposited film. Another assumed the plasma deposited film was stable but with additional film growth due to the oxidation. And the last allowing for both film growth and modification of the plasma film. The results obtained from these models were correlated to x-ray photoelectron spectroscopy results.

#### AS-TuP7 Surface-attached Polymer Brushes via Physisorbed Monolayers of Macroinitiators, *T. Stöhr*<sup>2</sup>, *J. Rühe*, Max-Planck-Institute for Polymer Research, Germany

Block copolymer adsorption is a frequently used procedure to modify the surface of solid substrates.@footnote 1@ Such systems, usually A-B block copolymers, consist of an anchor block which allows attachment to the substrate surface and a buoy block which carries the desired surface properties. Since one part of the molecule has to have only a weak interaction with the surface and the other a strong one, the two blocks should be rather different from a chemical point of view. This renders the task of finding a suitable solvent process non-trivial. Monolayers prepared by this technique are inherently very thin with thicknesses typically between 3 and 5 nm. The reason for this is a kinetic hindrance for the attachment of polymer chains due to a diffusion barrier created by the already attached molecules. Recently radical polymerization using chemisorbed azo-type initiators has been established.@footnote 2@ In this case the polymer is grown directly at the surface of the substrate. We present a macroinitiator system that allows to create hydrophobic layers on hydrophilic substrate surfaces. Here a hydrophilic anchor block bearing initiator groups is physisorbed to a hydrophilic surface. The hydrophobic buoy block is polymerized in situ resulting in a block copolymer monolayer. A poly(epsilon-caprolactone) macroinitiator containing azo moieties was synthesized and adsorbed to silicon oxide surfaces. The surface-attached monolayer was subsequently used for the polymerization of n-alkyl methacrylates resulting in thicknesses up to 100 nm. By this route the limitations of the block copolymer physisorption process, such as solubility problems of the block copolymer and intrinsic limitations of the layer

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thickness, can be overcome. @FootnoteText@ @footnote 1@ Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. Polymers at Interfaces; Chapman & Hall: London, 1993; Chapter 6. @footnote 2@ Prucker, O.; Rühe, J. Macromolecules 1998, 31, 592.

AS-TuP8 Observing Damage Produced during XPS Measurements, M.H. Engelhard, D.R. Baer, G.C. Dunham, Pacific Northwest National Laboratory An increasing amount of studies in our laboratory involve analysis of polymers, self assembled monolayers (SAMS) with different terminations, insulators and other materials for which some properties of the specimens degrade with time during x-ray exposure. When damage is observed, a series of parameter tests are conducted to determine the conditions and time for which reliable data can be collected. In this paper we will report measurements made on SAMS with CH@sub 3@, OH and COOH, as well as some test coupons of PCEMA, PTFE and PVC. Most of these measurements were made on a Physical Electronics Quantum 2000 for which a variety of different x-ray flux densities can be arranged. In addition, the beam can be moved around to examine the regions over which damage occurs. Measurements for COOH terminated SAM show a damage production directly related to the flux per unit area. These, and other results, suggest that damage on many materials is not simply due to specimen heating. However, tests on PCEMA show damage to occur outside the region that was exposed to the x-ray beam. These tests will be described along with a new series of experiments being undertaken to determine if specimen cooling provides a way to decrease specimen damage. This work was conducted in the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facilty sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research.

#### AS-TuP9 Role of Temperature in the Surface Oxidation Chemistry of IN-738 Superalloy, *L. Bracho<sup>1</sup>*, *S. Seal*, *V. Desai*, University of Central Florida

Super-alloys are used in high temperature industrial applications because of their strength, high resistance to high-temperature oxidation and hot corrosion, and longer durability than other conventional alloys. Although super-alloys possess these characteristics, they are still subjected to high temperature degradation when exposed to aggressive environments. The current research includes the high temperature oxidation behavior of IN-738 at 850, 900, and 950°C in air for a period of 300 consecutive hours. The oxidation kinetics is parabolic in nature. Due to its parabolic nature, the lattice diffusion is prominent in the various oxide formations. This leads to selective oxidation of various elements present in the alloy. The decrease in oxidation rate observed at higher temperatures is due to more alumina formation. The surface oxide formation is investigated using using XPS, AES, XRD, SEM, and EDS. It is expected to find external oxides rich in chromium, aluminum, nickel, and titanium. The thickness of the oxide and the gamma' depleted layers are expected to increase with temperature.

# AS-TuP10 Noncontact AFM Imaging of Al-Adsorbed Si(111) Surface, S. Orisaka, T. Minobe, K. Makimoto, Y. Sugawara, S. Morita, Osaka University, Japan

Recently, several groups including ourselves have reported true atomic resolution imaging using noncontact atomic force microscope (NC-AFM) operating in ultrahigh vacuum. In order to apply the NC-AFM as a scientific tool in variety of fields such as surface science, it is very important to understand the imaging mechanism of the NC-AFM on various sample surfaces. On the Si(111)7x7 reconstructed surface, we clarified that the tipsample interaction force is dominated by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom on the surface. In the present experiments, we investigated force interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface. As a sample surface with empty orbitals, Al-adsorbed Si(111) surface was used. We obtained strong contrast of NC-AFM images on Al-adsorbed Si(111) surface. Furthermore, we observed the characteristic discontinuity in the distance dependence of the frequency shift. So far, similar discontinuity has been observed on Si(111)7x7 surface, and it can be explained by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom. So, the discontinuity in the distance dependence of the frequency shift on Al-adsorbed Si(111) surface seems to be originated from the chemical bonding interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface.

AS-TuP11 Characterization of Chemically Heterogeneous Samples Using XPS Imaging and Small Area Analysis, A.C. Ferryman<sup>2</sup>, J.E. Fulghum, Kent State University

Recent advances in XPS instrumentation allow for the rapid acquisition of photoelectron images with a spatial resolution of a few microns. This capability both expands the range of samples which can be characterized using XPS, and provides additional complications in data interpretation and analysis. For samples which have a surface roughness comparable to the depth- of-focus within the image, care must be taken to distinguish between surface roughness effects and changes in chemical state or elemental distribution. Sandstones coated with a commercial perfluoropolyether for protection from weathering were characterized using imaging and small area XPS. Polymer impregnation into the stone, and uniformity of the polymer coating were characterized through analysis of both cross-sections and the surface of the sandstone. Variations in polymer distribution on both macro- and micro-scales will be discussed and evidence for polymer segregation between components of the sandstone evaluated. This system provides an example of the information which can be obtained, and artifacts which must be considered, in the analysis of a chemically heterogeneous sample which also contains significant surface roughness.

AS-TuP12 Characterisation of Oxide on GaAs Wafer Surfaces with TOF-SIMS and ARXPS, B. Burkhardt, O. Brox, Universität Münster, Germany; W. Fliegel, Freiberger Compound Materials GmbH, Germany; L. Wiedmann, Universität Münster, Germany; A. Kleinwechter, Freiberger Compound Materials GmbH, Germany; A. Benninghoven, Universität Münster, Germany

Molecular-beam epitaxy (MBE) on GaAs requires a thermally removable oxide. Therefore reliable techniques are needed to control oxides on the GaAs wafer surface in the production process. The quantitative oxide characterization (thickness and stoichiometry) can presently only be achieved by ARXPS. In this paper we compare results achieved with TOF-SIMS and ARXPS. The experiments were performed in a reflectron based TOF instrument equipped with an 8" manipulator for macroscanning and a dual beam source for depth profiling (sputter beam: 500eV Cs@super +@, analysis beam: 10kV Ar@super +@). For ARXPS we used a spherical electron analyzer with multichannel detector and monochromator X-ray source (AI K@alpha@: 1486,6 eV). For ARXPS data interpretation we assumed a 4-layer-system for the GaAs oxide. Separating the XPS signal into different oxide states we determined thickness and stoichiometry of each layer. Dual beam depth profiling was used to characterize the oxide layer by means of SIMS. The integrals of the secondary ions AsO@sub n@@super -@ and GaO@sub n@@super -@ over the sputter depth can be correlated to the oxide thickness and the various oxide phases as identified by ARXPS. The use of SF@sub 5@@super +@ primary ions allowed the detection of Ga@sub m@As@sub n@@super ±@ cluster ions with more than 40 atoms. The Ga/As ratio of these clusters changes with storage time and can be taken as a measure of stoichiometry changes in the uppermost atomic layer. Using ARXPS for calibration TOF-SIMS has shown to be a suitable technique to control the oxide layer on GaAs wafer.

## AS-TuP13 Surface Energy Change and Hydrophilic Formation of PE, PS and PTFE Films Modification by Hydrogen Ion Assisted Reaction, J. Cho, K.H. Yoon, Yonsei University, Korea; S.K. Koh, KIST, Korea

The Polyethylene (PE), Polystyrene (PS) and Polytetrafluoroetyhylene (PTFE) surface modification has been investigated by hydrogen ion assisted reaction with oxygen environment. The IAR is a kind of surface modification technique using ion beam irradiation with reactive gas environment. The hydrogen ion beam energy was 1 keV, ion dose were varied from 5ï,'1014 to 1ï, 1017 ions/cm2, and amount of oxygen blowing gas fixed 4 sccm (ml/min). Wettability was measured by water contact angles of water contact angle measurement, and the surface functionality was analyzed by x-ray photoelectron spectroscopy. The contact angle of water to PE modified by argon ion beam only decrease from 95 to 52 degrees, and surface energy was not changed significantly. But, the contact angle using hydrogen ion beam with 4 sccm oxygen environment was stiffly decreased to 8 degree and surface energy 65 ergs/cm. In case of PS, the contact angle and surface energy changes were similar results of PE, but the contact angle of PTFE samples decreased with ion dose up to 1ï, 1015 ions/cm2, increased at higher dose, and finally increased to the extent that no wetting was possible at 1ï, 1017 ions/cm2. The PTFE samples irradiated with argon with oxygen environment had lower contact angle than hydrogen with oxygen, even though the samples with oxygen environment

<sup>2</sup> ASSD Student Poster Competition Participant

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developed hydrophilic groups on the irradiated surfaces. This results was due to the hydrogen ion beam that affect the surface cleaning for removing the impurities on PE surface and, then hydrogen ion beam was activated with C-H bonding to make some functional groups in order to react with the oxygen gases, finally, unstable PE surface can be changed from hydrophobic to hydrophilic formation such as C-O and C=O from the XPS analysis, and the ion assisted reaction is very effective tools to attach reactive ion species to form functional groups on C-C bond chains of PE.

### AS-TuP14 Control of Intracellular Signal Transduction Using Self-Assembled Monolayers of Alkylthiolates on Gold, *K.B. McClary*<sup>1</sup>, *D.G. Grainger*, Colorado State University

Self-assembled monolayers of terminally-functionalized alkylthiolates on gold have been used to interrogate cell-biomaterial surface interactions at the extracellular and intracellular level. The goal of this research is to provide molecular level information on the surface determinants necessary to produce predictable, controllable biological responses to implanted materials. Various aspects of "outside-in" communication between cells and material surfaces have been investigated. Formation of focal contacts and stress fibers, early indicators of effective intracellular signaling, was observed to be surface-chemistry dependent, and correlated with protein behavior on different surface chemistries. The primary cellular regulators of these events were examined using well-controlled alkylthiol surface chemistries. Activation states of the GTPase RhoA were determined and shown to be surface chemistry-dependent. RhoGDI levels and intracellular localization were also shown to be surface-chemistry dependent. Cells cultured on -CH3 terminated SAMs, which normally exhibit a low growth phenotype, were transfected with a constitutively active RhoA mutant. Transfected cells exhibited significant increases in cell length. However, no focal contact formation was observed. These results show that genetic alteration of intracellular regulators is incapable of overcoming the lack of extracellular stimuli, in the form of adsorbed ECM proteins, present on -CH3 terminated SAM surfaces. In summary, extracellular and intracellular information indicates that surface chemistry is capable of modulating communication between a cell and its extracellular environment. These data provide new, valuable molecular level information necessary to develop rational cause and effect relationships between a material's surface chemistry and biological response.

#### AS-TuP15 Core-level Satellites and Outer Core-level Multiplet Splitting In Mn Model Compounds, *A.J. Nelson*, *J.G. Reynolds*, Lawrence Livermore National Laboratory; *J.W. Roos*, Ethyl Petroleum Additives

We report a systematic study of the 2p, 3s and 3p core-level photoemission, satellite structures and valence bands of Mn model compounds. Charge-transfer from the ligand state to the 3d metal state is observed and is distinguished by the prominent shake-up satellite about 5 eV higher than the Mn 2p@sub 3/2@ peak for of all the Mn@super +2@ species and MnPO@sub 4@. The Mn 3s final state configuration can be either 3s3d@super 5@ or 3s3d@super 6@L depending on final state screening effects due to the ligand. We observe that the Mn 3s multiplet splitting becomes smaller as the Mn oxidation state increases, except for the Mn-phosphate species. Also, the 3s final state has @super 7@S and @super 5@S symmetry. In the @super 7@S state, the remaining 3s electron is well correlated with 3d electrons of parallel spin, while in the @super 5@S state the two spins are antiparallel. This electron correlation reduces the branching ratio of the @super 7@S:@super 5@S states as experimentally observed. In addition, as the ligand electronegativity decreases, the spin state purity is lost in the 3s spectra and the spectra becomes representative of mixed unscreened (3d@super N@) and locally screened (3d@super N+1@) final states. Our results are best understood in terms of configuration-interaction (CI) calculations including intrashell electron correlation, charge-transfer and final-state screening.

#### AS-TuP16 Optimizing Signal Intensities in REELM and SAM Microscopies: A Comparision of Instruments Operated in Fixed-Analyzer-Transmission (FAT) and Fixed-Retard-Ratio (FRR) Modes, *E. Paparazzo, L. Moretto,* Consiglio Nazionale delle Ricerche, Italy; *S.A. Lea, D.R. Baer,* Pacific Northwest National Laboratory

Signal intensity is the main factor for chemical contrast in reflected electron energy loss microscopy (REELM) and scanning Auger microscopy (SAM) images of surfaces. We report here on REELM and SAM signal intensities measured as a function of the primary beam energy (Ep) for two Auger microprobes: one operated in the fixed analyzer transmission (FAT) mode (Cameca 'Nanoscan 50', Rome), the other in the fixed retard ratio

(FRR) mode (PHI '680 Auger Nanoprobe', Richland). The aim of this work is to guantitatively determine the extent to which each type of microprobe affects the relative intensities of REELM and SAM signals. To accomplish this task we conducted a comparative analysis in the two laboratories using atomically-clean Al metal as a sample. We measured the intensity ratio between the first bulk plasmon signal and the Auger Al LVV signal (KE ~ 70 eV) as a function of Ep, which was chosen at several values within the range 200-2000 eV. We found that for both the FAT and FRR microprobe this ratio decreases by a factor  $\sim$  10 upon increasing Ep from 200 to 2000 eV. These findings are discussed in light of both the energy resolution and response function associated with the FAT and FRR operation modes in the KE range considered, and they are used to account for the chemical contrast of REELM and SAM images acquired in the two microprobes at differing Ep's. We show that our work can help devise an optimal compromise between chemical contrast, surface-specificity and chemical speciation in both REELM and SAM imaging, whether the two methods are performed in FAT or FRR Auger microprobes.

#### AS-TuP17 The Develpment and Application of a High Speed Etching Source for Destructive Depth Profiling, *A.J. Roberts, C.J. Blomfield, S.C. Page, D.J. Surman,* Kratos Analytical, UK

The development and application of a low energy argon ion beam source for destructive depth profiling, combined with X-ray photoelectron spectroscopy (XPS) are presented. This compact Kaufman ion source which combines extremely high sputter rates and low ion beam acceleration potentials, reduces ion induced mixing of the surface atoms. The properties of this ion source mean that concentration depth profiling through several hundred nanometer thick layers is possible, whilst retaining good interface resolution. Rotation of samples during sputter profiling is shown to improve interface resolution. The depth profiling capabilities of this high speed etching source will be demonstrated through a number of challenging samples. Atomic concentration profiles through a three layer sample have been performed as a function of ion acceleration voltages, and the effect on interface resolution is discussed. A further example of depth profiling through an inorganic material with a thin metal underlayer on polyester is shown. Chemical state information is retained from the inorganic oxide layer, with some reduction of the oxide layer observed due to the preferential sputtering of oxygen from the surface during profiling. Data presented shows no decrease in the sputter rate due to positive charging of electrically insulating samples during the sputtering process.

#### AS-TuP18 A Dual Anode Monochromatic X-ray Source, S.C. Page, C.J. Blomfield, B.J. Tielsch, D.J. Surman, Kratos Analytical, UK

High energy Ag L@alpha@ X-rays have several advantages over the more commonly employed Al K@alpha@ source. A photon energy of 2984.3eV means that a Ag source can generate higher energy core levels, Auger series and has a greater excitation volume. A further advantage over other high energy sources is that the Bragg condition may be satisfied via a second order diffraction within the confines of the conventional Al K@alpha@ monochromator body with only minor modifications. We have now for the first time implemented a Ag monochromator as a modification to the standard Al monochromator on a modern magnetic lens based electron spectrometer, the Axis Ultra. The anode of the Al monochromator has been adapted to have both a conventional AI face as well as an additional Ag face, thus changes between source may be made by minor adjustment without breaking vacuum. The great improvement gained in photoelectron collection efficiency by employing magnetic lens technology improves the sensitivity and ultimate usability of the Ag source making it a viable alternative for the measurement of deep 1s core levels and Auger parameters. The results presented show the performance of the Ag source to give resolution better than 0.9 eV FWHM on Ag and a sensitivity greater than 4,300 CPS on Au at a resolution of 1.3eV. Further results highlighting the usefulness of the source on practical samples will be presented.

#### AS-TuP19 Scanning Tunneling Microscopy and X-ray Photolectron Spectroscopy Studies of WO3 Thin Films Submitted to Various Thermal Treatments in Air and Ultra High Vacuum, S. Santucci, L. Lozzi, M. Passacantando, University of L'Aquila and INFM, Italy; L. Ottaviano, INFM, Italy; C. Cantalini, L. Odorisio, University of L'Aquila, Italy

The gas sensitive properties of WO3 thin films seem to be due to a loss of oxygen at the surface, which determines the presence of active sites for the reaction with gases (Co,NOx,ozone). The reactivity of the WO3 films is strongly influenced by the morphology and surface properties. In this work the surface electronic and structural properties of about 150 nm thick WO3 films, deposited in high vacuum by thermal evaporation onto Si substrates, have been studied in UHV by means of XPS and Scanning Tunneling

Microscopy/Spectroscopy (STM/STS). After the deposition these films have been annealed in atmospheric owen for 24 h at different temperatures ( 300 and 500° C) to stabilise the film morphology. The XPS measurements, by using a monochromatic Al source to follow W 4f, O 1s peaks and the valence band, have been performed on these samples both as prepared and after a re-annealing in UHV at temperatures ranging from 50 to 600 ° C, . The UHV re-annealing procedure strongly modifies the W 4f peak of both the as deposited and 300 ° C samples, showing the loss of oxygen. Moreover, at the Fermi edge, before the UHV annealing there is a small signal due to the presence of metallic states. This signal after the UHV annealing strongly increases, indicating the presence of an high density of states at the Fermi edge. Instead the 500 ° C sample, after the heating in UHV has shown a substantial stability of the nearly stoichiometric WO3 phase. Using STM in UHV we have investigated the morphology of the samples at room temperature and while scanning at elevated temperatures up to 600 °C. In particular we have simoultaneously taken I-V curves at the boundaries and centers of the typical grains of the polycrystalline sample. Our findings on the electronic structure of the samples close to the Fermi level are in agreement and allow clearer understanding of the findings from a parallel XPS study.

#### AS-TuP20 Radiation Damage Study of n-Alkanethiols Deposited on Platinum, N. Franco, T. Van Buuren, C. Bostedt, L.J. Terminello, Lawrence Livermore National Laboratory

The potential technological applications of Self Assembled Monolayers (SAM's) has increased dramatically in the past few years. Most of these applications exploit the flexibility and simplicity of the monolayer film growth. Alkanethiols adsorbed on nobel metals are perhaps the best example of theses ordered interfaces and, in these cases, it has been shown that the stability of the adsorbed molecules is strongly related with the dimension of the carbon chain. We performed valence band and core level synchrotron radiation spectroscopy studies of different n-alkanethiols adsorbed on platinum in order to investigate the stability of these films under a Ultra Violet (UV) or soft X-ray exposure. Additionally we measured the change in the empty states by X-ray Absorption Spectroscopy (XAS) and we imaged the surface by Atomic Force Microscopy (AFM) to determine surface morphology. We will present results that suggest a change in the structure of the molecules adsorbed caused by irradiation. This change is related to the photon flux and is not energy dependent. @FootnoteText@ C. Bostedt is supported by the German Academic Exchange Service DAAD, N. Franco by the Spanish education and culture office. The work is supported by the US-DOE, OBES Material Sciences under contract W-7405-ENG-48, LLNL.

#### AS-TuP21 Surface-initiated Anionic Polymerization: Investigation of Functionalized Surfaces and In-situ Polymer Films, R.C. Advincula, University of Alabama at Birmingham, US; Y. Nakamura, S. Inaoka, Q. Zhou, J. Mays, University of Alabama at Birmingham

The surface initiated anionic polymerization is a "grafting from " approach to tethering polymer chains to surfaces. Although various surface-initiated polymerization schemes have appeared recently, we seek to utilize the anionic polymerization approach with its potential to forming monodispersed polymers of controlled MW through "living" polymerization. In this report, we describe the synthesis of the initiator; diphenylethylene (DPE) silane derivative, the activation towards initiation, polymerization mechanism, and characterization of the polymers bound on the substrate. An important focus is the analysis of the substrate before and after formation of the self-assembled-monolayer (SAM) of the initiator. We have utilized electrochemical methods, contact angle, quartz crystal microbalance (QCM), ellipsometry, atomic force microscopy (AFM), and surface plasmon resonance spectroscopy (SPS) to characterize the surfaces. We then correlated the initiation and the polymerization mechanism with the properties of the functionalized substrate. In particular we were interested in observing the density and distribution of the initiating species on the surface in a mixed system (alkylsilane) We have observed a dependence on the domain size and mixture composition of the initiator to the microstructure and physical properties of the resulting polymer (polystyrene and PMMA) films. Further characterization will be done on the polymer films by scale-up (using silica particles) and detachment from the surface.

AS-TuP22 Surface Limiting Factors of the Growth of Metallic Nanoparticles, *R. Tannenbaum*, Georgia Institute of Technology; *H. Rotstein, A. Novick-Cohen*, Technion-Israel Institute of Technology, Israel Chemical synthesis of metal clusters, unlike UHV methods, offers a great deal of flexibility in manipulating cluster properties, such as the oxidation state and the reactivity of the metal clusters due to particle size variations, all within the bounds of the nanoscale regime. Stabilization and control of the size of metallic colloidal particles are achieved in polymer solutions, due to the adsorption of the polymer to the coagulating metal fragments, to form a layer which separates the particles sufficiently in order to keep van der Waals forces below thermal energy levels. Among the most promising chemical avenues, is the thermal decomposition of metal carbonyls in the presence of polymers with relatively low reactivity (e.g. polystyrene) under controlled inert atmosphere, resulting in the formation of zero-valent metallic particles. During the decomposition reaction of the metal carbonyl precursors highly reactive intermediates are formed, resulting in two major subsequent reaction pathways: (a) Aggregation to form small clusters; and (b) Interaction with the polymer. The final particle size and particle size distribution will be a direct function of the various facets of this complex mechanism. For the growth of zero-valent cobalt clusters, there is an inverse correlation between cobalt cluster particle size and the polystyrene concentration in the reaction solution. The increase in the concentration of polystyrene in solution will result in an increase of the concentration of the adsorbed polystyrene layer, and hence a decrease in the final cobalt cluster size. The thickness of the adsorbed polymer layer is calculated by using a combination of TEM and STM measurements. The difference in the particle size diameters calculated by the two methods provide an indication of the thickness of the polymer layer. We will present working models for the correlation between the final cobalt nanocluster size and the extent of metal-polymer surface interactions.

#### AS-TuP23 Time-Resolved Observations of Failure along Polymer-Glass Interfaces in Humid Environments@footnote 1@, J.T. Dickinson, N.Z. Hertelendy, S.C. Langford, Washington State University

Adhesive interfaces play a critical role in microelectronic packaging, as well as in aerospace, automotive, and civil structures. The accelerated failure of strained adhesive bonds due to moisture is of considerable interest. By studying very small bonded zones (area @<=@ 1 mm@super 2@) one greatly enhances the influence of environmental attack, allowing for accelerated testing. To measure failure kinetics, we compare videotaped micrographic records of failure along ethylene vinyl acetate/soda lime glass interfaces in humid atmospheres with simultaneously acquired measurements of applied force. The interface is viewed through the glass substrate with an optical microscope. With increasing applied stress and relative humidity, the time required to produce an observable defect and the total time to failure decrease in a monotonic fashion. With increasing stress, the size of the crack at the onset of unstable critical crack growth also decreases. Visible crack growth prior to unstable failure is rate limited by the diffusion of water to the crack tip. The time required to produce a visible defect can be accounted for on the basis of chemically assisted failure, where the crack velocity depends directly on the change in surface energy due to water sorption (not transport limited). A quantitative model for the dependence of failure on stress and humidity is presented. @FootnoteText@ @footnote 1@This work is supported by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

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