Monday Morning, October 2, 2000

Material Characterization Room 207 - Session MC-MoM

Depth Profiling

Moderator: F.A. Stevie, Lucent Technologies

8:20am MC-MoM1 Valence Model Based Correction of Ultra Shallow Depth Profiles, *O. Brox*, University of Muenster, Germany; *D. Gehre, E. Zschech*, AMD Saxony Manufacturing GmbH, Germany; *A. Benninghoven*, University of Muenster, Germany

In recent years lateral and in-depth dimensions of microelectronic devices have shrunk by orders of magnitude. The reduction in depth scale was supported by the application of ultra low implantation energies of dopant materials. As a consequence a significant part of the implanted species is located in the uppermost monolayers. The entire thickness of the shallow implants used nowadays of less than 10 nm implanted in oxides with a thickness up to 3 nm complicates the establishment of quantitative SIMS depth profiles. Changing conditions regarding the oxidation state require corrections of the concentration- and depth scale. Distortions can occur also due to the very high peak concentrations (distinctly higher than 1%) resulting from the ultra low implantation energies and from contamination layers as hydrocarbons e.g. For all experiments we used TOF instruments, equipped with flexible gas ion sources and cesium sources (0.6 - 10 keV) for crater formation. Additional gas ion sources (Ar@super +@, 11 keV) have been applied for the analysis of the crater bottom. We have investigated the possibility to compensate the falsification caused by changes of the secondary ion yield in the transient region by applying a suitable correction procedure based on the so-called lattice valency model.@footnote 1@ The success of this correction will be demonstrated by a quantitative depth profile of a 10 keV As-implant into a 3 nm screening oxide. The sputter behavior of undefined organic contaminations as well as of well defined polymer overlayers has been investigated. Sputter yields, damage cross sections, and thermal desorption behaviors will be reported. They allow an estimation of possible depth scale distortions. . @FootnoteText@ @footnote 1@ C. Plog, L. Wiedmann, A. Benninghoven, Surf. Sci. 67 (1977) 565.

8:40am MC-MoM2 Analysis of Ultra-thin Oxynitride Layers by TOF-SIMS, *E. Niehuis, T. Grehl, R. Möllers,* ION-TOF GmbH, Germany; *O. Brox,* University of Münster, Germany

The analysis of very thin oxynitride layers with a thickness below 3 nm becomes increasingly important. Methods are needed to determine the layer thickness, the nitrogen content and the nitrogen distribution in a quantitative manner. The film thickness can be measured with high reproducibility by Ellipsometry, but the SiO@sub 2@/Si interface properties and contamination layers can influence the accuracy. The total N content for very thin films can be quantified using XPS. However, no analytical technique can give the quantitative N distribution with sufficiently high depth resolution and sensitivity. SIMS depth profiling using Cs primary ions in the energy range of 500-1000 eV has been used extensively to study oxynitrides. However, the transient width in this energy range is still above 3 nm. In order to reduce it below the thickness of the film, very low energies of 100-300 eV and/or high impact angles are required. The low sputter yield in this energy regime leads to extremely high Cs surface concentration and to significant sputter rate changes in the transient regime. We have investigated the capabilities of Cs depth profiling at very low energies using TOF-SIMS depth profiling in the dual beam mode. A Cs beam with an energy below 300 eV has been used for the erosion while the center of the sputter crater is analysed with a high energy Ga beam. We have used a new Cs-Xe co-sputtering method to control the Cs surface concentration and keep it in the optimum range for the formation of MCs@super +@ cluster ions. The achievable depth resolution, the sensitivity for nitrogen and the accuracy of the thickness measurement will be discussed in detail.

9:00am MC-MoM3 Ion Beam Studies of Ultrathin Metal Oxide Dielectrics, E. Garfunkel, B. Busch, H. Schulte, T. Gustafsson, Rutgers UniversityINVITED

There is a strong need to find silicon-compatible high dielectric constant (high-K) replacements for silicon dioxide in microelectronics. This presentation describes recent results on the structure, composition, growth and annealing behavior of high-K combinations of Zr, Hf, Y, and La oxide films. Results will be presented from ion scattering, scanning probe microscopy, photoelectron spectroscopy, electron microscopy and several other surface and thin film methods. It is found that only by crosscorrelating several different methods can a definitive analysis of structure and composition (including the depth profile) be given. The interaction of isotopically labeled oxygen with ultrathin oxides at elevated temperatures shows oxygen exchange and diffusion in the films, as well as deleterious silicon dioxide interface growth (that unfortunately accompanies many post-growth anneals). Problems associated with crystallization, interdiffusion, electrical breakdown, and interface structure will also be addressed.

9:40am MC-MoM5 Matching the High Dose Ultra Shallow As Doping Profiles Measured by X-ray Photoelectron Spectroscopy, Magnetic Sector Secondary Ion Mass Spectrometry and Low Energy Quadrupole Secondary Ion Mass Spectrometry, J. Zhao, C.M. Jones, T. Neil, Advanced Micro Devices; D. Zhou, University of Central Florida

SIMS has proven to be a powerful technique for dopant depth profile analysis, however, quantification of dopant concentrations in the outermost several nanometers is still not at all trivial. A major problem arises because SIMS analysis exhibits a surface transient before reaching equilibrium in the sputtering process. Ion yields and sputtering-rate vary significantly during the transient zone and after reaching the equilibrium. The surface transient can be reduced to a few nanometers if a low-energy primary ion beam is used, but a further reduction is hindered by the presence of native oxide of varying thickness on Si wafers. For ultra-shallow As doping profiles using Cs@super +@ primary ions, which increases the negative secondary ion yields, surface oxide significantly depress the As@super ?@ negative ion yield. In the present work, an attempt of using XPS depth profiling to determine the high dose ultra-shallow As dopant profile, with particular interests in the dopant distribution and concentration within the surface transient region, was reported. XPS guantification is free from the ion yield and erosion rate variations of SIMS quantification, and a detection limit of 3e19at/cm@super 3@ for As is demonstrated. XPS results show higher As concentration up to ten times at the sample surface region (<10nm) than that of magnetic sector SIMS result. In addition, the feature of As piled up at the interface of surface oxide and Si substrate was clearly detected in the XPS depth profile, but missed in the magnetic sector SIMS depth profile. After the first 10nm, XPS and magnetic sector SIMS depth profiles match each other, and magnetic sector SIMS demonstrates a superior detection limit down to 5e16at/cm@super 3@. A comparison of the As dopant profiles measured by low energy quadrupole SIMS and magnetic sector SIMS, which was corrected by XPS for the surface transient region, will be further discussed in the paper.

10:00am MC-MoM6 XPS Characterization of NO Oxynitride Films using Chemical Profiling, *I.S. Choi*, *H.J. Kim*, *S.Y. Lee*, Hyundai Electronics Industries Co., Ltd., Korea

For the fabrication of MOS devices, the incorporation of nitrogen into thin SiO2 dielectric films has been shown to improve the electrical and structural property of the films. Some benefits of these oxynitrides are as following: (a) resistance to boron diffusion, (b) immunity to hot carrier effects, (c) higher charge-to-breakdown voltage, and (d) reduced charge trapping. These improvements are owing to accumulation of nitrogen atoms at the dielectric/silicon interface. The depth profile and chemical environment of nitrogen in oxynitride films is a critical information to the process control so that a lot of technique to study this material have long been used.@footnote 1,2,3@ However, Ar ion sputtering usually used to acquire depth profile may affect the actual concentration and the bond characteristic of N. In this X-ray photoelectron spectroscopic study of oxynitride films, we adopted successive delicate etching of the films with dilute HF solution as a technique for profiling. It was believed that this kind of chemical profiling would not affect the actual concentration and chemical environment of the films. The etch step was finely controlled to have etch rate of ~0.5 ¢ ?/sec and the thickness of every slicely etched films were measured by XPS. With the help of this chemical profiling technique, we observed, for the first time, the selectivity of the etch rate between the thermal oxide and oxynitride films. Much difference between the etch rate of two films was used to remove upper oxide layer and study remained pure oxynitride film. Therefore we could directly observe the thickness of NO oxynitride interlayer to be about 6¢®?.@footnote 4@ We also have studied the bond structure, thickness, and composition of the oxynitride layers by deconvoluting Si2p and N1s XPS spectra. The results of the study on the composition and the chemical environment of the oxynitride films will be discussed in this presentation. @FootnoteText@ @footnote 1@ Rama I.Hegde, Philip J. Tobin, Kimberly G. Reid, Bikas Maiti, and Sergio A. Ajuria, Appl. Phys. Lett. 66(21), 2882 (1995) @footnote 2@ E. P. Gusev, H. C. Lu, T. Gustafsson, E. Garfunkel, M. L. Green, and D.Brasen, J.

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Appl. Phys. 82(2), 896 (1997) @footnote 3@ M. R. Frost, C. W. Magee. Appl. Surf. Sci. 104/105, 379 (1996) @footnote 4@ E. A. Irene, Q. Liu, W. M. Paulson, P. J. Tobin, and R. I. Hegde, J. Vac. Sci. Technol., B14, 1697 (1996)

10:20am MC-MoM7 The Effect of Ion Acceleration Voltage on Interface Resolution During Depth Profiling and the Application of Advanced Data Analysis Techniques, *S.J. Hutton*, Kratos Analytical, UK; *N. Fairley*, CASAXPS Ltd, UK; *D. Surman*, Kratos Analytical, UK

The effect of ion acceleration voltage on interface resolution during destructive depth profiling of a challenging multilayer sample was investigated. A compact, high speed, Kaufman ion source combined with Xray photoelectron spectroscopy (XPS) enabled efficient concentration depth profiling through several hundred nanometer thick layers. The Kaufman source exhibits extremely high sputter rates at low ion beam acceleration potentials reducing ion induced mixing of the surface atoms. Atomic concentration profiles through inorganic oxide layers were recorded as a function of ion acceleration voltage. The improvement in interface resolution with decreasing acceleration voltage was clearly demonstrated. Chemical state information was retained with some reduction of the oxide layer observed due to preferential sputtering of oxygen from the surface during profiling. A detailed examination of the O 1s envelopes was also performed using principal component analysis (PCA) and non-linear least-square curve fitting (NLLSCF). It was shown that while four abstract factors characterised the O 1s data only two were of chemical significance with the remaining pair describing trends associated with the measurement process. Sub-sampling the periodic nature of the data matrix allowed underlaying line-shapes to be identified which were used to support the NLLSCF data reduction.

10:40am MC-MoM8 Quantitative Comparison between AES and SIMS Depth Profiles of a Double Layer Structure of AlAs in GaAs Using the MRImodel, *S. Hofmann*, Max-Planck-Institute for Metals Research, Germany; *A. Rar*, University of Alabama; *D.W. Moon*, Korea Research Institute of Standards and Science, Korea; *K. Yoshihara*, National Research Institute for Metals, Japan

Application of the so called mxing-roughness-information depth (MRI)model@footnote 1@ to the quantitative reconstruction of the in-depth distribution of composition, is demonstrated by a comparison of SIMS and AES depth profiles. A GaAs/AlAs reference sample consisting of two layers of AIAs (1 ML and 36 ML) separated by 44 ML of a GaAs matrix was depth profiled using almost identical sputtering conditions: Ar+ ions of 3 keV impact energy and 52 (SIMS: CAMECA 4f) and 58 deg. (AES: VG Microlab 310F) incidence angles. Both the Al+ intensity of the SIMS profile and the Al (LVV) intensity of the AES profile were quantified by fitting the measured profiles with those calculated with the MRI model, resulting in the same mixing length of 3.0 nm ± 0.3 nm, similar roughness parameter (1.4-2 nm), and negligibly small information depth (0.4 nm)for SIMS. Whereas practically no matrix effect was observed for Al+ in the SIMS profile, quantification using dimer ions (Al2+) shows a marked nonlinearity between concentration and intensity.@footnote 2@ @FootnoteText@@footnote 1@S. Hofmann, Surf. Interface Anal. 27,(1999)825. @footnote 2@A. Rar, D.W. Moon and S. Hofmann, J. Surf. Anal. 6,(1999)29.

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Biomaterial Interfaces

Room 202 - Session BI+MC-MoA

Characterization of Biomaterial Interfaces Moderator: L. Hanley, University of Illinois at Chicago

2:00pm BI+MC-MoA1 Surface Tools for the Characterisation of Biomaterials, M.C. Davies, S.J.B. Tendler, C.J. Roberts, P.M. Williams, S. Allen, University of Nottingham, UK INVITED Understanding the interfacial chemistry of biomaterials has long been a goal in the search for optimum biocompatibility. The interfacial

environment has a major control on materials properties and the exploitation of nanosurface engineering, to tailor the optimum surface behaviour and function has made a significant impact in the biotechnological and biomedical sciences over the last decade. This talk will explore the role of advanced surface tools for the characterisation of modern biomaterial materials and review the limitations and advantages of different approaches, highlighting fruitful areas for future activity.

2:40pm BI+MC-MoA3 Electrochemical SPR for Biomaterial Applications, R.M. Georgiadis, Boston University, usa; R.J. Heaton, Boston University

Electrochemical SPR is the combination two powerful surface specific techniques which together provide the basis for many surface modification and detection schemes with new applications to biomaterial interfaces. Although the general effect of an applied electrochemical potential on the surface plasmon resonance response from a simple metal surface is well known, the response from more complex interfaces has not been studied in detail. Yet, such studies are crucial for many applications such as quantifying binding at interfaces in the presence of an applied electrochemical field. We show that very useful information can be obtained directly from the potential dependent SPR optical data: the potential of zero charge can be determined in the presence or absence of anions can also be distinguished. We report results for a series of modified interfaces including self assembled monolayer films and for thiol bound DNA oligomer films in various electrolytes.

3:00pm BI+MC-MoA4 Characterization of Surface Modified Microporous PTFE Biomembranes using Surface Charge, Topography and Chemistry Studies, *I.D. Baikie*, *B. Lägel*, Robert Gordon University, UK

Functionalised microporous PTFE membranes have many applications involving cell growth and adhesion such as skin grafting and cell scaffolds. Key factors in promoting cell growth are the chemistry and topography of the surface, however a much overlooked surface parameter is that of surface charge. Using a multitip scanning kelvin probe (SKP)@footnote 1@ we have performed surface potential/charge topographies of bare and surface modified bio-membranes prior to Human Skin Fibroblast growth. Additionally surface characterization with SEM and XPS provided topography and chemistry information on the top-most layers. Subsequent video-microscopy growth data indicates an extraordinary correlation between a regime of homogeneous negative surface charge profiles and confluent HSF films. Indeed the optimum growth surface displays two dimensional charge transport characteristics. Up to now little work has been performed on the electrical properties of modified polymers due to the difficulties in obtaining accurate surface potential data. The SKP features a truly noninvasive charge imaging measurement mode and we anticipate many future applications both in monitoring biomaterials and biological interfaces. @FootnoteText@ @footnote 1@I. Baikie, P.J.S. Smith, D.M. Porterfield and P.J. Estrup, Rev. Sci. Instrum. 70, 1842 (1999).

3:20pm BI+MC-MoA5 Enhanced TOF-SIMS Imaging of a Micropatterned Protein by Stable Isotope Protein Labeling, *A. Chilkoti*, Duke University; *A. Belu*, Physical Electronics; *Z.P. Yang*, Imation Inc.; *R. Aslami*, Duke University

Patterning of biomolecules on surfaces is an increasingly important technological goal. Because the fabrication of biomolecule arrays often involves step-wise, spatially resolved derivatization of surfaces, spectroscopic imaging of these arrays is important in their fabrication and optimization. Although imaging time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a powerful method for spatially resolved surface analysis of organic molecules on surfaces, TOF-SIMS images of micropatterned proteins on organic substrates can be difficult to acquire because of the lack of high intensity, protein specific molecular ions that are essential for imaging under static conditions. In contrast, low mass ions are of suitable intensity for imaging, but can originate from different chemical species on the surface. A potential solution to this problem is

utilize stable-isotope labeled proteins, an approach that has heretofore not been explored in TOF-SIMS imaging of micropatterned proteins and peptides. In order to investigate the feasibility of stable isotope enhanced TOF-SIMS imaging of proteins, we synthesized @super 15@N-labeled streptavidin by metabolic labeling of the protein during expression from a recombinant gene. The spatial distribution of streptavidin bound to biotin micropatterns, fabricated on a polymer and on a self-assembled monolayer on gold, was imaged by TOF-SIMS. Imaging of high intensity, low m/z secondary ions (e.g., C@super 15@N@super -@ and C@super 15@NO@super -@) unique to streptavidin, enabled unambiguous spatial mapping of the micropatterned protein with a lateral resolution of a few microns. TOF-SIMS imaging of micropatterned @super 15@N-labeled streptavidin also illustrated the exquisite sensitivity of TOF-SIMS to low fractional coverage of protein (0.5 nm effective thickness) in the background regions of the protein micropattern.

3:40pm BI+MC-MoA6 Quantitative Chemical Mapping of Lipid-protein Langmuir-Blodgett Layers by Laser-SNMS, *N. Bourdos, F. Kollmer, R. Kamischke, H.-J. Galla, A. Benninghoven,* Westfälische Wilhelms-Universität, Germany

Quantitative molecular mapping of chemically modified or functionalized surfaces is still an important challenge in surface analysis. We demonstrate that analyzing sputtered neutrals may be a big step forward in the quantitative mapping of laterally structured overlayers of organic molecules or biomolecules, respectively. We studied samples consisting of phospholipids and a small 34-residue peptide, the surfactant protein C (SP-C). These overlayers are phase-separated into a fluid and condensed phase. They were prepared on Au substrates with the Langmuir-Blodgett (LB) technique and investigated using a combined SIMS/SNMS instrument equipped with a reflectron-type TOF analyzer, a 30 keV Ga+ primary ion source, and an excimer laser for resonantly enhanced multiphoton postionization of neutrals. Laser-SNMS was applied for the first time to study LB layers. The SP-C clearly engenders typical amino acid-specific neutral fragments, by which it can be identified and localized on a surface. Most of them result from the cleavage of the COOH group, e. g., CH@sub4@N, C@sub 4@H@sub 8@N or C@sub 5@H@sub 12@N. The small CN is not typical of a certain amino acid but the entire molecule. It is the most intense peptide-based secondary particle and therefore gives excellent maps of SP-C-rich domains formed in the overlayer. It is possible to calculate the protein content in a lipid layer by histogram evaluation. The yields and damage cross-sections calculated from TOF-SIMS measurents indicate that the lateral resolution may be far below instrument limitations (beam focus). A quantitative comparison of the secondary particle emission from SP-C-rich and SP-C-free domains (on the same substrate) allowed some insight into the process of secondary ion and neutral generation from the molecular overlayer as well as from the substrate.

4:00pm BI+MC-MoA7 Probing the Spatial Organization of Mixed Lipopeptide/Phospholipid Monolayers : Complementarity of AFM and XPS, Y.F. Dufrene, Universite Catholique de Louvain, Belgium; M. Deleu, P. Jacques, Faculte Universitaire des Sciences Agronomiques de Gembloux, Belgium; P. Thonart, Centre Wallon de Biologie Industrielle, Belgium; M. Paquot, Faculte Universitaire des Sciences Agronomiques de Gembloux, Belgium

Surfactin is a surface-active bacterial lipopeptide, with important biological properties, which is known to interact with lipid membranes. To gain insight into the spatial organization (miscibility, molecular orientation) of mixed surfactin/dipalmitoyl phosphatidylcholine (DPPC) monolayers, the morphology and chemical composition of mixed monolayers transferred on mica were determined by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. AFM topographic and friction images revealed phase-separation for mixed monolayers prepared at 0.1, 0.25 and 0.5 surfactin molar ratios. The step height measured between the surfactin and the DPPC domains was about 1.2 nm, pointing to a difference in molecular orientation: while DPPC had a vertical orientation, the large peptide ring of surfactin was lying on the mica surface. These data were in excellent agreement with the monolayer properties at the air-water interface and with computer simulation data. The N/C atom concentration ratios obtained by XPS for pure monolayers were consistent with two distinct geometric models: a random layer for surfactin and for DPPC, a layer of vertically-oriented molecules in which the polar headgroups are in contact with mica. XPS data for mixed systems were accounted for by a combination of the two pure monolayers, considering respective surface coverages that were in excellent agreement with those measured by AFM. Finally, exciting new possibilities offered by dynamic AFM imaging modes (force modulation, phase imaging) to

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investigate the film nanomechanical properties will be presented. This work demonstrates the complementarity of AFM imaging and XPS analysis to directly probe the molecular organization of multicomponent monolayers.

4:20pm BI+MC-MoA8 Detection of Intact Biomolecules with Matrix-Enhanced ToF-SIMS, D.G. Castner, P. Kingshott, J. Nesiba, S.L. Golledge, B.D. Ratner, University of Washington

An improved understanding of the interfacial interactions between biomolecules and surfaces is important for the successful design of the next generation of biomaterials. This study combines the high surface sensitivity and chemical specificity of ToF-SIMS with the 'soft' ionization capabilities of MALDI. Model peptides with beta-sheet and alpha-helix structures were used in conjunction with MALDI matrix molecules [2,5dihydroxybenzoic acid (DHB) and sinapinic acid (SA)] to facilitate generation of molecular ions with the SIMS Cs+ ion source. The positive ToF-SIMS spectra from the beta-sheet peptide incorporated into crystals of DHB show peaks representative of sodium-adduct ions of the peptide (M-H+Na+) (m/z 1096.7). The spectrum from the bulk beta-sheet contains only fragment ions and no molecular ions, suggesting that there is a synergistic effect in producing sodium adduct molecular ions when both Na and matrix molecules are present. When sodium is eliminated from the system, peaks that can be assigned to the M+ ion $(m/z \ 1074.7)$ can still be detected. Molecular ions from the alpha-helix peptide were also detected when DHB was present. The use of SA as matrix failed to generate peptide molecular ions, suggesting the matrix-specific nature of this MALDI-SIMS technique. Imaging-SIMS indicated that the peptides are incorporated within the DHB matrix crystals, but are not fully incorporated into the SA crystals. This shows the importance of good mixing between the peptides and matrix molecules for detection of intact molecular ions.

4:40pm BI+MC-MoA9 Molecular Orientation of Annealed Artificial Joint Polymers: Characterization by Soft X-ray Absorption, S. Sambasivan, SUNY Stony Brook; *D.A. Fischer*, National Institute of Standards and Technology; *M. Shen*, University of Maryland; *J.A. Tesk, S. Hsu*, National Institute of Standards and Technology

For the past 30 years ultra-high molecular weight polyethylene (UHMWPE) has remained the dominant polymer in artificial joints due to its outstanding wear resistance properties. It has been recognized that wear of UHMWPE contributes to the loosening of the implants and is the main cause for the failure of long-term implants. Hence, there is an urgent need to understand the mechanism and the surface morphology leading to wear and failure of the artificial joint. Hubbard et al.@footnote 1@ and Hastings et al.@footnote 2@ have demonstrated that the molding and annealing the UHMWPE at safe elevated temperatures resulted in increased mechanical strength. Also, cross-linking of UHMWPE has been demonstrated to reduce wear significantly. We have previously measured molecular orientation as a function of wear motion.@footnote 3@ Molecular orientation in biomaterials is thought to be critical in characterizing the precursors of wear and the production of debris during the wear process. While the link between molecular orientation and wear has not been clearly established, molecular orientation has been recognized as an important parameter in wear resistance. This study examines the change of molecular orientation caused by annealing UHMWPE. Our technique utilizes soft x-ray absorption spectroscopy at a synchrotron beamline to non-destructively characterize the molecular orientation of the UHMWPE surface layer. Current methods of inferring or deducing orientation are not accurate and often rely on staining and cutting specimens.@FootnoteText@ @footnote 1@Hubbard et al., Trans. 25th Soc. For Biomaterials, 325(1999). @footnote 2@Hastings et al., Trans. 25th Soc. For Biomaterials, 328(1999). @footnote 3@Fischer et al., Trans. 25th Soc. For Biomaterials, 351(1999).

5:00pm BI+MC-MoA10 Titanium-Alginic Acid Chemistry of Adhesion Using X-ray Photoelectron Spectroscopy, *R.A. Brizzolara*, David Taylor Research Center, NSWC

The interfacial chemistry between alginic acid and a titanium surface has been examined using x-ray photoelectron spectroscopy (XPS). This study is motivated by the effort to mitigate effects of seawater biofouling on heat transfer surfaces via materials or surface modification strategies. Alginic acid is a predominant adhesive in bacterial biofilms, and titanium is a common material in naval ship cooling and piping systems. XPS has been used to quantify the alginic acid adsorbed to the titanium surface from aqueous solution. The experiments were performed at various solution pH's to examine the effect on alginic acid adsorption of changing the charge state of the ionizable groups on the alginic acid and of the titanium surface. The effects of ions in the solution were investigated by performing the alginic acid adsorption in the presence of calcium chloride. To separate the effects of the carboxyl and hydroxyl moieties present in alginic acid, XPS has also been used to measure caproic acid (carboxyl) and glucose (hydroxyl) adsorption as a function of solution pH. High-resolution XPS spectra have been utilized to separate the various carbon and oxygen chemistries present, and angle-resolved XPS spectra and advancing contact angle measurements were used to elucidate molecular orientation effects. Atomic force microscope (AFM) images were obtained to determine adsorbate morphology and surface coverage. These data will be interpreted in light of potential alginic acid - titanium adsorption mechanisms such as hydrogen bonding and anion exchange. This information regarding the biofilm-surface chemical interaction will be useful in developing fouling resistant surfaces. The NSWC Carderock Division In-House Laboratory Independent Research Program supported this work.

Material Characterization Room 207 - Session MC-TuM

Real World Surface Analysis

Moderator: A. Belu, Physical Electronics

8:20am MC-TuM1 Surface Interaction, Coverage and Performance of Quaternary Amine Treatments on Hair, *B.C. Beard*, Akzo Nobel Chemicals; *D. Tang*, Akzo Nobel Surfactants America; *J. Hare*, Akzo Nobel Chemicals

Surface analysis by Xray Photoelectron Spectroscopy (XPS) has shown specific one to one (ionic) interaction between cationic quaternary alkyl conditioning molecules and the anionic sulfonate groups present on the hair surface. Conditioning cationic quaternary molecules incorporating ester and alcohol functionality (ester quat) demonstrate a lower number of surface quaternary nitrogen per sulfonate group, indicating an altered surface interaction mechanism. Relative conditioner surface coverage for the ester quat is not reduced despite the apparent decrease in ionic interaction at the surface. Molecular dynamics modeling of the conditioner-hair surface interaction indicate higher adsorption energies for ester quaternary amine conditioning molecule. Industry standard tests demonstrate the superior performance of ester quats, in keeping with the increased surface coverage.

8:40am MC-TuM2 Chemical Characterization of Modified Nanotips by TOF-SIMS and Laser-SNMS, *R. Kamischke*, *F. Kollmer*, Physikalisches Institut der Universitaet Muenster, Germany; *R. Stark*, *W. Heckl*, Institut fuer Kristallographie und Mineralogie der Universitaet Muenchen, Germany; *A. Benninghoven*, Physikalisches Institut der Universitaet Muenster, Germany

For many applications of nanotips detailed information on their chemical surface composition with high sensitivity is a key issue. This holds e.g. for their use as chemical sensors, where the tip surface is chemically modified, or for nanoextraction of sample material by direct contact with the tip. TOF-SIMS and Laser-SNMS are the most sensitive techniques for chemical surface mapping with high lateral resolution. The large fraction of sputtered neutrals and their efficient Laser-postionization results in a high Laser-SNMS sensitivity. In this contribution we summarize and compare results of TOF-SIMS and Laser-SNMS characterization of chemically modified as well as metal loaded Si@sub 3@N@sub 4@ and Si AFM cantilever tips. All experiments were carried out in a reflectron based time of flight instrument with a fine focused Ga@super +@-LMIS (@>=@80 nm). For nonresonant postionization an excimer laser (248 and 193 nm) was applied. Special efforts had to be put on the sample preparation. Distortion of the extraction field, shadowing effects, charging, and presputtering during sample adjustment had to be reduced to a minimum. On surface modified cantilevers it is not possible to characterize the tip itself, because of the lateral resolution being limited to at best 80 nm. However, imaging the tip pyramid provides detailed information on the surface composition, and in this way on the results of surface modification efforts. For Nanoextraction of metals (Co, Cu, Ag) the sample is imaged by AFM and material is extracted by applying a loading force of several µN and scanning over the surface for some μm . The extracted amount of material adhering to the top of the tip can be characterized down to the sub-amol range. Most important advantages of Laser-SNMS compared to SIMS are enhanced ion yields for elements (@<=@10@super -2@), the ease of quantification and the fact that sputtered neutrals are not affected by electrostatic fields in the vicinity of the sample.

9:00am MC-TuM3 Real World Surface Analysis, B. Hagenhoff, TASCON GmbH, Germany INVITED

Most surface analytical techniques like photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) have left their academic origins and are routinely applied in university and industry laboratories. Whereas in former times most analyses were performed at model systems having only one or few known compounds, nowadays surface analytical techniques are used to solve daily occurring problems in industrial environments. Materials to be analyzed in these cases mostly contain several components and the respective samples may have undergone additional surface treatments. The talk will concentrate on the special requirements to be dealt with when working on practical problem solving. Issues covered will include sample preparation, selection of the suited analytical technique, set-up of the equipment and data evaluation. Case studies taken from semiconductor and glass industry will be used to explain

how both, XPS and TOF-SIMS, can successfully be used to solve "real world" problems.

9:40am MC-TuM5 Thermal Degradation of IM7/BMI5260 Composite Materials: Characterization by X-ray Photoelectron Spectroscopy, S. Ohno, M.-H. Lee, K.Y. Lin, F.S. Ohuchi, University of Washington

High performance polymeric composites (IM7/BMI5260) are being considered for use in structures for high speed aerospace vehicles. In this application, composite components are exposed to elevated temperatures for a long time period. This results in physical and chemical degradation of the polymers. In this paper, experimental studies were conducted to investigate the effects of isothermal aging of the IM7/BMI5260 exposed at 150 - 200°C using x-ray photoelectron spectroscopy (XPS). During the XPS measurements, binding energies for the carbon-fibers are uniquely determined because of their electrically conducting nature, whereas binding energies for the polymeric matrix are shifted by the amount of bias voltage applied to an electron flood gun. This effect turns out to be useful to separate out the contribution from carbon fibers and polymeric matrix, thus we have established a unique experimental protocol to analyze the composite material surfaces. Experimentally, the composite specimens were oxidized in an environmental cell specially designed to mimic the aging conditions, and analyzed to learn intrinsic nature of the chemical reactions. These data were further compared with those obtained from long-aged specimen (7 months at 205 °C in air). Our results indicate that degradation of the IM7/BMI5260 is initiated by preferential oxidation of the carbon sites in the BMI to form the carbonyl species, followed by the oxidation to CO@sub2@ leading to degradation.

10:00am MC-TuM6 Pt-Metal Oxide Aerogel Catalysts: An X-ray Photoemission Investigation, A.J. Nelson, J.G. Reynolds, Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy was used to study Pt-metal oxide aerogel catalysts that have been developed to respond to increased NO@sub x@ emissions of lean-burn engines. Lean-burn engines, critical components of low and zero emission vehicles, produce much higher levels of engine-out NO@sub x@ and current three-way catalytic converters are not sufficient to meet Clean Air Act standards. Platinum catalysts were formed by the reaction of modified Pt coordination compounds with selected transition-metal alkoxides through sol-gel techniques into aerogels. Photoemission measurements on the valence band electronic structure and Pt 4f, Si 2p, Ti 2p and O 1s core lines were used to evaluate the chemistry of the material after each processing step. Results indicate Pt-O bonding and reduced Pt disbursed in the aerogel. In addition, Si 2p, Ti 2p and O 1s binding energies indicate an oxo-bridged network structure.

10:20am MC-TuM7 Quantification of the Changes in the Air-formed Oxide/Hydroxide Film at the Surface of Aluminium on Exposure to Ambient Conditions, *M.R. Alexander*, *G.E. Thompson*, UMIST, UK; *G. Beamson*, RUSTI, CLRC, UK; *A.J. Roberts*, Kratos Analytical, UK

The performance of coated and bonded Al is dependent on its surface chemistry. XPS is a powerful tool for characterising of the surface airformed film. It is apparent that agreement exists in the literature on the method to calculate the oxide thickness from the clearly resolved metal and oxide components of the XPS Al2p core level.@footnote 1@ However, there is no consensus on the approach for fitting the unresolved oxide and hydroxide components of the O1s, indeed some suggest that it is not advisable.@footnote 2@ Recently, a method based on defining the separation between the O1s and Al2p components has been developed using an oxyhydroxide standard.@footnote 3@ Here, the film formed at the surface of magnetron sputtered Al is characterised. Importantly, this sample allows reliable definition of the age of the surface film and control of the alloying elements. Curve fitting of the O1s and Al2p core levels from samples after a range of atmospheric exposure times revealed the gradual formation of hydroxide ions in the surface film, an increase in its thickness and the adsorption of adventitious hydrocarbon. Interestingly, it was determined that atmospheric moisture influences strongly the hydroxyl concentration and the rate of film growth. Changes in the wetting of the surface were measured through the water contact angle, which increased from about 10° to 80° over a 24-h period. This was assigned to the formation of a continuous overlayer of hydrophobic adventitious hydrocarbon onto the hydrophilic oxide/hydroxide surface film. Characterisation of this "ageing" of the Al surface forms the basis for an investigation into the effectiveness of plasma cleaning and the atmospheric stability the resultant surface. @FootnoteText@ @footnote 1@ B Strohmeier Surf. Interface Anal. 15 51 (1990). @footnote 2@ PMA

Sherwood Surf. Sci. Spect. 5 (1) 1 (1998). @footnote 3@ MR Alexander, GE Thompson and G Beamson, Surf. Interface Anal., 29 (7) in press (2000).

10:40am MC-TuM8 Scanning Auger Microscopy Studies of an Ancient Bronze, *E. Paparazzo*, Consiglio Nazionale delle Ricerche, Italy; *A.S. Lea*, *D.R. Baer*, Pacific Northwest National Laboratory; *J.P. Northover*, University of Oxford, UK

We have conducted a scanning Auger microscopy (SAM) analysis on a Syrian bronze of the early I millennium BC. The objective was to derive a picture of modifications of the object's surface composition, induced by chemical attack by the ambient. Understanding degradation of ancient materials dating from a well-defined historical context provides information about long-term corrosion phenomena that is not possible from laboratory data. Such information is also useful for restoration and conservation efforts. While corrosion processes in the bulk are understood, this is not true for localized intergranular and transgranular surface corrosion in these materials. This requires information about local chemical composition and movement of ionic species that has not generally been available, and we find AES useful in accomplishing this task. SAM images of Cu, Sn and O, ~ 100-nm spatial resolution, and Auger point spectra show that Sn acts as a barrier against O@sub 2@ attack, as it entirely traps this gas into a SnO@sub 2@-like oxide, thus minimizing copper oxidation. Submicron spectromicroscopic evidence is given that S-induced corrosion occurs mainly via chemical attack along grain boundaries, where Sn has a low abundance and copper sulfides are detected. Lateral segregation of Sn and Cu domains is imaged with a spatial resolution of 15 nm. This result marks the best spatial resolution any analytical method has yet achieved in highlighting lateral chemical heterogeneities of ancient bronzes. Although archaeomaterials lie outside the mainstream applications of Auger techniques, this study provides convincing evidence that SAM can greatly advance our understanding of these materials.

11:00am MC-TuM9 Practical Applications of Surface Analysis Techniques in Electroplating, C. Xu, J.A. Abys, Lucent Technologies

Electroplating has been widely used to deposit thin metal films on various substrates either to achieve certain functionality (wear resistance, solderability, wire bondability, corrosion resistance) or specific appearance. The materials properties are critical to the functionality and are dependent on the electroplating process. These properties are determined by the elemental, and chemical composition, and deposit structure. Surface analysis techniques are unique in their ability to provide specific diagnostic tools to study electrodeposited films. In this paper, the potential of various surface analysis techniques for investigating failure modes and new products development in electroplating industries will be discussed and demonstrated using various case studies. A comparison of techniques such as AES and XPS to traditional failure mode analysis methods such as Scanning Electron Microscopy (SEM) will be made.

11:20am MC-TuM10 Surface Chemistry and Physical Properties Related to Adhesion of Various Soldermask Materials, *C.A. Bradbury*, *Y. Du*, *T. Jiang*, Micron Technology Inc.

In Flip Chip (FC) Ball Grid Array (BGA) packages, adhesion between soldermask material to mold compound, underfill and liquid encapsulant materials are critical to package reliability. Delamination will result in package crack and solder joint failure. In this study, the adhesion of several different types of soldermask materials to an underfill polymeric material was evaluated. The surface chemical properties of the soldermask materials were characterized using x-ray photoelectron spectroscopy (XPS) and surface tension test. The surface chemistry was correlated to the interfacial fracture toughness obtained by Mixed Mode Bending (MMB) test.

Surface Science Room 210 - Session SS3+MC-TuM

Technique Innovations: Experiment, Theory and Simulation

Moderator: S.B. Sinnott, The University of Kentucky

8:20am SS3+MC-TuM1 Twenty-First Century Modeling: Multiscale Coupling and its Impact on Surface and Interface Science, E.A. Carter, University of California, Los Angeles INVITED

Multiscale modeling is all the rage among computational material scientists in this new century. This refers to a type of simulation which considers phenomena whose length and/or time scales span several - possibly many -

orders of magnitude. Examples of such phenomena include, e.g., time scale disparities in surface diffusion and thin film growth, length scale disparities in corrosion-induced cracking of solid materials, etc. In the first example, surface diffusion is "fast" while the flux of material is "slow". In the second example, corrosion involves chemical reactions on the atomic scale while cracking takes place on the meso-to-macroscale. Future materials modeling will account for the complexities across scales. An overview will be given of new techniques being developed that: (i) provide a first principles quantum mechanical description of thousands of atoms (via a linear scaling kinetic energy density functional - KEDF - theory); (ii) couple atomic level interactions, described by KEDF molecular dynamics simulations, to guasicontinuum simulationsof behavior on the micron scale; and (iii) connect first principles quantum mechanics calculations to cohesive zone continuum mechanics simulations of crack propagation in solids. The impact of such coupled simulations on understanding how surface and interface phenomena affect materials behavior on scales beyond the atomic will be emphasized.

9:00am SS3+MC-TuM3 The KMLYP Density Functional Approximation: A New Method for Accurate Prediction of Activation Barriers and Enthalpies of Reaction, J.K. Kang, C.B. Musgrave, Stanford University

We develop the KMLYP hybrid DFT method which is shown to predict activation energies and enthalpies of reaction with smaller errors than B3LYP, G2, QCISD(T), CCSD(T), and CBS-APNO. The accuracy of the method is demonstrated on over 100 reactions. The KMLY P exchange functional is a hybrid functional that combines Hartree-Fock exact exchange with Slater exchange. The correlation functional is a hybrid functional combining Lee-Yang-Parr (LYP) correlation and Vosko-Wilk-Nusair (VWN) correlation. For reactions with reliable experimental data, the RMS deviation of the activation energies are 0.64 kcal/mol, 1.59 kcal/mol, 3.20 kcal/mol, and 3.10 kcal/mol for the KMLYP, CBS-APNO, G2, and B3LYP methods, respectively. The RMS deviations from experiment of the entha lpy of reaction are 1.57 kcal/mol, 2.24 kcal/mol, and 2.87 kcal/mol for the KMLYP, G2 and B3LYP methods, respectively. The KMLYP maximum absolute deviation of the activation barriers is 1.2 kcal/mol while the KMLYP maximum absolute deviation of the enthalpy of reactions is 3.8 kcal/mol. Furthermore, KMLYP is significantly more efficient than the G2, QCISD(T), CCSD(T), and CBS-APNO methods and is practical for the simulation of surface reactions using relatively large clusters.

9:20am SS3+MC-TuM4 Probing Chemical Interactions at the Single Bond Level, *M.K. Weldon*, Bell Laboratories, Lucent Technologies; *J.D. Batteas*, City University of New York, College of Staten Island; *K. Raghavachari*, Bell Laboratories, Lucent Technologies

The measurement of chemical bond strengths is a fundamental goal of much of chemistry; indeed the making and breaking of bonds between atoms is the essence of chemical science. Despite this, the direct measurement of bond strengths has remained an elusive goal due primarily to the inherent difficulty in localizing the requisite excitation along a single bond coordinate. Here we demonstrate a methodology for measuring the strength of individual chemical bonds at solid surfaces. We have used atomic force microscopy (AFM) to probe the pH-dependent changes in the surface chemistry of silica in the single bond limit. We observe quantized adhesion forces that, when referenced to the results of ab initio quantum chemical cluster calculations, can be unambiguously assigned to single neutral hydrogen bonds (OH..OH), single ionic hydrogen bonds (OH@super -@..OH) and single covalent bonds (Si-O-Si) between the tip and surface. We have subsequently extended this work to measure the interaction (bond) energetics in a number of aqueous and organic solvent systems. Remarkably, we find that we able to observe individual H@sub 2@O..H@sub 2@O hydrogen bonds under the appropriate conditions, as well as the attendant isotopic shift and bond weakening upon raising the temperature, again demonstrating the potential of this approach for exploring the nature of chemical bonds in solution. In summary, this breakthrough in chemical analysis is predicted to be generalizable to all solution reactions for which the constituent reagents can be chemically functionalized onto a solid surface. To this end, we are currently investigating the interaction energetics in a variety of reactive organic systems.

9:40am SS3+MC-TuM5 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation, Experiments and Calculations, *P. Uvdal*, *M.P. Andersson, R. Asmundsson*, Lund University, Sweden; *A.D. MacKerell, Jr.*, University of Maryland

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment

conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The latter may reveal surface induced changes of activation barriers of importance for the understanding of e.g. heterogeneous catalysis. The former reveal dynamical properties of the system as the extent of coupling governs the dissipation and randomization, within the molecule, of the energy initially localized in a single bond excitation. Using methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces as model systems we will demonstrate binary intramolecular modes in the presence and absence of Fermi resonance coupling. We will also show a combination mode consisting of the C-O stretch and the hindered motion of methoxy with respect to the surface.

10:00am SS3+MC-TuM6 Time Resolved Fourier Transform Infrared Spectroscopy, *M. Kovar, P.R. Norton,* University of Western Ontario, Canada

We have developed a data acquisition system based on digital signal processing for a broadband time-resolved Fourier Transform Infrared Spectrometer. In FTIRS, broadband infrared radiation is modulated by means of a Michelson interferometer. The position of the moving mirror is tracked by the fringe pattern of a reference He/Ne laser, whose beam follows the same optical path as the infrared radiation. Pulses used for time resolution as fast as 500 ns are modulated on a reference He/Ne laser signal. We have chosen a slower mirror speed which permits observation of an external perturbation of a system under investigation which often limits the mirror speed. Different external perturbations can be used, such as thermal, mechanical, photochemical or those caused by external potential. We discuss characteristics of time resolved FTIRS and its performance. The system will permit grazing incidence IR reflection-absorption measurements of surface and thin film processes with sub-microsecond time resolution.

10:20am SS3+MC-TuM7 Momentum Space Line Narrowing by Angle Resolved Auger-photoelectron Coincidence Spectroscopy, A. Danese, R.A. Bartynski, Rutgers University; R. Gotter, Lab. Nazionale TASC-INFM, Trieste, Italy; S. Iacobucci, CNR-IMAI Montelibretti, Italy; G. Stefani, U. di Roma III, Italy

We have measured the Ag N@sub 23@VV Auger electron diffraction pattern from the Ag(100) surface in coincidence with Ag 4p photoelectrons under high energy and angular resolution conditions. Measurements were performed using the ALOISA beamline at the ELETTRA synchrotron in Trieste. It is well known that the Auger and photoemission spectra associated with the shallow 4p (3p) core levels of the late 4d (3d) transition metals are unusually broad in energy owing to the rapid decay of the core hole. Furthermore, it has been shown for the Cu 3p and Ag 4p levels that this energy broadening can be eliminated in Auger-photoelectron coincidence (APEC) energy distribution curves. However, this lifetime broadening is expected to generate a concomitant momentum broadening and the resultant Auger diffraction pattern has only a very weak intensity modulation of ~15%. By performing an APEC measurement with high energy and angular resolution, this momentum broadening should be eliminated. In our APEC angular distribution curves, intensity modulations are enhanced to ~50%, consistent with a significant reduction of the momentum uncertainty of the outgoing Auger electrons. These results provide direct evidence that the photoexcitation/Auger decay of these levels is a coherent process. The implications of these results in the context of Auger electron diffraction will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF grant NSF-DMR9801681 and NATO grant CRG97-0175.

10:40am SS3+MC-TuM8 A Microarray Technique for Measuring Adsorption/Desorption Kinetics, *M.C. Wheeler, R.E. Cavicchi, G.E. Poirier, S. Semancik,* National Institute of Standards and Technology

We have developed a novel method for characterizing the kinetics and thermodynamics of adsorption and desorption that uses a 340-element array of micromachined Si hotplates as the sample platform. The method takes advantage of the microhotplates' rapid heating characteristics (10@super 6@ °C/s), intermediate between traditional temperature programmed desorption methods and pulsed laser desorption. The method is isobaric, particularly useful for studying many systems where the

desorption rate is significant at room temperature, and readily automated to efficiently produce large data sets for adsorption systems. Under constant gas exposure, all of the array elements are simultaneously subjected to square temperature pulses as short as 5 ms. An example sequence is a high-T cleaning pulse (as high as 800 °C), a low-T adsorption pulse, an intermediate-T desorption pulse, and a final high-T cleaning pulse. Variation of the pulse amplitude and duration allows determination of the adsorption and desorption rate constants and energies. Signal-to-noise is enhanced by using a large array of microhotplate devices and averaging of repeated pulse sequences. The pressure range is extended to over 10@super -5@ Torr using a differentially pumped mass spectrometer system (even higher effective pressures can be achieved with a directed doser). We illustrate the technique by mapping adsorption isotherms and extracting parameters for methanol on CVD-deposited SnO@sub 2@ polycrystalline films, such as are used in gas sensing; however, wide ranges of materials and adsorbates can be investigated with this technique. In addition to emphasizing the convenience, flexibility, simplicity, and efficiency of this automated technique, we will also discuss challenges that we have had to address - the most significant relating to temperature calibration and uniformity.

11:00am SS3+MC-TuM9 Scanning Probe Energy Loss Spectroscopy: Spectroscopic Analysis of Reflected Electrons in Field Emission STM, B.J. *Eves*, University of Birmingham, UK; *F. Festy, K. Svensson*, University of Birmingham, UK, U.K.; *R.E. Palmer*, University of Birmingham, UK

Spectroscopic (i.e. chemical) analysis is a key frontier in scanning probe microscopy. We have employed a scanning tunnelling microscope (STM) operating in field emission mode to act as a nanometre scale electron source while the resulting backscattered electrons have been detected with a hemispherical energy analyser. Angular measurements show that the flux of reflected electrons peaks parallel to the surface, consistent with simulations which include the long range field generated by the tip bias voltage. The measured energy loss spectra contain information on the surface and bulk plasmons, and other surface excitations. The Si (111)-7x7 surface was found to show losses at 5, 7.5, 11, 15, and 18 eV. These inelastic losses correspond to an interband transition (5 eV), two surface states (7.5 and 15 eV), and the surface and bulk plasmons (11 and 18 eV, respectively). Spectra have also been measured for a number of different exit angles. With improvements it is believed that the scanning probe energy loss spectrometer (SPELS) can be built to perform electron energy loss spectroscopy with spatial resolution on the scale of 5-50 nm.

11:20am SS3+MC-TuM10 Application of a Direct Method in Surface X-ray Crystallography, *P.F. Lyman*, *R. Harder*, *D.K. Saldin*, University of Wisconsin, Milwaukee; *C.-Y. Kim*, *K.W. Evans-Lutterodt*, Lucent Technologies

The electron density of the near-surface region of a crystal could be recovered from x-ray scattering data if the phases of the scattered radiation were known. In the case of surface scattering, the diffracted intensities arise from the square of a linear combination of bulk and surface amplitudes. Since the phases and amplitudes of the bulk component can be calculated accurately, it is possible to use the bulk scattering as a reference wave, and to thereby estimate the phases of the surface component, in analogy with holography. We have developed an algorithm to estimate the most likely set of surface phases, and to thereby recover the electron density of the near-surface region. We present preliminary applications of this method to (2x1)-reconstructed Ge(001) surfaces. It has been shown that the (001) face of Ge or Si can be passivated by 1 ML of a group V element. Although there is general acceptance of the existence of symmetric group V dimers for most adsorbate/substrate combinations, a controversial result of asymmetric Sb dimers for the Sb/Ge(001) system was concluded from an x-ray scattering study: Each Sb dimer was found to have shifted along the axis of the Sb-Sb bond.@footnote 1@ However, a number of first-principles calculations have found no evidence for the shift. We will use our direct reconstruction algorithm on experimental x-ray scattering data to address the possibility of shifted dimers in a model-independent way. @FootnoteText@ @footnote 1@ M. Lohmeier, H.A. van der Vegt, R.G. van Silfhout, E. Vlieg, J.M.C. Thornton, J.E. Macdonald and P.M.L.O. Scholte, Surf. Sci. V. 275, p.190 (1992).

11:40am SS3+MC-TuM11 Line of Sight Techniques: Providing an Inventory of all Species Arriving at and Departing from a Surface, *R.G. Jones*, University of Nottingham, UK, U.K.; *A.S.Y. Chan, M.P. Skegg*, University of Nottingham, UK

Line of sight techniques comprise those methods in which species emanating from a surface (atoms, molecules and radicals) undergo just a single pass through the ionisation volume of a mass spectrometer before being pumped. This is achieved by enclosing the mass spectrometer within a cryoshield fitted with appropriate apertures, such that line of sight is established only between a patch on the sample surface (ca 7 mm diameter) and the ionisation volume. All LOS techniques are inherently angle resolved, free from extraneous signals and have approximately equal detection probabilities for all species. Line of sight temperature programmed desorption (LOSTPD)@footnote1@ is a particularly reliable way of obtaining TPD data. By applying an over pressure of gas to the sample and monitoring the reflected flux, we get line of sight sticking probability (LOSSP) measurements@footnote 2@ giving S to an accuracy of 0.02; while monitoring of the reaction products at constant temperature gives line of sight product desorption (LOSPD) data. These techniques provide new, powerful and reliable ways of studying all aspects of surface kinetics, by allowing an inventory of all species arriving at and departing from a surface, for any combination of partial pressures, surface temperature, surface composition and surface structure. In this paper we illustrate these methods using the reactions of 1-bromo-2-chloroethane (BCE) and ioodotrifluoromethane with Cu(111). For BCE we show that it undergoes non-activated dissociative adsorption with a transition state 13 kJ/mol below zero (0 = molecule at infinity). For CF@sub3@I we observe emission of CF@sub3@ radicals and coupling reactions forming, among others, C@sub2@F@sub4@. @FootnoteText@ @footnote 1@ R.G. Jones and S. Turton, Surface Sci. 377-379 (1997) 719. @footnote 2@ R.G. Jones and C. J. Fisher, Surface Sci. 424 (1999) 127.

Material Characterization Room 207 - Session MC-TuA

Quantitative Surface Analysis

Moderator: S. Hofmann, Max-Planck-Institute for Metals Research

2:00pm MC-TuA1 Molecular Secondary Particle Emission from UHV-Prepared Molecular Overlayers, A. Schnieders, M. Schröder, K. Rüschenschmidt, A. Benninghoven, H.F. Arlinghaus, Physikalisches Institut der Universität Münster, Germany

Secondary particle yields in organic SIMS and SNMS are not determined by the surface concentration of the respective particles only. Furthermore, the chemical interaction between substrate and adsorbed molecules determines the secondary particle emission, in particular from the first molecular monolayer. Especially the intrinsic ionization but also the fragmentation of the sputtered particles is influenced by this so-called matrix effect. Additionally, secondary particle emission depends on primary ion properties such as species or energy. In continuation of recent investigations, mainly focussing on the sputter process, we used UHVprepared molecular overlayers of adenine and alanine prepared on liquidnitrogen cooled substrates. We extended our investigations to a broader range of substrate/molecule combinations to determine the influence of the matrix effect. The flux of sputtered secondary neutrals and secondary ions in dependence on the layer thickness was continuously monitored under static sputtering conditions during overlayer formation. The detection of the sputtered neutrals was achieved by efficient laser postionization. As substrates we chose Au, Ag, Cu, Ni, Si, Al and C surfaces to cover different types of surface chemistry. A comparison between secondary ion and secondary neutral emissions showed a distinct ionization matrix effect depending on the respective substrate material for @beta@-alanine but not for adenine.

2:20pm MC-TuA2 Detection of Trace Metal Contamination on Si Wafers by TOF-SIMS, R. Möllers, T. Grehl, E. Niehuis, ION-TOF GmbH, Germany

According to the ITRS roadmap, the detection of metal trace impurities on wafer surfaces is becoming increasingly important. Analytical techniques with detection limits for transition metals and alkali metals well below 5E8 atoms/cm@super 2@ are required in the coming years. At present, TXRF is widely used for the detection of transition metals on blank wafers but it seems that its detection limits will no longer be sufficient in the future. The VPD based methods collect the contamination from the oxide of the entire wafer and techniques like VPD-AAS and VPD-ICMS can achieve detection limits in the low E8 range. However, they can not give information on the lateral distribution and do not discriminate against particle contamination. Time-of-Flight SIMS is an attractive candidate for the detection of trace metals. The analysed area is only about 50 to 100 μ m in size and the analysis for all elements in parallel takes only a few minutes per position on a wafer. Detection limits in the low E8 range can be achieved for a number of important metals. In combination with a stage raster, mapping of contaminants on large areas is possible. In contrast to the established techniques, TOF-SIMS can be applied to patterned wafers and the wafer back-side as well. On the other hand, the quantification in TOF-SIMS surface analysis has been a concern due to the well known matrix effect of SIMS and the rather small sampling depth of only 1-2 monolayers. In this contribution, we will discuss the capabilities of TOF-SIMS for trace metal analysis in more detail. We will focus on analytical protocols that give quantitative results and minimise the influence of the initial chemical state of the surface (organic contamination level, oxidation state etc.). The results will be compared to the established analytical techniques.

2:40pm MC-TuA3 Comparative Ion Yields by Secondary Ion Mass Spectrometry from Microelectronic Films, *C. Parks*, IBM Corporation

Secondary Ion Mass Spectrometry (SIMS) is reported from multipleelement ion implants. The implants include a thirteen element metal set dubbed the Universal Metal Standard (UMS) and a six element gas set called the Universal Gas Standard (UGS). These implants were made into films of interest for microelectronics (silicon, silicides, wiring layers, liner metals, organic dielectrics, and polymer dielectrics.) Because species are co-implanted, the relative sensitivity factor (RSF) for many elements are generated with each SIMS profile. Because the implant sets are selfconsistent, ion yields can be readily compared from matrix to matrix. The literature has compared ion yields within single matrices using the RSF. This study performs a broader comparison across matrices and requires a more general metric. In SIMS, the useful ion yields of potassium positive ions and chlorine negative ions approach a yield-saturating limit. To compare matrices, we obtain normalized useful yields (NUY), where the normalization is to the potassium or chlorine yields from silicon. In this paper we document the ion implants sets themselves, we show some of the SIMS profiles, and we note trends in ion yields and implications for SIMS analysis.

3:00pm MC-TuA4 Quantitative Surface Analysis Using Ion Implantation, F.A. Stevie, J.M. McKinley, C.N. Granger, Lucent Technologies; F. Hillion, CAMECA Instruments; D.S. Simons, P. Chi, National Institute of Standards and Technology; B. Schueler, Physical Electronics; C.B. Vartuli, T.L. Shofner, Lucent Technologies; L.A. Giannuzzi, University of Central Florida INVITED This paper summarizes current uses of ion implantation to quantify analytical data. SIMS is emphasized, but the methods are applicable to other techniques. SIMS requires secondary standards for calibration. Ion implantation has been traditionally used to create SIMS standards because any element can be implanted and the dose and energy tailored for the application. High reproducibility has been demonstated for SIMS measurements using these standards. Absolute dose measurements can be made for boron and arsenic using NIST reference materials. Quantification at a surface can be achieved using implantation through a removable layer by selecting the implant energy so that the peak of the implant is at the interface between the removable layer and the substrate. This mehod has been successful for surface SIMS, time-of-flight SIMS, and TXRF measurements. The dose can be increased to provide detection and quantification by other analytical methods, such as AES, XPS, and EDS. High dose quantification can also be used to quantify SIMS in the concentation range of a few percent. This is especially of interest for semiconductor materials, such as PSG, BPSG, and FSG, that are difficult to profile by other methods. SIMS line scan measurements can be quantified by first scanning over a series of depth profiles made at increasing depth into an ion implanted reference. Focused ion beam (FIB) workstations can be used to prepare cross sections of ion implanted standards that can be lifted out and mounted perpendicular to the analysis beam. Secondary ion images of the cross sections provide quantification of the element of interest. FIB prepared cross sections of high dose implanted standards can be used for AES and EDS calibration asnd for determination of detection limit.

3:40pm MC-TuA6 Comparison of ISS, XPS, and QUASES-XPS Techniques for Determination of Growth Mechanisms: Application to Thin Iron Oxide Films Deposited on SiO2, F. Yubero, A.R. Gonzalez-Elipe, Inst. for Material Science of Sevilla; S. Tougaard, University of Southern Denmark, Denmark We have studied the formation of iron oxides on SiO2 under varying growth conditions by X-ray photoemission spectroscopy (XPS) and ion scattering spectroscopy (ISS). Three different procedures for quantitative analysis of the experimental data were used: 1) traditional analysis of the XPS-peak intensity by assuming a layer formation that covers the surface completely, 2) combination of the XPS-peak and ISS intensities assuming a Poisson distribution of island heights, and 3) Tougaard-method (QUASES@footnote 1@) to determine in-depth profiles from analysis of the peak and background. The difference between the three methods lies mainly in the a priori assumptions made on the surface morphology. In contrast to method 1) and 2), the Tougaard-method is free from assumptions about the growth structure of the overlayer. By a critical comparison of the results, it is concluded that the Tougaard-method gives the most complete and reliable information. It is found that iron oxides on SiO2 grow with strong island formation, whose height depends on the preparation conditions of the deposit. The growth mechanisms are proposed. Thus, for example, if iron oxide is deposited on SiO2 at room temperature in a PO2 of 2Â'10-6 mbar, islands of ~22@Ao@ homogeneous thickness are formed for surface coverages below 20%. If the samples are annealed at 773K in a PO2 ~4Â'10-5, higher islands are formed (~32 @Ao@). For iron oxide treated by a plasma of oxygen, ~40 @Ao@ tall islands are formed for surface coverages below 30%. Besides, even ~35 @Ao@ of iron oxide does not fully cover the SiO2 substrate surface. Strong shadowing effects are observed in the ISS signal from the iron oxide deposits on SiO2 due to the tall island formation. As expected, the shadowing effects are stronger when taller islands have been formed. @FootnoteText@ @footnote 1@ http://www.quases.com

4:00pm MC-TuA7 Quantitative Depth Profiling with Angle Resolved XPS: The Effect of Surface Roughness, S.M. Hunt, Montana State University; B.J. Tyler, University of Utah

A major limitation of conventional XPS is that sample concentrations are calculated based on the assumption that the elemental concentrations are homogeneous in the outer 100 angstroms, an assumption that is frequently

inaccurate. By exploiting the angular dependence of the XPS sampling depth, it is easy to get a qualitative assessment of surface uniformity, however, quantitative use of the data can be problematic. The objective of this work has been to explore the limits to which ARXPS data can be used for quantitative analysis of depth profiles and in particular to explore the influence of surface roughness on quantitation. Because calculating concentration depth profiles for ARXPS data is a mathematically unstable problem, modeling studies are necessary to determine how various sources of error propagate through the calculations. Assessing the influence of different types of error is of importance because even relatively small errors in the data might propagate into large errors in the calculated profiles. The influences of random error and surface roughness have been investigated. Monte Carlo simulations were used to explore the effects of random error. To explore the influence of roughness, simulations were used to calculate the XPS signal intensities from surfaces described by a 2 dimensional wave function. Various amplitude to wavelength ratios were explored. The influence on both the measure signal intensities and the calculated depth profiles has been investigated. The results have been validated on a series of samples consisting of self-assembled monolayers. Except at glancing angles, surface roughness has a minimal effect. At angles greater than 70 degrees from the surface normal, even minimal surface roughness can result in changes in the measured signal intensity of greater than 1000%. Optimum parameters for ARXPS experiments and the calculations have been identified.

4:20pm MC-TuA8 Intercomparison of IMFPs Determined by Elastic Peak Electron Spectroscopy, S. Tougaard, University of Southern Denmark, Denmark; M. Krawczyk, A. Jablonski, Polish Academy of Sciences; J. Pavluch, Dept. Electronics and Vacuum Physics, Czech Rep.; J. Toth, D. Varga, G. Gergerly, M. Menyhard, A. Sulyok, Hungarian Academy of Sciences

We have evaluated the consistency and accuracy of IMFPs determined from comparison of the intensity of elastically reflected electrons with theoretical calculations. The scatter in determined IMFPs with experimental geometry, spectrometer energy resolution and the procedure for background subtraction was determined. Four spectrometers with widely different geometries and energy resolutions, placed in four different laboratories in three countries were used. Four background subtraction methods (Shirley, linear, Tougaard, and ELPSEP) were applied to isolate the elastic peak intensity from the reflected electron spectra. The RMS deviation of the IMFP from a function fitted to the data is 3.01 - 4.11 A depending on the background subtraction method and it is smallest for the Tougaard method. The RMS deviation from IMFP values calculated by Tanuma et al is 3.41 - 4.41 A again with the smallest value for the Tougaard method. The mean percentage deviation from the Tanuma et al values is ~ 18 %. The results point to the conclusion that the major contribution to the inaccuracies in IMFPs determined with the elastic peak method is not the background subtraction procedure but rather lack of accuracy of the presently available models for elastic electron scattering, i.e. atomic elastic scattering cross sections and effects of crystallinity that are not included in the presently applied models. @FootnoteText@ @footnote@ Work supported by EU contract INCO COPERNICUS ERBIC15CT960800.

4:40pm MC-TuA9 Measurement of Silicon Dioxide Film Thicknesses by XPS, *C.J. Powell*, National Institute of Standards and Technology; *A. Jablonski*, Polish Academy of Sciences

It is now customary for the effects of elastic-electron scattering to be ignored in measurements of overlayer thicknesses by XPS. It is known, however, that elastic scattering can cause the effective attenuation length (EAL), needed for the thickness measurement,@footnote 1@ to be appreciably different from the corresponding inelastic mean free path.@footnote 2@ We have investigated the effects of elastic-electron scattering in measurements of the thicknesses of SiO@sub 2@ films on Si from XPS measurements with Al and Mg K@alpha@ x rays. Calculations have been made of substrate and oxide Si 2p photoelectron currents for different oxide thicknesses and emission angles using an algorithm based on the transport approximation.@footnote 3@ This algorithm accounts for the occurrence of elastic scattering along electron trajectories in the solid. It was found that the average EAL, determined from the substrate currents with and without an oxide overlayer of a certain thickness, varied weakly with oxide thickness and emission angle for a restricted range of emission angles. For emission angles greater than about 60°, corrections need to be made to this average EAL in order to determine the oxide thickness. These corrections will be described.@FootnoteText@ @footnote 1@A. Jablonski and C. J. Powell, Surf. Interface Anal. 20, 771 (1993). @footnote 2@A. Jablonski and C. J. Powell, J. Electron Spectrosc. 100, 137 (1999).

@footnote 3@I. S. Tilinin, J. Zemek, and S. Hucek, Surf. Interface Anal. 25, 683 (1997).

5:00pm MC-TuA10 A New Angle on Angle Dependent XPS, K.S. Robinson, G. Jones, R. White, J. Wolstenholme, VG Scientific, UK

Angle dependent XPS offers the ability to determine relative distributions, compositions and layer thickness for layers thinner than the XPS analysis depth. In practice, the use of angle dependent XPS is limited by the need to acquire data at several angles, usually requiring the sample to be tilted. The analysis of small features is also difficult because tilting the sample changes the analysis area as the projected shapes of the X-ray spot and / or analysis area on the sample change. We previously presented results@footnote 1@ from a commercial instrument where the electron input lens could be used to sequentially define two angles; a surface sensitive angle and a bulk sensitive angle, allowing angle dependent XPS without moving the sample. This method has now been extended to allow simultaneous collection of angle dependent XPS data from a range of angles. We present data from this instrument which shows the application to oxide thickness measurements and more complex structures. @FootnoteText@@footnote 1@QSA-10 at University of Surrey, UK, 1998.

Processing at the Nanoscale/NANO 6 Room 302 - Session NS+NANO6+SS+MC-TuA

Self-assembly and Self-organization

Moderator: R. Wiesendanger, University of Hamburg, Germany

2:00pm NS+NANO6+SS+MC-TuA1 Dip-Pen Nanolithography: A New Tool for Generating and Studying Soft Nanostructures, C.A. Mirkin, S.A. Brennan, L.M. Demers, S. Hong, P.V. Schwartz, D.A. Weinberger, Northwestern University INVITED

A new type of ultrahigh resolution soft-lithography, Dip-Pen Nanolithography (DPN) that is interfaceable with biomolecules and biofunctionalized building blocks will be presented. This soft lithography allows one to routinely pattern structures, in serial or parallel fashion, with sub 50 nm spatial and line-width resolution with near-perfect alignment. Implications in materials synthesis, electronics, and biodiagnostics will be discussed.

2:40pm NS+NANO6+SS+MC-TuA3 A Step Toward Making and Wiring-up Molecular-Scale Devices with a Self-Directed Growth Process, G.P. Lopinski, D.D.M. Wayner, D.J. Moffatt, National Research Council of Canada; **R.A. Wolkow**, National Research Council of Canada, Canada

Our understanding of and control over molecular adsorption on silicon has advanced very significantly in the last several years. It is now possible to provide a microscopic picture of structure and bonding in covalently attached molecule-silicon surface systems. This detailed understanding of adsorbate-surface structures was entirely lacking when the first wave of enthusiasm for molecular devices crested roughly 20 years ago. While many ideas for molecule-scale devices have been put forward in the past, the tools - both synthetic and analytical - to pursue those ideas did not exist. Now, the control necessary to begin exploring ways to incorporate organic function into existing technologies or, eventually, to make new molecule-scale devices is within reach.@footnote 1@ Experimental and modeling methods have emerged that effectively extend the resolution of STM to see the details of adsorbed molecule structure and bonding. In the next several years it is now realistic to expect structures and concepts dreamed about for decades to begin to be realized. This talk will focus on a self-directed growth process for creating molecular nanostructures on silicon.@footnote 2@ @FootnoteText@ @footnote 1@ Controlled Molecular Adsorption on Si: Laying a Foundation for Molecular Devices, R.A. Wolkow, Annual Review of Physical Chemistry, volume 50, 413-41, 1999. @footnote 2@ Self-Directed Growth of Molecular Nano-Structures on Silicon, G.P Lopinski, D.D.M. Wayner and R.A. Wolkow, Nature in press.

3:00pm NS+NANO6+SS+MC-TuA4 Control of Spatial Distribution of Self-Assembled Diacetylene Compounds by Co-deposition with Fatty Acid Molecules, Y. Kuwahara, G.-M. Zhang, J.-W. Wu, M. Akai-Kasaya, A. Saito, M. Aono, Osaka University, Japan

Control of self-assembled surface structure of functional organic molecules has been attracting intensive interest from a viewpoint of future applications such as novel material structures for nanometer-scale molecular devices. We have investigated self-assembled surface structures of two different chain organic molecules co-adsorbed on HOPG by use of scanning tunneling microscopy. The subject molecule was 10,12-

tricosadiynoic acid, which is one of the diacetylene compounds possessing the possibility of being polymerized into macromolecular wire and/or sheet, and several kinds of fatty acids were used as buffer molecules. We used Langmuir Blodgett method for the fabrication of the molecular monolayers. In order to achieve the parallel molecular arrangement, the surface pressure for the deposition was deliberately controlled much lower than the saturate pressure and the substrate was horizontally oriented. A variety of molecular patterns inside the two-component monolayers were revealed, which could be briefly grouped into 'phase separation pattern', where microscopically pure 10,12-tricosadiynoic acid and fatty acid were observable respectively, and 'alternative pattern', in which the lamellae of the two sorts of molecules emerged alternatively. In order to evaluate the mechanism for the two dimensional surface ordering, we have also done the ab-initio molecular orbital calculation and the proposed structural model of the surface self-assembly is in good agreement with the theoretical simulations. Consequently, the possibility of controlling the spatial distribution of the diacetylene compounds on the solid surface has been demonstrated.

3:20pm NS+NANO6+SS+MC-TuA5 The Interaction of Metal Atoms with Self-assembled Organic Monolayers, A.V. Walker, B.C. Haynie, N. Winograd, The Pennsylvania State University

Organic monolayers show great promise as materials for a wide range of technological applications. An understanding of the nature of the metal atom - organic monolayer interaction is vital in the development of molecular electronic devices. Recently it was demonstrated that deposited Al atoms can penetrate through an n-alkyl monolayer to the monolayer / Au (111) interface. This phenomenon is believed to occur via thermally activated transient defects in the monolayer. In this paper, we explore the thermodynamics of this system using time-of-flight secondary-ion-mass-spectrometry (TOF SIMS) and demonstrate that at low temperatures the rate Al atom penetration into the monolayer is reduced. We have also studied the interaction between other promising molecular wire candidates and metal atoms.

3:40pm NS+NANO6+SS+MC-TuA6 Chiral Surface Reconstruction by Largish Molecules, *M. Schunack*, *L. Petersen*, *A. Kühnle*, *E. Laegsgaard*, *I. Steensgard*, *F. Besenbacher*, University of Aarhus, Denmark

Temperature-controlled scanning tunneling microscopy studies provide insight into the bonding, ordering and mobility of large organic molecules at metal surfaces. This is illustrated by investigations of disc-like molecules on a Cu(110) surface with a variable temperature STM, which can be operated down to 25 K.@footnote 1@ Hexa-tert-butyl decacyclene (HtBDC) self-assembles upon deposition onto Cu(110) above 250 K and forms a double-row structure in two directions surrounded by fast-diffusing single molecules. Nano-manipulation experiments with the STM at low temperatures revealed an underlying chiral reconstruction of the Cu surface. This consists of holes of approximately 14 Cu atoms pulled out of the surface. Surprisingly, the observed reconstruction is chiral. By gently annealing of the molecule structure at higher coverages. large enantiomerical pure domains with two different orientations build up. By means of simple effective medium theory calculations, we estimate the lower bound of the adsorption energy to be E@sub ad@ = 0.45 eV, and can give a plausible explanation for the observed structure. @FootnoteText@ @footnote 1@ L. Petersen, M. Schunack et al., submitted to Review of Scientific Instruments.

4:00pm NS+NANO6+SS+MC-TuA7 From Functionalisation of Single Molecules to Self-organisation of Nano-structured Thin Films, *Q. Guo*, University of Birmingham, U.K. INVITED

The combination of functionalisation of individual molecules with selforganisation of the molecules into functional structures is a promising route for the fabrication of nanoscale electronic and optoelectronic devices. In this talk I will present experimental findings of nanostructured thin films prepared using this method. The dependence of the structure of molecular monolayers on the functionality of individual molecules will be demonstrated using chemisorbed acetate and benzoate species on TiO@sub 2@ surfaces as an example. Both acetate and benzoate attach to the substrate through strong bonding between the carboxyl end of the molecules and the metal cations at the surface of TiO@sub 2@. In the case of benzoate, the phenyl ring offers an extra functionality for intermolecular linkage, leading to the formation of dimerised rows of benzoate. Self assembled monolayers (SAMs) of functionalised alkanethiols adsorbed on Au(111) surfaces will also be discussed. Functionalisation of the tail group of thiol molecules gives rise to SAMs with different surface energies, allowing the fine tuning of the reactivity of the surfaces towards binding of

deposited atoms and molecules. The formation of nano-particles of gold on carboxyl terminated SAMs has been investigated using scanning tunnelling microscopy (STM) and electron energy loss spectroscopy(EELS) and results will be presented to demonstrate the important role of functionality of individual molecules on nano-structure formation.

4:40pm NS+NANO6+SS+MC-TuA9 Ion Beam Assisted Self-Organization of Periodic Nanowire-Arrays on CaF2 Substrates, *M. Batzill⁴*, *F. Bardou, K.J. Snowdon*, University of Newcastle, UK

The fabrication of well ordered nanowire arrays over large areas is a challenge with many potential applications. Here we report a novel glancing incidence ion beam assisted self-organisation approach to form periodic wire-arrays over large areas on a CaF2(111) substrate. Preferential erosion of fluorine by the ion beam creates a surface enriched in calcium. The calcium self-organises in elongated island structures of preferential width and separation. If the sample is irradiated along a fixed azimuth we observe formation of nanowires with ~10 nm periodicity and wire lengths of at least several micrometers oriented along the azimuthal direction of ion beam incidence. Electrical conductivity measurements reveal a three order of magnitude lower conductivity normal to the wires than along the wires.

5:00pm NS+NANO6+SS+MC-TuA10 Quantum Engineering of a Pb Nanostructure: Controlling the Thickness with Monolayer Precision, *C.-S. Jiang*, *H.-B. Yu*, *X.-D. Wang*, *C.-K. Shih*, University of Texas at Austin

We report a novel quantum engineering of Pb mesas on Si(111), designing the quantum number (N) of the electron resonator of Pb by modifying its thickness with monolayer precision. Pb deposition on Si(111) forms mesas on the surface, and the mesas serve as electron resonators because of the strong quantization along the surface normal direction. To modify the mesas into desired thickness, mass-transfer was first triggered by an STMtip under controlled conditions. The triggering lead to the formation of single layer with annular shape at the edge of the mesa by transferring the Pb mass from the wetting layer. Once triggered, the mass transfer from the wetting layer to the top of the mesa continue until the new layer involving millions of atoms is completed. Once this layer is completed, no more mass transfer is observed unless a new triggering is performed. Each triggering leads to addition of one complete monolayer on top of the plateau. Using this process, the Pb mesa thickness can be engineered in a quantized fashion. Detailed mechanisms involved in the engineering will be discussed.

¹ NSTD Student Award Finalist

Material Characterization Room Exhibit Hall C & D - Session MC-TuP

Poster Session

MC-TuP1 Quantitative Detection and Mapping of SiOH Groups on Si using Chemically Labeled TOF-SIMS Method, *T. Mitsuoka*, *M. Ikai*, *T. Ohwaki*, *Y. Taga*, TOYOTA Central Research and Development Laboratories Inc., Japan

This paper first demonstrates an accurate quantitative detection and mapping of SiOH by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) combined with phenyldimethylchlorosilane (PDMCS) treatment to detect the amount of SiOH on a Si wafer. We found that we can detect the quantity of SiOH on a Si wafer without the influence of adsorbed water by the labeled TOF-SIMS method. Furthermore, we could map the 2D distribution of SiOH on the Si surface. The quantitative analysis of SiOH by TOF-SIMS was confirmed as follows. H and OH terminated surfaces were prepared by dipping a Si wafer into hydrofluoric acid (HF) solution and H@sub 2@O@sub 2@:H@sub 2@SO@sub 4@=4:1 solution, respectively. Contact angles of the SiOH surface became smaller with dipping time in deionized water. Surface chemical characteristics and adhesion force of the surfaces thus treated were examined by attenuated total refraction (ATR) of IR and Atomic Force Microscopy (AFM). The yields of characteristic ions (C@sub 6@H@sub 5@Si@super +@, C@sub 6@H@sub 5@(CH@sub 3@)@sub 2@Si@super +@)emitted from the labeled SiOH surfaces were compared with the data of contact angles, ATR and AFM. There was a good correlation between the amount of these fragment ions and contact angles. In conclusion, quantitative detection and mapping of SiOH groups on Si were demonstrated by the sophisticated labeled TOF-SIMS method.

MC-TuP2 Secondary Ion Emission from Well Defined Molecular Overlayers Under Molecular Primary Ion Bombardment, *D. Stapel, A. Benninghoven*, University of Muenster, Germany

Molecular primary ions have been shown to enhance the yield Y(X@sub i@@super q@) of organic secondary ions considerably. The simultaneous increase in the corresponding damage cross section @sigma@(X@sub i@@super q@) is much smaller. This holds in particular for thick molecular samples like LB multilayers or polymers. For LB multilayers we found yield increases up to a factor of 1000, when changing from Ar@super +@ to SF@sub 5@@super +@ bombardment. This phenomenon is important for practical analytical applications of TOF-SIMS, because yields, damage cross sections, and the resulting ion formation efficiencies E=Y/@sigma@ determine the achievable sensitivity as well as the achievable lateral resolution. In recent years we have investigated in some detail this secondary ion emission behavior for a variety of LB layers under atomic and molecular primary ion bombardment. Basic studies were performed with three series of LB layers (n = 1, 3, 5, 7, 9; n : number of monolayers) under 0.5 - 11 keV Ne@super +@, Ar@super +@, Xe@super +@, O@sub 2@@super +@, CO@sub 2@@super +@, SF@sub 5@@super +@, C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 8@@super +@, C@sub 6@F@sub 6@@super +@ and C@sub 10@F@sub 8@@super +@ bombardment. Y(X@sub i@@super q@) as well as @sigma@(X@sub i@@super q@) were determined. We found a more pronounced Y and E enhancement for multilayers (n>1). Y, @sigma@ and E increases with increasing mass of atomic primary ions and with growing number of constituents up to 6 heavy atoms. Y, @sigma@ and E features a saturation behaviour for molecular primary ion species containing more than 6 atoms. We could not find an influence of the chemical composition of the primary ion on this enhancement under static SIMS conditions. We found that the molecular secondary ions are emitted from the 1@super st@ and 2@super nd@ layer and a pronounced decrease in Y and E was determined for 1 keV SF@sub 5@@super +@ bombardment.

MC-TuP3 A SIMS Study on the Negative Boron Cluster Secondary Ion Yield Change in Boron Implanted Silicon, *S. Hayashi*, Nippon Steel Corporation, Japan; *Y. Okamoto*, SHARP Corporation, Japan; *F. Toujou*, Matsushita Technoresearch Inc., Japan; *Y. Homma*, NTT Basic Research Laboratories, Japan

To establish standard protocols in depth profiling, the linearity of the ion intensity using the ion-implanted silicon specimens with a variety of ion dose have been investigated. In these round-robin test, we have been studying secondary ion emission mechanism and found the irregularity of the production of negative boron cluster in boron implanted silicon specimens. These phenomena have been reported only the positive secondary ion emission in the high dose specimen.@footnote 1@ In this

study we applied the boron implanted silicon wafer to quantify the amounts of boron in silicon with a wide concentration range. Cs@super +@ ion beam was used to detect negatively charged boron cluster ion signals, ie, B@super -@, B@sub 2@@super -@, B@sub 3@@super -@ ,etc.. The dependency of negative secondary ion yields on a variety of ion doses was estimated in order to compare with the detection of boron cluster ion counts. The higher dose of boron was implanted into silicon, the larger production efficiency of boron cluster ion was. Especially, the efficiency of B@sub 2@@super -@ exceeded the one of boron atomic ion in the high dose, 1x10@super 17@ions/cm@super 2@ specimen which was implanted B@super +@ with 50keV as an accelerating voltage. Such an enhancement of negative dimer ion emission yield cannot be explained on the basis of the recombination mechanism because B@sub 2@@super -@ yield is larger than the B@super -@ ion yield. The emission mechanism of boron negative cluster ion will be discussed, comparing with the dependence of the boron negative cluster ion yields on the implanted doses, the shape of the implanted depth profile, and boron positive secondary ion emission. @FootnoteText@ @footnote 1@M. Tomita, F. Takahashi and Y. Homma, Nucl. Instrum. Methods Phys. Res., B85(1994), 399.

MC-TuP4 Fabrication and Characterization of Boron-Doped Silicon Thin Film as a Reference Material for Secondary Ion Mass Spectrometry Quantification, K.J. Kim, D.W. Moon, H.K. Kim, Korea Research Institute of Standards and Science, Korea; C.J. Park, Korea Research Institute of Standards and Science

Secondary ion mass spectrometry(SIMS) is one of the most powerful techniques for the determination of the concentration of minor impurities in solid materials. Ion implanted reference materials are generally used for the quantification of impurities by SIMS. In this study, we will present a new type of reference material for the quantification of minor impurities by SIMS. Uniformly-doped silicon thin films with three levels of boron concentrations were fabricated by ion beam sputter deposition. A Si target with a small BN was sputter deposited simultaneously on a Si(100) and a polyester substrate by 1 keV Ar ion beam. The boron concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS) using the isotope dilution method. The boron concentration measured by ICP-MS was compared with that by SIMS using a boron ion implanted standard reference material.

MC-TuP5 Development of Secondary Ion Mass Spectrometry Methodology for the Film Thickness Measurement of Sub-2nm SiO@sub 2@ Interlayers, C.M. Jones, J. Zhao, Advanced Micro Devices

Film thickness of interfacial SiO@sub 2@ in poly-emitter devices and thickness of gate oxide in transistors is crucial to device performance and speed. The thickness regimes (0-1nm and 1.5-2.5 nm, respectively) are too thin to allow for accurate measurement by electron microscopic techniques. In the present work, we report the development of secondary ion mass spectrometry (SIMS) methodology for the film thickness measurement of sub-2nm SiO@sub 2@ interlayers. The SiO@sub 2@ interlayer structure is polycrystalline Si / SiO@sub 2@ / Si substrate. The polycrystalline Si layer can be up to a few hundred nano-meters thick. The sample is analyzed by SIMS and a concentration depth profile of oxygen is acquired. High-energy Cs bombardment is used, so that the thin SiO@sub 2@ layer is diluted by ion beam mixing. A 14.5 kV net impact energy provides sufficient mixing to change the composition of the interface from that of stoichiometric SiO@sub 2@ to Si with a high dose of oxygen. The areal density of the interfacial oxygen peak may be calibrated against a SIMS oxygen ion implant standard with a precision of better than 3%. The SiO@sub 2@ thickness is then calculated with equal precision, using the formula derived. A statistical measurement of the same sample over a period of several weeks demonstrated a superior reproducibility.

MC-TuP6 Analysis of Delta Multilayer Profiles Measured by Secondary Ion Mass Spectrometry, A. Takano, Y. Higashi, NTT Advance Technology Corporation, Japan; Y. Homma, NTT Basic Research Laboratories, Japan; J. Kikuma, S. Soga, Y. Okamoto, R. Oishi, S. Hayashi, R. Saito, M. Tomita, Y. Ueki, S. Seo, F. Toujou, S. Yoshikawa, J. Kinoshita, SIMS-Depth Profiling WG, Japan; D.W. Moon, Korea Research Institute of Standards and Science, Korea

Delta-doped multilayers are potential reference materials for the evaluation of depth resolution in secondary ion mass spectrometry (SIMS). For this purpose establishing standard procedures of depth resolution evaluation is necessary, as well as developing reliable delta multilayers. We tested a theoretical model, mixing-roughness-information depth (MRI) model@footnote 1@ for extracting depth resolution parameters from the measured profiles in the round-robin study using a delta-multilayer

specimen that includes five GaAs-doped delta layers separated by amorphous Si layers. The measured arsenic profiles were analyzed using the MRI model. For SIMS, information depth in the model can be regarded to be very small, so we used the only two parameters concerning mixing and roughness. The mixing parameters showed very little in-depth variation but dependence only on primary-ion energy and impact angle, irrespective of the instrument types used. This means that the mixing parameter may be regarded as a physical quantity. The roughness parameter and its in-depth dependence, on the other hand, varied among participating laboratories, reflecting the measurement conditions and surface roughening. @FootnoteText@ @footnote 1@ S. Hofmann, Surf. Interface Anal. 21 (1994) 673

MC-TuP7 Comparison of Improved Spreading Resistance Profiling and Secondary Ion Mass Spectrometry in the Characterization of Ion Implanted Dopant Profiles, *L.C.P. Tan*, The National University of Singapore, Republic of Singapore; *L.S. Tan*, *M.S. Leong*, The National University of Singapore; *C.W. Lee*, ST Microelectronics Ltd.

Spreading resistance profiling (SRP) is a well-established technique for the determination of dopant profiles in silicon wafers. The dopant profile can then be recovered from the spreading resistance profile by using an iterative algorithm. It has been noticed that for certain dopant profiles, especially shallow ion implanted profiles, the junction depth determined from SRP often do not agree with those predicted by process simulators such as SUPREM3. In addition, the sheet resistance as measured using fourpoint probes is also sometimes different from that deduced from dopant profiles recovered by SRP. The discrepancy may arise if the algorithm used to convert the spreading resistance profile into the dopant profile does not take into an account a phenomenon known as the carrier redistribution effect. In this work, we describe the results of a set of experiments carried out to compare the dopant profiles obtained from SRP and secondary ions mass spectrometry (SIMS) as well as those predicted by SUPREM3. SRP is an electrical characterization technique that responds to the presence of electrons and holes. The p-n junction indicated by the spreading resistance profile is the electrical junction, where the electron concentration is equal to the hole concentration. SIMS, on the other hand, is a physical characterization technique that measures the profile of dopant atoms, and the junction obtained by SIMS is the metallurgical junction where the donor concentration is equal to the acceptor concentration. The electrical junction and the metallurgical junction do not necessarily coincide because of the carrier redistribution effect, especially in shallow ion implanted profiles. However, we shall show that by using a new algorithm that correctly models the carrier redistribution effect, the disagreement in the dopant profiles obtained by SRP, SIMS and SUPREM3 can be significantly reduced.

MC-TuP8 Characterization of Si Distribution at the Tungsten / Titanium Nitride Interface Using Secondary Ion Mass Spectrometry - An Investigation of the Dynamic Response of a Chemical Vapor Deposition Chamber, C.M. Jones, J. Zhao, Advanced Micro Devices

In sub-micron MOS IC processing, tungsten lines or contact (via) plugs are formed by blanket chemical vapor deposited tungsten thin film fill into the narrow SiO@sub 2@ trenches or small contact openings on the titanium nitride (TiN) layer with the underlying structure. The blanket CVD tungsten thin film is typically accomplished as the following: a thin nucleation layer (~50nm) is grown by silane (SiH@sub 4@) reduction of tungsten hexafluoride (WF@sub 6@), and the bulk deposition is accomplished via hydrogen (H@sub 2@) reduction of WF@sub 6@. The TiN layer serves as an adhesion layer that promotes uniform W growth as well as a diffusion barrier between W and underlying Si or silicide layers. For the common CVD deposition chamber, such as a batch-processing machine, the deposition process parameters, such as gas flow, temperature and pressure, are monitored in the inlets of the chamber usually at a distance from the wafer surface where the reaction takes place. The small SiH@sub 4@ gas flow that controls the Si concentration in the nucleation layer, in particular, will have certain modulating effects from the chamber, in terms of time and concentration, in the course of transport. In the present work, simultaneous SiH@sub 4@ and H@sub 2@ reduction of WF@sub 6@ formed the tungsten nucleation layer with a nominal thickness of 60nm. A two-step SiH@sub 4@ gas flow scheme was used to determine the effects of magnitude and duration of SiH@sub 4@ flow on the Si concentration at the W/TiN interface. The results amply demonstrate that SIMS analysis can be used to evaluate the deposition process so as to meet the fill and barrier protection requirements for narrow trench or small via. Issues of SIMS analysis such as depth resolution, interference from molecular ions, memory effect, and quantification are discussed.

MC-TuP9 SIMS/XPS Depth Profiling of a Fluoride-Modified Epoxycoating, W.J.H. Van Gennip, R.D. Van de Grampel, R. Van der Linde, Eindhoven University of Technology, The Netherlands; P.C. Zalm, Philips Research, The Netherlands; J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands, Netherlands

The surface of an epoxy resin has been modified by the addition of a small amount of a polymerizable monomeric surfactant. The difference between the surface free energy of the epoxy and surfactant caused the surfactant, by definition the component with the lower surface free energy, to segregate preferentially to the solid/air interface. Curing caused the surfactant to bind to the crosslinking agent, thus permanently modifying the surface of the epoxy. Initial XPS measurements showed that the surface is indeed fluoride-modified. This was confirmed by contact angle measurements. Only a small amount of surfactant is necessary to saturate the surface. These exploratory measurements were used as reference to study, explain and confirm the depth profiles we subsequently acquired using depthprofiling SIMS. Although depth profiling of semiconductors has become a widely used technique, the application of depthprofiling SIMS to polymers is much less common. The preliminary results obtained thus far indicate that depthprofiling through polymers can deliver useful results unobtainable by other techniques.

MC-TuP10 Strategies for Reducing the Effects of Topography in Depth Profile Analysis of Polycrystalline Thin Film CdTe/CdS Photovoltaic Materials and Devices, *S.E. Asher*, *M.R. Young*, *H. Moutinho*, *T. Gessert*, *R.G. Dhere*, *P. Sheldon*, National Renewable Energy Laboratory

Polycrystalline thin film materials are promising for low-cost, large area manufacturing of photovoltaic modules. Surface analysis methods are critical tools to measure the distribution of contaminants and dopants in these materials. However, the native t opography and heterogeneity can present significant challenges for depth profile analysis, particularly by SIMS. We have developed several methods that have proved useful for SIMS examinations of CdTe/CdS solar cells made by different thin film depositio n methods. Depth profile results obtained after chemical etching, controlled polishing and back-side analysis show strengths and limitations of each method. These methods have allowed us to study diffusion and composition in 100 nm CdS layers buried under up to 10 µm of CdTe. In the films studied, the CdTe may have an initial average surface roughness of @>=@ 200 nm or more. The depth profile results from sample preparation methods listed above will also be compared to depth profiles obtained with sample rotation. We find that sample rotation in these materials is complicated by lateral inhomogeneities, even when the rotation speed is well matched to the cycle time of the analysis.

MC-TuP11 Comparison of Sputter Rate and Interfacial Resolution in a Multi-instrument Surface Science Laboratory, *M.H. Engelhard*, *A.S. Lea*, *D.J. Gaspar*, *G.C. Dunham*, *T. Thevuthasan*, *D.R. Baer*, Pacific Northwest National Laboratory

A multi-instrument, multi-technique laboratory faces a wide variety of analysis needs. Although much is known about the parameters that influence sputtering and the ability of a technique to resolve an interface, variations among different instruments reflect the geometry and design of each instrument, as well as the conditions convenient for operation and actual performance of an ion gun. Each instrument has advantages and limitations for specific types of analyses. In order to determine the actual performance of various instruments found in the Environmental Molecular Sciences Laboratory, we have measured interfacial resolution and sputtering rates produced for common operating and a few optimized sputter conditions for several instruments. The capabilities of these instruments include X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and accelerator based materials analysis. Samples used for these studies included Si/SiO@sub 2@, Ta/Ta@sub 2@O@sub 5@ and Ni/Cr multilayer standards. For instruments with sample rotation capability, data has been collected with and without rotation. Using this data, we have developed a matrix describing the performance of the various techniques and instruments. We utilize this matrix to choose the appropriate instrumentation to acquire the desired information at the required accuracy for a wide range of scientific studies in the minimum time.

MC-TuP12 XPS Investigation of Counterion Exchange in SiO@sub 2@ Solgel Films Doped with Tris(2,2'-bipyridine)Ruthenium(II), X. Wen, M. Sykora, T.J. Meyer, R.W. Linton, University of North Carolina at Chapel Hill SiO@sub 2@-based sol-gels provide an attractive matrix for doping a variety of molecules. Ru complexes are among the most attractive dopant

molecules for SiO@sub 2@ sol-gels due to their unique photophysical and redox properties. Applications of sol-gel films doped with Ru complexes are mostly based on the properties related to the metal-to-ligand charge transfer (MLCT) excited state of the complex. The MLCT excited states are very sensitive to not only the physical nature but also the compositions of the sol-gel matrix. This research work investigates the possible new method of tailoring the compositions of SiO@sub 2@ sol-gel thin films doped with [Ru(bpy)@sub 3@]Cl@sub 2@, which involves the exchange of the original counterions of Ru complexes with new counterions. SiO@sub 2@ sol-gel films doped with [Ru(bpy)@sub 3@]Cl@sub 2@ were prepared by spin-coating from sol/[Ru(bpy)@sub 3@]Cl@sub 2@ mixtures. XPS coupled with Ar@super +@ sputtering was used to study both the surface compositions and depth profiles of the sol-gel films before and after the counterion exchange experiments. The results indicated the original counterion, Cl@super -@, of Ru(II) complex completely leached out of the film after exposing the film to water. Cl@super -@ ion could be reintroduced into the film by putting the Cl@super -@ deprived film back in HCl solution. New counter ions, such as PF@sub 6@@super -@, were incorporated into the sol-gel film by immersing the Cl@super -@ deprived film in HPF@sub 6@ solution. The incorporation of PF@sub 6@@super -@ ions was both time and pH dependent. In addition, cations such as Na@super +@ could also be incorporated into the film by putting the solgel film in basic solutions such as Na@sub 2@HPO@sub 4@/NaH@sub 2@PO@sub 4@. This approach was used to calculate the ratio of total Si to the number of SiO@super -@H@super +@ sites that can be exchanged in the SiO@sub 2@ sol-gel films.

MC-TuP13 SiO2 Growth on Si(100) and (111) Investigated by QUASES-XPS Analysis, B. Semak, C. Gundlach, P. Morgen, University of Southern Denmark; S. Tougaard, University of Southern Denmark, Denmark

It is well known that the growth of SiO2 on Si is an activated process. It must involve heating and it may be strongly influenced by the presence of small amounts of catalysts like alkali metals. A fundamental problem for the growth of very thin SiO2 films with heating is the formation of oxide islands and trenches at their perimeters. The parameters of oxide growth are varied in a series of experiments to determine their influence on the morphology and interface structure of silicon oxide on Si(111) and Si(100). Here we have used the QUASES-XPS technique@footnote 1@ to analyze the surface morphologies of 0 to 10 nm thin SiO2 films. The SiO2 growth is determined for different cycles of alkali-metal evaporation-, oxygen exposure- and annealing- procedures. @FootnoteText@ @footnote 1@ http://www.quases.com.

MC-TuP14 Influence of Ar@super +@ Ion Bombardment on the Chemical States of SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Films Fabricated by Metal-Organic Decomposition, Y.B. Park, K.Y. Min, S. Heo, C.H. Lim, M.K. Lee, H.J. Kim, S.Y. Lee, Hyundai Electronics Industries Co., Ltd., Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@(SBT) belongs to a Bi-layered perovskite structure where double Ta-O octahedron layers are sandwiched between (Bi@sub 2@O@sub 2@)@super 2+@ lavers were analyzed for the characterization of chemical states with the help of x-ray photoelectron spectroscopy (XPS) during the depth profiling analysis. When the sputter etching was performed to SBT films by Ar@super +@ ion bombardment, the chemical states of constituents were changed as a function of the applied Ar@super +@ ion beams energy from 1kV to 4kV. Among the constituents of SBT film, the Sr 3d peak was slightly changed by the change of Ar@super +@ ion beams energy. On the other hand, the change of Ta 4f and Bi 4f peak were obviously dependent on the applied Ar@super +@ ion beams energy. In particular, Bi 4f peak was dramatically changed from Bi@sub x@O@sub y@ oxide states to Bi metallic states by the lower Ar@super +@ ion energy than the cases of Sr and Ta. These changes of chemical state within SBT film resulted from the preferential sputtering of oxygen atoms. Following out present study, Preferential sputtering of oxygen atoms was found to depend on thermal stability and mass difference between oxygen and each constituent within SBT film.

MC-TuP15 XPS Analysis of Plasma-Modified Polymers for Enhanced Cellular Response, *R. White*, VG Scientific, UK; *R.L. Williams, T. Markkula,* University of Liverpool, UK; *G. Jones, J. Wolstenholme,* VG Scientific, UK

Gas plasmas are a convenient way of modifying the surface properties of polymers without significantly altering their bulk properties. As such they have been proposed as a means of modifying the surface properties of polymers to enhance the cellular response to the materials for particular applications. XPS has been used to determine both the elemental composition and chemical state functionality of PET and PTFE polymers modified using two different RF plasma systems (Capacitor Plate and Inductive Coil) with nitrogen and ammonia gases. Initial results indicate significant differences in modification of the polymers with the respective treatments.

MC-TuP16 Surface Potential Measurement with High Spatial Resolution using a Scanning Auger Electron Microscope, Y. Sakai, M. Kudo, JEOL Ltd., Japan; *C. Nielsen,* JEOL USA Inc.

The microscopic surface potential distributions were measured from the onset energies of secondary electron spectra using a scanning Auger electron microscope. An equipment used in this experiment was a scanning Auger electron microscope (JEOL Model JAMP-7830F) attached with a hemispherical electron energy analyzer with an input focusing lens system and a secondary electron detector to take SEM images. The electron gun is a Schottky field emission type and electrons emitted from a cathode tip are focused onto the specimen surface. The hemispherical electron energy analyzer with a high detection efficiency in the region lower than several ten eV was used at an ultra-high vacuum pressure. Such a technology makes possible to measure the work function change caused by different crystal orientations, the surface potential profile depending on microelectronic structures of semiconductor devices, etc. The typical applications of the work function measurement are presented in this paper. The four grains of poly-crystal Ni (99.9% purity) with different crystal orientation were prepared for testing a spatial resolution of work function mapping. The initial rises of secondary electron emission for the four grains of Ni are observed by the primary electron beam at 10 keV and 1.3 n A., and the onset energies are 5.55, 5.60, 5.65, and 5.50eV, respectively. If we put the work function of the analyzer equal to 5.60 eV, the work functions of Ni are 4..95, 5.04, 5.22 and 5.35 eV, respectively. The mapping of work function distribution was carried out by measuring intensities of secondary electron emission at the fixed point of. 5.70eV. The observed work function images show a spatial resolution of several tens nm estimated from the image contrast. The measurement of work function and imaging of the surface potential at a spatial resolutions of several tens nm and a sensitivity of 0.05V have been established by using a scanning Auger electron microscope of ultra-high vacuum.

MC-TuP17 Satellite Structure of KLL Auger Spectra in Fluorides, L. Kövér, Institute of Nuclear Research of the HAS, Hungary; M. Uda, Waseda University, Japan; I. Cserny, J. Tóth, Institute of Nuclear Research of the HAS, Hungary; K. Ogasawara, H. Adachi, Kyoto University, Japan

Considerable chemical effects have been found on the satellite structures of the F KLL Auger spectra in fluorides recently,@footnote 1-3@ which could be important for surface chemical identification and could provide information on the origin and the atomic or molecular character of the particular Auger satellite lines. In the case of the alkali fluorides unassigned satellites were found and interpreted on the basis of a new concept, the resonant orbital rearrangement.@footnote 3@ In the present work we study the structure of the Auger satellites induced from rutile-type fluorides. F KLL Auger spectra were excited by Al K@alpha@ and Cu L@alpha@ X-rays from polycrystalline powder samples of MgF@sub 2@. ZnF@sub 2@, NiF@sub 2@ and CoF@sub 2@ and measured by a high luminosity electron spectrometer.@footnote 4@ Excitation by Cu L@alpha@ increased the peak to background ratio in the spectra significantly. Similarly to the alkali fluorides, a satellite has been found in the high kinetic energy part of the measured F KLL spectra. From the satellite intensities the fluorescence yield for the doubly ionized states in MgF@sub 2@ has been determined. An inverse proportionality has been found between the satellite/diagram X-ray and the corresponding Auger intensity ratios, while the latter ratios have been found to be proportional to the energy width of the new Auger satellites. These observations indicate the resonant nature of the Auger transition identified. For determining the energy difference between the molecular orbitals in resonance, Discrete Variational X@alpha@ cluster molecular orbital calculations have been performed. This work was supported by the projects OTKA T026514, MTA-JSPS 24/1998. @FootnoteText@ @footnote 1@ O. Benka and M. Uda, Phys. Rev. Letters, 56 (1986) 1667, @footnote 2@ H. Aksela, E. Kukk, S. Aksela, A. Kikas, E. Nommiste, A. Ausmees and M. Elango, Phys. Rev. B 49 (1994) 3116, @footnote 3@ M. Uda, T. Yamamoto and T. Takenaga, Adv. in Quant. Chem. 29 (1997) 389,@footnote 4@ L. Kövér, D. Varga, I. Cserny, J. Tóth and K. Tökési, Surf. Interface Anal. 19 (1992) 9.

MC-TuP18 XPS and XRD Characterization of CuO-TiO2-CeO2 Catalyst System, M.S.P. Francisco, Universidade de Sao Paulo, Brazil; P.A.P. Nascente, Universidade Federal de Sao Carlos, Brazil; V.R. Mastelaro, Universidade de Sao Paulo, Brazil; A.O. Florentino, Universidade Estadual Paulista, Brazil

The CuO-TiO@sub 2@ system has been widely studied due to its catalytic properties on methanol oxidation. However, disadvantages are related to TiO@sub 2@ as support: thermal instability, its sintering and the sintering of the active phase. The cerium addition to this system is known to stabilize the active phase in a fine dispersed state and to improve both the resistance to thermal loss of surface area and the catalytic activity of supported catalysts. The influence of loading cerium and cooper to TiO@sub 2@ on its superficial composition and on its structure have been studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The analyses revealed that with increasing amount of cerium on titania, cerium occurs mainly in a dispersed superficial specie and just a little as CeO@sub 2@ phase (cerianite). At higher loading of cerium, the CeO@sub 2@ phase increases and the Ce/Ti atomic rate is smaller than the bulk rate, as a consequence of cerium agglomeration. We have concluded that a limited amount of cerium can be spread on the titania surface. The Cu/(Ce+Ti) atomic rate showed no influence from cerium on the dispersion of cooper. For CuO-TiO@sub 2@ samples with low concentration of cerium, we could observe that cerium is found as Ce@super 3+@, at least partly. Also the XPS spectra confirmed the presence of a second titanium specie with a spin-orbit component at higher binding energy than the one presented by Ti@super 4+@ in CuO-TiO@sub 2@ samples rich in cerium. The structural results obtained by XAS were in good agreement with those obtained by XRD and XPS.

MC-TuP19 Structural Characterization of V@sub 2@O@sub 5@/TiO@sub 2@ Catalysts, C.B. Rodella, Universidade de Sao Paulo, Brazil; P.A.P. Nascente, Universidade Federal de Sao Carlos, Brazil; V.R. Mastelaro, M.R. Zucchi, R.W. Franco, C.J. Magon, J.P. Donoso, Universidade de Sao Paulo, Brazil: A.O. Florentino, Universidade Estadual Paulista. Brazil

Vanadia supported on titania constitutes a well-know catalytic system for selective oxidation of o-xylene, ammoxidation of hydrocarbons and selective reduction of NO@subx@ with NH@sub3@. A series of V@sub2@O@sub5@/TiO@sub2@ samples was synthesized by sol-gel and impregnation method with different contents of vanadia and treated in different calcination temperature. The samples were characterized by X-ray diffraction (XDR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electronic paramagnetic resonance (EPR). XDR detected rutile as the predominant phase for pure TiO@sub2@ prepared by the solgel method when calcined at 450@super0@C. The structure changed to anatase when the vanadia loading was increased. Also anatase was the predominant phase for samples obtained by the impregnation method. XPS results indicated that the Ti ions were surrounded tetrahedrally by oxygen ions. The V/Ti atomic ratios showed that V ions were highly dispersed on the vanadia/titania surface obtained by sol-gel method. Raman measurements identified three species of surface vanadium: monomeric vanadyl (V@super4+@), polymeric vanadates (V@super5+@) and V@sub2@O@sub5@ crystalline. EPR analysis detected three V@super4+@ ion types: two of them were located in axial symmetry sites substituting the Ti@super4+@ in the rutile structure, and the third one was constituted by a magnetically interacting V@super4+@ ions in the form of pairs or clusters. For the materials with higher concentrations of vanadium, a partial oxidation of V@super4+@ to V@super5+@ was evident from EPR analysis.

MC-TuP20 Investigation of Oxide Layers Formed on NiTi Shape Memory Alloys at Elevatated Temperatures, *R.G. Vitchev*, *G. Firstov*, *H. Kumar*, Katholieke Universiteit Leuven, Belgium; *Y. Liu*, Nanyang Technological University, Singapore; *B. Blanpain*, *J. Van Humbeeck*, Katholieke Universiteit Leuven, Belgium

NiTi shape memory alloys have attracted considerable attention as materials for medical implants. It is known that the biocompatibility of the implants fabricated from NiTi depends on their surface composition since nickel often causes allergic and toxic effects. The purpose of this study is to characterise the thermally grown oxides on the surface of an NiTi alloy (50 at. % Ni). The samples were heat treated in air in the temperature range 473-1073 K. Thermo-gravimetry measurements were carried out to investigate the kinetics of oxidation. X-ray photoelectron spectroscopy and Auger electron spectroscopy combined with sputter depth profiling were used to investigate the surface composition and chemical state of the constituent atoms and their depth distribution. X-ray diffraction was used to determine the phases formed in the oxide layers. The influence of the

surface treatment of the alloy on the oxidation process was also studied. Thermodynamic calculations were carried out to explain the oxidation behaviour of the NiTi alloy.

MC-TuP21 Reduction of Artifacts in Temperature Programmed Desorption Measurements of Field Generated, Real-Life, Powdered Samples, V.S. Smentkowski, A.L. Linsebigler, General Electric Corporate Research and Development Center

Temperature programmed desorption (TPD) is a powerful surface analytical technique used for studies of adsorbate systems under controlled, high vacuum, conditions. Even under controlled, high vacuum, conditions background events such as desorption from the mounting wires and/or the heater assembly can contribute to the TPD signal and complicates data analysis. Researchers often need to determine the desorption characteristics of field generated, real-life, samples that have been prepared under ambient conditions and TPD measurements are often utilized to provide the desorption characteristics. Since real-life samples are generated under ambient conditions, the potential for background effects is significantly enhanced. In many cases, background effects and their implications on data analysis are not considered. It will be demonstrated that background effects are very significant for real-life, field generated samples when traditional TPD measurements are performed. We have devised a novel experimental protocol to reduce background effects during TPD measurements of field generated, real-life, powdered samples. The novel experimental apparatus and procedures will be described. TPD spectra measured using the new protocol will be compared with spectra measured using traditional protocol.

MC-TuP22 A New Look at the Steel Cord-Rubber Adhesive Interphase by Chemical Depth Profiling, G.E. Hammer, The Goodyear Tire & Rubber Company

The adhesive interphase formed between brass plated steel cord and sulfur crosslinked rubber is known to be a complex layer of metal oxides, sulfides, and rubber. Hostile aging of this system produces changes in the structure, morphology, thickness and mechanical properties of this layer. In a previous publication it has been shown that the overall thickness of the sulfide layer as measured by depth profiling with Auger electron spectroscopy could be used to characterize the degradation of the adhesive bond.@footnote 1@ In this work multivariate statistical analysis of the sulfur Auger electron spectra was used to produce chemical depth profiles of the individual copper and zinc sulfide layers. These chemical depth profiles give new insight into the adhesion degradation mechanism on the nanometer scale. Particularly, the percentage of copper sulfide in the layer was found to be an accurate predictor of adhesion degradation. @FootnoteText@ @footnote 1@G. E. Hammer, R. M. Shemenski, J.Vac. Sci. Technol. A, 12(4), 2388 (1994).

MC-TuP23 Electrical Property of TiN@sub x@/SiO@sub 2@/Si Structure for Metal Gate Electrodes, K.S. Kim, Y.C. Jang, K.J. Kim, Sungkyunkwan University, South Korea; N.-E. Lee, S. Youn, K. Roh, Y. Roh, Sungkyunkwan University, South Korea, Korea

Recently, there have been growing research interests in the gate structures utilizing metal gate electrode materials including W in Si MOS devices. In order to avoid the strong interactions of F during W CVD with gate oxide layer leading to the destruction of gate oxide integrity, TiN@sub x@ diffusion barrier layer has been employed between the metal electrode and the gate oxide due to its excellent electrical property and structural stability. In this work, we investigated the interface formation between TiN@sub x@ and SiO@sub 2@ and electrical properties of TiN@sub x@/SiO@sub 2@ as a function of annealing temperature. Thermal gate oxide with the thickness of 110 Å was grown at 850 °C in the O@sub 2@ atmosphere by RTP on p-type Si. Then, TiN@sub x@ layers with the film thickness of 1000 Å were deposited at room-temperature by reactive d.c. magnetron sputtering with the Ar and N@sub 2@ gas mixture ratios of 6:1, 6:3, and 6:6. To minimize the radiation-induced damage of thermal gate oxide, plasma power was kept as low as 100 W during sputtering. Annealing of TiN@sub x@/SiO@sub 2@/Si structures was performed for 180 sec at 600, 700, and 800 °C by RTA in order to investigate the structural and chemical stability. AES and 4-point probe were performed to measure the chemical composition and sheet resistance (R@sub s@) of TiN@sub x@/SiO@sub 2@ films, respectively. The results of R@sub s@ measurements as a function of annealing temperature indicated that the R@sub s@ values of TiN@sub x@ films decreased at the annealing temperature below 600 °C but started to increase above 700 °C compared to those of as-deposited films. Increased R@sub s@ of the samples annealed at elevated temperature above 700 °C was attributed to the

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increased oxygen concentration in TiN@sub x@ layers, judged from the AES results. Microstructures of TiN@sub x@/SiO@sub 2@ interfaces investigated by cross-sectional TEM showed a good structural integrity.

MC-TuP24 The Observation of Ferroelectric Domains using Scanning Capacitance Microscope, *M.K. Lee*, Hyundai Electronic Industries Co. Ltd., Korea; *P. DeWolf, R. Alvis,* Digital Instruments, Veeco Metrology Group; *W.S. Yang, C.H. Lim, S. Heo, T.K. Lee, Y.B. Park, H.J. Kim, K.Y. Min, S.Y. Lee,* Hyundai Electronic Industries Co. Ltd., Korea

The ferroelectric domain structure affects the ferroelectric properties like as hysteresis loop characteristic that is of importance in manufacturing of ferroelectric random access memory (FeRAM). However, the domain images cannot be easily seen using a general analytic method. We have investigated the ferroelectric domain structure of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) using a scanning capacitance microscope (SCM) combined with an atomic force microscope (AFM). The ferroelectric domains were imaged by optimizing AC and DC bias between sample and cantilever tip. Integrating a dc/dv signal from single domain makes a microscopic ferroelectric hysteresis loop that corresponds well with a macroscopic one obtained from the same film. We also try to image the leakage current of SBT film by means of tunneling AFM (TunA). As the result, the weak point passing by the high currents was observed. Further study on the chemical composition or the structure of the weak point will be helpful to understand the leakage current mechanism of ferroelectric materials.

MC-TuP25 Improved Local Capacitance Detection and a Quantitative 1-D Carrier Profile Extracted from the Scanning Capacitance Microscopy dC/dV versus V Curves, E.-S. Kang, J. Kang, H.-J. Hwang, Chung-Ang University, Korea

We have quantitatively extracted 1-dimensional carrier profile from the scanning capacitance microscope (SCM) dC/dV versus V curves using the SCM modeling and an inversion modeling. This is based on the spherical capacitor model, not the common parallel-plate capacitor model. We physically analyzed the spherical capacitor and calculated the rate of capacitance change with bias. Our modeling data have resulted in the capacitance-voltage (C-V) curves different from the conventional C-V curves. The method for a quantitative carrier profiling can be applied directly th the 2- or 3-dimensional dopant profile extractions. Since the current SCM system has a poor reproducibility and sensibility for obtaining the local dC/dV curves, this problem will prevent us from acquiring carrier depth information. For a better quantity of the carrier profiling, for example, to obtain a carrier profile more than 10x18 cm@super -3@, we have designed a new capacitance detector operating at 1.8GHz voltagecontrolled oscillator. It consists of an vco, a microstrip resonator, and a peak detector. It will bring a greater enhancement for the SCM sensitivity and performance.

MC-TuP26 Dynamic Force Microscopy Investigations on Molecular Structures and Electrical Properties of Organic Ultrathin Films, K. Kobayashi, T. Fukuma, H. Yamada, T. Horiuchi, K. Matsushige, Kyoto University, Japan

Dynamic force microscopy (DFM) was used to investigate the nanometerscale structures and electrical properties of organic molecular films, which should be elucidated for their promising applications for molecular electronics. Frequency modulation (FM) detection method which can give high sensitivity especially in a vacuum environment was used in our DFM. The samples used in this study were organic ultrathin films such as selfassembled monolayers (SAMs) of alkanethiol molecules on Au(111) surface and fullerene crystalline islands deposited on Si(111) surface. On fullerene crystalline islands, we successfully obtained molecularly-resolved images, in which molecules were hexagonally packed. Local variation in surface potential (SP) was also mapped using Kelvin null method in DFM, which allowed us to study the local charge transfer between fullerene thin films and the substrate. In the SP image, a small contact potential difference (CPD) between the fullerene crystalline islands and monolayer-covered Si(111) surface was measured. In addition, we obtained molecularlyresolved images on both SAMs of short-chain alkanethiol molecule (octanethiol) and long-chain molecule (hexadecanethiol). The fact that the latter long-chain SAMs could not be imaged by scanning tunneling microscopy (STM) due to the poor electrical conductivity demonstrates a remarkable advantage of DFM for the studies of organic thin films.

MC-TuP27 Conservative and Dissipative Tip-sample Interaction Forces Reconstructed from Dynamic Atomic Force Microscopy Data, B. Gotsmann, H. Fuchs, University of Muenster, Germany

The conservative and dissipative forces between a tip and a surface are characteristic for the materials involved and contain information on several material parameters. In order to determine these forces quantitatively at all tip-sample distances dynamic atomic force microscopy (AFM) can be used. We based our analysis on a combination of computer simulations and experimental AFM data obtained by the frequency modulation technique. In this way it became possible to reconstruct complete force versus distance curves and damping coefficient versus distance curves from experimental data (frequency shift and energy dissipation) without using free parameters and without using a predefined model for the interaction.@footnote 1@ As an example the interaction between an Al-tip and a Au(111)-sample under UHV conditions was analyzed. It turned out that the parts of the force curves that correspond to long range van-der-Waals-forces as well as strong repulsive contacts can be described well with known contact models. However in the transition regime between attractive and repulsive contact an additional short range force can be found. Similarly, the friction coefficient can be determined quantitatively up to a distance of several nanometers exhibiting an inverse power law. At closer contact both velocity dependent friction and adhesion hysteresis lead to energy dissipation. A strategy to distinguish between the two in AFM experiments will be discussed briefly. @FootnoteText@ @footnote 1@ B. Gotsmann, C. Seidel, B. Anczykowski, H. Fuchs, Phys. Rev. B 60 (1999) p.11051.

MC-TuP28 Challenges in Insulator Surface Analysis, M. Reichling, C. Barth, Universit@um a@t M@um u@nchen, Germany; M. Huisinga, R. Lindner, FU Berlin, Germany

The application of high end ultraviolet optical materials as required for next generation optical lithography is extremely demanding in terms of preparing defect free surfaces. We report about major progress in insulator surface analysis with respect to both, characterizing the electronic and geometric surface structure. This is exemplified for crystals with the fluorite structure (CaF@sub 2@, SrF@sub 2@, BaF@sub 2@) that are important materials for advanced ultraviolet optical applications. Results from highest sensitivity ultraviolet photoelectron spectroscopy revealing defect states are presented. Supported by additional evidence from ultrafast laser spectroscopy, we demonstrate that for any preparation there are occupied and unoccupied states throughout the band gap where the density of states strongly decreases with energy above the valence band edge. The sources of the band gap states as well as their implications for optical absorption in the ultraviolet are discussed. We recently presented atomic resolution in imaging defects on a fluoride surface with scanning force microscopy in the ultra-high vacuum.@footnote 1@ With such measurements and controlled gas exposure we can show that chemical interactions between gas molecules and surface defects play a major role in the degradation of surfaces exposed to air. We, furthermore, demonstrate that it is now possible to resolve not only defects on terraces of cleaved surfaces but also features like step edges and kinks with atomic resolution and that we are able to locate positions of individual ions and vacancies along steps. We present recent results where we resolved individual atoms in regular nanometer-sized surface clusters that are a result of cleavage. @FootnoteText@ @footnote 1@ M. Reichling, C. Barth, Scanning force imaging of atomic size defects on the CaF@sub 2@(111) surface, Phys. Rev. Lett. 83(4), 768 (1999).

MC-TuP29 Controlled Surface Charging as an Analysis Tool in XPS of Mesoscopic Systems, *H. Cohen*, *K. Shabtai*, *S.R. Cohen*, *I. Rubinstein*, Weizmann Institute of Science, Israel

A novel application of X-ray photoelectron spectroscopy (XPS) is presented, using controlled surface charging (CSC) in dielectric/conductive mesoscopic heterostructures. The method is based on the induction of well-defined potential gradients by means of the electron flood gun. The resultant local potential variations are projected on the photoelectron energy scale, directly detected as XPS line shifts, providing high-quality spatial information down to nanometer scale resolution. The method is applicable to a large variety of systems, offering important advantages over existing XPS-based techniques. Applications of the method will be demonstrated.

Wednesday Morning, October 4, 2000

Material Characterization Room 207 - Session MC-WeM

Methods of Data Analysis

Moderator: D.G. Castner, University of Washington

8:20am MC-WeM1 Interpretation of the Shirley Background in XPS INVITED Analysis, J.E. Castle, University of Surrey, U.K.

The feature that is perhaps the most characteristic of an XPS spectrum, i.e. the step in background which accompanies every peak, is also its most enigmatic. The simple interpretation given in early texts was that the step is created by extrinsic losses as the electron travels through the material has not survived the work of Tougaard@footnote 1@ who has shown that the extrinsic losses build up rather slowly on the low kinetic energy side of the peak. In fact when the Tougaard function is subtracted from a typical peak there remains a peak with a considerable tail. Interpretation of this tail in a quantitative manner has always posed problems, mainly because the standards used for sensitivity factors do not include the tail and in most cases of analysis the tail extends beyond the window used for the narrow scan. Thus to undertake quantification in XPS analysis it is normal to remove a background which is based on the original Shirley algorithm,@footnote 2@ i.e. an integration of the peak lying above background using an integration constant which allows the background to merge with the experimental data at some point close to the peak. A browse through a collection of standard xp spectra of the elements quickly reveals what many of us recognise from experience: That the intensity removed by the Shirley background differs from one element to another. Over the past few years, working with Pr.A.M.Salvi, we have shown that this part of the background structure varies in a systematic manner across a row of the periodic table. In this review we bring together results published in several journals@footnote 2-6@ in an attempt to give a unified account of the progress so far made. It will be shown that the intensity of the background can be distinguished from the Tougaard, extrinsic loss, background and characterised by a single parameter. This 'shape' parameter can be of value in peak fitting, especially when fitting over lapping peaks as occurs with oxide films on metals. There is also an element of chemical state information contained in the peak itself. For example we have shown that when aluminium participates in the formation of an aluminide with one of the 3d transition metals, then the aluminium gains the background imprint typical of the 3d elements. Similar findings occur in the formation of other covalent compounds and in the chemisorption of molecules to transition metal substrates. In conclusion the review will show that the Shirley background, far from being part of the spectrum to be discarded, actually contains information of a secondary nature which can be useful in interpretation of the primary analytical results. @FootnoteText@@footnote 1@S. Tougaard, Applied Surface Science, 100/101, pp 1-10 (1996) @footnote 2@D.A. Shirley, Phys.Rev.B, 5 4709 (1972) @footnote 3@Anna Maria Salvi and James E Castle, J. Elec Spec & Related Phenomena, 94 pp 73-88 (1998) @footnote 4@Anna Maria Salvi and James E Castle, "The intrinsic asymmetry of Photoelectron Peaks: Dependence on Chemical State and Role in Curve Fitting", J. Elec Spec & Related Phenomena, 95 pp 45-56 (1998) @footnote 5@J.E.Castle, S.J.Greaves, M.R. Guascito, and A.M.Salvi, "A New Probe of Bonding States in Intermetallic Compounds" Phil Mag. 79, pp 1109-1129 (1999). @footnote 6@J.E.Castle, A.M.Salvi*, M.R. Guascito, "A Substrate-Related Feature in the Loss Structure of Contamination-C1s" Surface and Interface Analysis, 27, 753 - 760 (1999) @footnote 7@J.E.Castle, H.Chapman-Kpodo, A.Proctor** and A.M.Salvi*"Curve-Fitting in XPS Using Extrinsic and Intrinsic Background Structure" J.Elec.Spec.and Rel Phenomena, 106 pp 65-80 (1999)

9:00am MC-WeM3 Formation of Potentially Protective Oxide-free Phosphate Films On Titanium Characterized by Valence Band X-ray Photoelectron Spectroscopy, J.A. Rotole, Kansas State University; K. Gaskell, Nottingham Trent University, UK; A. Comte, Ecole Nationale Superieure de Chimie de Clemont-Ferrand, France; P.M.A. Sherwood, Kansas State University

This paper reports the results of a continuing study focused on preparing novel surface chemistries on metal surfaces. In this paper we report how it is possible to prepare oxide-free titanium metal surfaces protected by a film consisting of phosphate. The surface is prepared by electrochemical treatment in an anaerobic cell which allows electrochemistry to be conducted on samples located in a vacuum system attached to an X-ray photoelectron spectrometer. When a clean metal surface is subjected to

electrochemical treatment in aqueous orthophosphoric acid an oxide-free phosphate film can be formed on the metal which is stable on subsequent air exposure. Compositional variations were found with potential and other factors. Identical electrochemical treatment of as received titanium foil in atmosphere yielded samples that had a surface consisting largely of oxide. The chemical composition of these surface films was studied by core level and valence band X-ray photoelectron spectroscopy. Valence band photoemission interpreted by band structure calculations was found to be especially effective in understanding subtle differences in surface chemistry, enabling the clear identification of phosphate (being able to distinguish between orthophosphate and metaphosphate films) and its distinction from surface oxide.@footnote 1@ @FootnoteText@ @footnote 1@ This work was funded by the National Science Foundation under grant CHE-9421068.

9:20am MC-WeM4 Chemometric Approaches to the Analysis of Surface Chemical Image Data, K.G. Lloyd, D.J. Walls, G.S. Blackman, N. Tassi, J.P. Wyre, E.I. DuPont de Nemours and Co., Inc. INVITED

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) provides a mass spectrum from the topmost 10-20 Angstroms of a sample, which is in effect a composite of mass spectra from all species that co-exist at the surface. This makes it difficult to track surface compositional changes in multi-component systems, especially when molecular ions are not observed. In the area of chemical imaging, the generally comparable secondary ion yields from most organic species result in little/no contrast observed in total ion images of organic/polymeric samples. Recent advances in technology now allow us to acquire an entire spectrum at each image pixel. This approach results in a huge amount of data and requires an objective, robust, and automated means of data analysis. For all these reasons, chemometric methods such as Principal Components Analysis (PCA) and Partial Least Squares (PLS) have come to play an important role in surface characterization, not just for ToF-SIMS, but for all the surface chemical imaging techniques. We have had considerable success with the use of chemometric approaches for visualizing chemical contrast in chemical images from ToF-SIMS, Raman, and ESCA data. Our work has focused on how to take advantage of the complementary information content of these data sets. This talk will present examples of how we are using these multivariate statistical techniques today, and how we might expect to use them in the future.

10:00am MC-WeM6 Multivariate Analysis of TOF-SIMS Data of Dodecanethiol SAMs: Detailed Spectral Analysis and Insight Into Fragmentation, D.J. Graham, B.D. Ratner, University of Washington

The analysis of novel engineered surfaces will require detailed, molecular specific characterization methods. The power of multivariate analysis in extracting such detailed information from TOF-SIMS spectra of a time series assembly of dodecanethiol SAMs was studied. PCA analysis of the negative spectra showed a relative increase in the intensity of molecular ion clusters and low mass hydrocarbon fragments (C to C3) with increasing time. This trend was also reflected in the positive data where a relative increase of C to C4 hydrocarbon fragments was seen at longer assembly times. This increase was accompanied by a relative decrease in the intensity of C5 and above hydrocarbon fragments. To assure these trends were not just an artifact of the PCA analysis we plotted the original spectral data from the peaks involved in the above trends. These plots verified that the trends seen in the PCA analysis reflected actual trends in the TOF-SIMS data. This data suggests that as the SAM surface becomes more ordered and crystalline the emission of longer fragments from the thiol chains is reduced relative to the emission of short fragments. Thus PCA is extracting information about the interaction and energetics of the surface. Using the PCA trends, a multivariate ratio (SAMratio) was created. This ratio was applied to a completely different set of thiol SAMs of varying chain length and head group. A correlation was found between the SAMratio and the parachor of the surfaces. Therefore PCA analysis was able to determine real data trends that lead to insight into the TOF-SIMS fragmentation process and a direct correlation with a thermodynamic property of the surface. The ability to extract this type information has the potential to revolutionize TOF-SIMS analysis by unlocking the information within the TOF-SIMS fragmentation pattern that is not accessible from univariate analysis.

10:20am MC-WeM7 Z-dol PFPEs on Magnetic Recording Disks: A PLS Study of TOF-SIMS Spectra, A. Spool, K. Kuboi, R. Waltman, P. Kasai, IBM Corporation

Statistical methods were used to show how variations in the peak intensities in the TOF-SIMS spectra of Z-dol Perfluoropolyether (PFPE)

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lubricant deposited on magnetic recording disks vary with the properties of the lubricant. Partial Least Squares analysis of a large number of spectra successfully modeled variations in lubricant thickness, molecular weight and the ratio of the 2 main repeating units in the Z-dol copolymer. The peaks of most significance (largest absolute regression factor) for each model were then examined to relate fragment structures to the physical property being modeled. This in turn was used to further our understanding@footnote 1,2@ of the spectra themselves. @FootnoteText@ @footnote 1@ A. M. Spool and P. Kasai, Macromolecules 29, 1691 (1996). @footnote 2@ P. H. Kasai and A. M. Spool, J. Phys. Chem. B 102, 7331 (1998).

10:40am MC-WeM8 Exploration of the Time-of-Flight Secondary Ion Mass Spectra of Combinatorially Designed Polyarylates by using a Novel Multivariate Statistical Approach, *B.J. Tyler*, Montana State University; *A. Belu*, Physical Electronics

In this study, a novel multivariate data analysis method has been used to explore relationships in the TOF-SIMS spectra from a series of polyarylates, with well-controlled and systematically varying chemistry. A series of 16 polyarylates was prepared from 4 distinct tyrosine-derived dipheols and 4 aliphatic diacids. This series is a subset of a library of 112 polyarylates described by Brocchini et al. These materials which have well controlled and systematically varying chemistry are ideal for evaluation by surface analysis techniques. The effects of incremental increase in polymer backbone length and polymer side-chain length can be evaluated. SIMS spectra of these polymers have been investigated by Belu, et al. These polymers show a series of peaks which are shifted by a mass characteristic of the particular polyarylate chemistry. Although principal components analysis and other multivariate methods have proved to be a very powerful aid for interpreting SIMS spectra, patterns which are shifted by a mass unit are invisible to these methods. A novel approach to multivariate analysis has been developed which is sensitive to characteristic shifts in the mass spectra rather than solely to peak positions. Details of the multivariate method as well as results for the polyarylate polymer series will be presented. @FootnoteText@ @Footnote 1@Brocchini S, James K, Tangpasuthado V, Kohn J, JACS, 1997; 119(19): 4553-4554 @Footnote 2@Belu A, Brocchini S, Kohn J, Ratner B, Rapid Communications in Mass Spectrometry, in press.

Processing at the Nanoscale/NANO 6 Room 302 - Session NS+NANO6+MC-WeM

Nanomechanical and Interface Measurements Moderator: R.J. Hamers, University of Wisconsin, Madison

8:20am NS+NANO6+MC-WeM1 Surface Acoustic Wave Investigation by UHV Scanning Tunneling Microscopy, *P.U. Voigt, S. Krauß, E. Chilla, R. Koch,* Paul-Drude-Institut für Festkörperelektronik, Germany

Recently we have shown that the scanning tunneling microscope can also be used to investigate surface acoustic waves (SAW) of 35 MHz by adding a high frequency sinusoidal signal to the dc tip voltage.@footnote 1@ Due to mixing with the SAW oscillation at the tunneling gap the tunneling current contains both amplitude and phase information of the SAW. Here we report on the first UHV compatible version of this technique including provisions for sample transfer and in situ surface preparation. Since both signal-to-noise ratio and spacial resolution are significantly enhanced, the acoustic oscillation of single atoms and monoatomic steps can be investigated. At present SAW frequencies up to 500 MHz have been successfully fed into the UHV system. @FootnoteText@ @footnote 1@ E. Chilla, W. Rohrbeck, H.-J. Fröhlich, R. Koch, K. H. Rieder, Appl. Phys. Lett.61, 3107 (1992).

8:40am NS+NANO6+MC-WeM2 Q-Control: Characterizing Highly Sensitive Surface Structures with the AFM, *B. Anczykowski*, NanoAnalytics WWU Münster, Germany; *L.F. Chi, H. Fuchs*, Physikalisches Institut WWU Münster, Germany

When operating an atomic force microscope (AFM) in a dynamic mode the oscillation of the cantilever is influenced by non-linear interaction forces between the probing tip and the surface. In principle the instantaneous forces exerted on the sample while scanning the surface can be either repulsive or attractive. Experimental findings and corresponding computer simulations of the tapping mode show that by choosing appropriate system parameters the AFM can continuously be operated in the regime of net-attractive interaction forces. Thereby the risk of modifying the sample surface by the probing tip is minimized. However, in most cases the range

in which the system parameters have to be adjusted is rather narrow and therefore a stable operation of the AFM in this interaction regime is difficult to achieve. With the help of the Q-Control module it is possible to reduce the damping of the dynamic system, i.e. to increase the effective quality factor of the oscillating cantilever and thereby to enlarge the regime of net-attractive interaction forces.@footnote 1@ This method allows to minimize the forces exerted by the probing tip on the sample surface. Therefore by applying Q-Control delicate and highly sensitive surfaces, such as ultrathin organic layers or DNA structures, can be characterized with high resolution. @FootnoteText@ @footnote 1@B. Anczykowski, J. P. Cleveland, D. Krüger, V. B. Elings, and H. Fuchs, Appl. Phys. A 66, S885 (1998).

9:00am NS+NANO6+MC-WeM3 Traceability for Nanoscale Properties, L.P. Howard, J. Pratt, National Institute of Standards and Technology INVITED The accuracy of nanoscale materials properties measurements ultimately depends upon the accurate determination of many SI units. When measurements are pushed into the nano-scale, many difficult circumstances arise due to what may be effectively described as a poor signal to noise ratio. This talk will highlight work involving the integration of interferometers into scanned-probe microscopes and work in traceable, sub-micronewton force measurements. Interferometry provides us the means to realize the meter. Several applications of sub-nanometer laser interferometry will be presented in the context of scanned-probe microscopes. Atomic lattice spacings have been measured using interferometers, and the expanding role of the atomic lattice in scannedprobe microscope metrology will be explored. Nanonewton force measurements are the subject of a new NIST project with the goal of improving traceability below the micronewton level. The unit of force is derived from the SI base units. Extending force measurement accuracy to the nanonewton level can require a combination of difficult dimensional, mass and electrical measurements. Our development of an electromagnetic balance capable of interfacing to scanned-probe instruments will be highlighted. With this new instrument (and a related electrostatic balance), we will explore the practical limits of using an electrical representation of the newton while attempting to extend our traceability chain back to a purely mechanical realization of force using mass and the earth's gravitational acceleration.

9:40am NS+NANO6+MC-WeM5 Low Temperature Scanning Force Microscopy of the Si(111) 7x7 Surface and Site-specific Measurements of Tip-Sample Interaction Forces, *M.A. Lantz*, *H.J. Hug*, *S. Martin*, *A. Abdurixit*, *A. Baratoff*, *R. Hoffmann*, *P. Kappenberger*, *P.J.A. van Schendel*, University of Basel, Switzerland; *Ch. Gerber*, IBM Research Division, Zuerich Research Laboratory; *H.-J. Guentherodt*, University of Basel, Switzerland

A low temperature scanning force microscope (SFM) operating in a dynamic mode in ultra high vacuum was used to study the Si(111)7x7 surface at 7.2K. Not only the twelve adatoms but also the six rest atoms of the unit cell are clearly resolved for the first time with SFM. In addition, the first measurements of the short-range chemical bonding forces above specific atomic sites are presented. The data is in good agreement with first-principles computations and indicates that the nearest atoms in the tip and sample relax significantly when the tip apex is within a few Å of the surface.@footnote 1@ New experiments with non-reactive tips reveal atomically resolved images with surprisingly different contrast from those obtained with a reactive tip. Careful analysis of frequency and damping versus distance curves clearly shows the obtained contrast does not result from the formation of a covalent bond, however atomic resolution is still obtained. This strongly suggests that true atomic resolution can be obtained with a new type of tip-sample interaction. The physical nature of this interaction mechanism will be discussed and compared to theoretical models.@FootnoteText@@footnote 1@Lantz et al., Phys. Rev. Lett 84, 2642 (2000).

10:00am NS+NANO6+MC-WeM6 Simultaneous STM/nc-AFM Imaging and Force Spectroscopy of Si(100)-(2x1) Surface with Small Oscillation Amplitudes, *H.O. Ozer, A. Oral,* Bilkent University, Turkey; *J.B. Pethica,* University of Oxford, UK

We have used a new, fiber interferometer based, high force resolution nc-AFM to image the Si(100)(2x1) surface with atomic resolution, using very small tip oscillation amplitudes down to 0.5 ?pp. The lever is dithered with the small oscillation amplitude at a frequency below resonance and the changes in the oscillation amplitude recorded simultaneously with force gradient and STM topography. With this method we can measure the force gradients quantitatively. Simultaneous images of Force gradient and STM topography have been recorded as a function of tunnel current and bias

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voltage. The effect of tunnel current and bias voltage on the force gradient contrast will be presented. We have also present force-distance curves between tip and Si(100) surface, measured with sub-Angstrom oscillation amplitudes.

10:20am NS+NANO6+MC-WeM7 A Liquid Helium Temperature Ultrahigh Vacuum Dual-tip Scanning Tunneling Microscope, *H. Okamoto, D. Chen,* Rowland Institute for Science

A dual-tip scanning tunneling microscope (D-STM) is a powerful instrument for investigating dissipative, diffusive, or ballistic transport phenomena of electrons in nanoscale structures.@footnote 1@ Here we present an ultrahigh vacuum compatible D-STM system working at liquid helium temperature for these new potential applications. Coarse positioning system consists of five rigid and compact inertial steppers, which has mechanical resonant frequency of ~900 Hz after integration. Each stepper has embedded capacitive position sensors with sub-micron resolution. An efficient new method, which we call tri-plane method, is used to navigate the two tips to proximity. The whole D-STM system is installed in a homemade vapor-cooled helium cryostat with a very low evaporation rate of 1.25 liter/day without liquid nitrogen radiation shield. @FootnoteText@ @footnote 1@Q. Niu et al., Phys. Rev. B 51 5502 (1995).

Material Characterization Room 207 - Session MC-ThM

Polymer Characterization

Moderator: B.C. Beard, Akzo Nobel Chemicals

8:20am MC-ThM1 Quantification of Polymer Surface Composition Based on ToF-SIMS Data, *P. Bertrand*, Université Catholique de Louvain, Belgium INVITED

Time-of-Flight Secondary Ion Mass Spectrometry is nowadays intensively used for polymer surface characterization. The fingerprint nature of ToF-SIMS spectra acquired in static conditions is now well established. Characteristic molecular fragment ions can be used for identification of polymer and organic materials present at the surface. The aim of this presentation is to discuss some issues related to surface quantification with this technique. This is of special importance for applications where copolymers and polymer blends are involved. First, we will discuss the use of end group ToF-SIMS signals. Our recent results obtained on monodisperse polystyrene samples show that ToF-SIMS is very sensitive to end groups. Their intensity can be used, after appropriate calibration, to quantify molecular weight at the surface. Some end groups (sec-butyl) are seen to influence also the intensity of main chain fragments. This is due to a specific interaction with the first neighboring repeat unit. It consists in a mechanism of H transfer, with no long-range (intermolecular) influence. So, the end group signals allowed us to quantify the surface composition of polystyrene blends with close molecular weights but different end groups. Second, we will discuss the use of characteristic fragment intensity and intensity ratios for blend and copolymer surface quantification. For polystryrene / poly (2,6-dimethyl-1,4-phenylene oxide) blends, which are miscible and do not exhibit any surface segregation, the intensity of the characteristic ions is seen proportional to homopolymer bulk concentration, allowing a staighforward surface quantification. But for random copolymers, different situations are observed. For random styrene butadiene rubbers, an appropriate choice of ions leads to "bulk like" surface composition, as expected. However, styrene / methyl methacrylate random copolymers, exhibit strong matrix effects due to a specific interaction between adjacent species taking place during the secondary ion emission. This outlines the need of understanding the fragmentation pathways in order to use ToF-SIMS intensities for surface quantification. Another approach would be the use of "full spectrum" chemometrics multivariate methods.

9:00am MC-ThM3 Characterisation of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), R. Kersting, B. Hagenhoff, TASCON GmbH, Germany; D. Rading, E. Niehuis, ION-TOF GmbH, Germany In continuation of our ongoing studies concerning the characterisation of polymer additives in their respective host polymers we have concentrated on the investigation of the influence of the primary ion parameters on the emission behaviour of characteristic additive ions. The additives, mostly antioxidants, were incorporated into low densitiy polyethylene (LDPE) or spin coated onto virgin LDPE in concentrations between approx. 500 and 2000 ppm. Thus ion emission from thick polymer materials could be studied. Reference samples without the polymer host were prepared by spin coating the additives onto bare Si wafers. Both, monoatomic (Ga@super +@, Au@super +@) and polyatomic (SF@sub 5@@super +@, Au@sub 2@@super +@) ions were used for sample excitation. Additionally, the energy of the respective primary ions was varied between 1 and 10 keV. The talk will describe the influence of the respective primary ion parameter onto yield and efficiency of the desorbed secondary ions. The consequences for the quantification of polymer additives in "real world" samples will also be discussed.

9:20am MC-ThM4 Surface Composition of Poly(imidesiloxane) Copolymers Containing Multiple Siloxane Lengths, *C.M. Mahoney*, State University of New York at Buffalo; *J Rosenfeld*, *S.R. Rojstaczer*, Occidental Chemical Corporation; *J.A. Gardella*, State University of New York at Buffalo Polyimidesiloxane copolymers (SIM) are becoming increasingly important materials for microelectronic applications due to their excellent adhesive properties, low dielectric constants and good overall thermal and mechanical properties. Hence it is of importance to study the surface and interfacial properties of this polymer system. More recently it has been shown through depth profiling using Electron Spectroscopy for Chemical Analysis (ESCA) that an increase in the siloxane chain length will result in an increase in the thickness of the siloxane layer at the surface.@footnote 1@ The effect of incorporating two or more different siloxane segment lengths into the same copolymer system, on the surface properties, has not been investigated. It is of importance to determine whether or not there is preferential segregation of certain segment lengths over others in SIM copolymers containing multiple siloxane lengths. A series of poly(imidesiloxane) (SIM) copolymers, based a,w'on aminopropylpoly(dimethylsiloxane) (PDMS) of varying molecular weights, 2,2-bis(4-[4-aminophenoxyl]phenyl)propane (BAPP), and 4,4'-oxydiphthalic anhydride (ODPA) was synthesized in our laboratories. In this series, the total composition of PDMS was maintained at 10%, while the segment length composition of the PDMS was varied (e.g. 5% Mw = 252g/mol, 5% Mw = 832.5g/mol vs. 1% Mw = 252g/mol, 9% Mw = 832.5g/mol). This polymer series was analyzed using ESCA and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). Angle-dependent ESCA results suggest that there is preferential segregation of the longer PDMS segment lengths to the surface. ToF-SIMS can be used to further confirm the occurance of this preferential segregation. The peel strength of the polymer series to a standard Ni/Fe alloy 42 was measured , and the results correlate well with the ESCA and ToF-SIMS data. @FootnoteText@ @footnote 1@ Zhao, J; Rojstaczer, S.R.; Chen, J.; Xu, M.; Gardella, J.A. Macromolecules. 1999, 32(2), 455.

9:40am MC-ThM5 High Spatial Resolution XPS and FTIR: An Approach to 3-D Characterization of Polymer Blends, K. Artyushkova, G. Czwerniec, J.E. Fulghum, Kent State University; B. Wall, J. Koenig, Case Western Reserve University

Correlative XPS and FTIR studies of the complex structure of PVC/PMMA polymer blends will be presented. The comparable lateral resolution and real-time imaging capabilities of both techniques allow for a direct comparison of surface (XPS) and bulk (FTIR) measurements of polymer blends. In order to eliminate substrate influence and film-to-film variations, the same areas on the polymer films were analyzed by both methods. The effect of PMMA molecular weight on surface separation and segregation was evaluated using six blends with a constant PVC molecular weight and a PMMA molecular weight varying from 75 kDa to 2,132 kDa. The imaging capabilities of both techniques were used for a qualitative comparison of the heterogeneous structure of the blends, while a quantitative comparison of bulk and surface compositions utilized small area spectroscopy from XPS and FTIR. Based on the quantitative analysis, we can conclude that surface segregation of PMMA increases with increasing molecular weight. Comparison of Attenuated Total Reflectance (ATR) FTIR, bulk FTIR and large area XPS analyses provides adiditional information about component distrubution in the blend. The combination of highspatial resolution XPS and FTIR provides a more complete method for characterizing complex polymer films containing differing surface and bulk compositions. This work has been partially supported by NSF ALCOM (DMR89-20147) and 3M. The XPS was funded by a grant from the Keck Foundation and by NSF CHE-9613880.

10:00am MC-ThM6 Iron Metallization of Fluorinated Organic Films; A Combined XPS and AFM Study, S.R. Carlo, A.J. Wagner, D.H. Fairbrother, Johns Hopkins University

The evolution of the metal-organic interface during iron mediated metallization of fluorinated organic surfaces has been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). Poly(tetrafluoroethylene) (PTFE) and a semi-fluorinated self-assembled (CF@sub3@(CF@sub2@)@sub7@(CH@sub2@)@sub2@SH, monolayer CF-SAMs) formed on Au were used as substrates. Reaction of Fe resulted in defluorination of each film, production of a carbonaceous overlayer and exclusive formation of iron (II) fluoride. A metallic iron overlayer was formed concurrently with FeF2 during deposition on CF-SAMs and following extended iron exposures with PTFE substrates. X-ray treatment of metallized PTFE caused an increase of the FeF@sub2@ content in the metal-organic region. Ex-situ AFM measurements revealed that the frictional characteristics of the surface increase during the initial stages of metallization associated with defluorination and FeF@sub2@ formation. At higher Fe exposures the surface friction decreased as a metallic overlayer evolved. Results of metallization using other metals will also be presented.

10:20am MC-ThM7 Interactions of Cu(I) with the Surface of a Novel Poly(imidazole), A.L. Marsh, D.J. Burnett, University of Michigan; D.A. Fischer, National Institute of Standards and Technology; P.G. Rasmussen, J.L. Gland, University of Michigan

The surface of a novel poly(imidazole), polyvinazene, was characterized using both X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) at both the C-K-edge and N-K-edge.

Polyvinazene, which is based on the monomer 2-vinyl-4,5dicyanoimidazole, is a novel polymer which has a high temperature stability and can be easily processed from solutions in concentrated aqueous ammonia into thin, yellow films. XPS was used to determine the chemical composition of the polyvinazene surface, while NEXAFS was used to determine the structure of the polymer surface before and after copper doping. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between the specific bonds present in the polymer, so the bonding sites for Cu(I) can be determined. In addition, the orientation of the imidazole ring has been determined since resonance intensities for NEXAFS obey electric dipole selection rules. Based on NEXAFS experiments, Cu(I) interacts favorably with the amide N on the imidazole ring. Also, the imidazole ring is oriented close to the surface and away from the surface normal, which supports the claim that the polymer chains are linked together through hydrogen bonds. Determination of the bonding site of Cu(I) to the polymer and the structure of the polymer surface hopes to aid in design for materials such as sensors, catalysts, and metallized polymer films.

10:40am MC-ThM8 Study of Semicrystalline Poly(ethylene terephthalate) by Atomic Force Microscopy, *M. Kovar, U. Gorodzinsky, P.R. Norton,* University of Western Ontario, Canada

We studied the surface topography of isothermally crystallized polyethylene terephthalate (PET) films by atomic force microscopy (AFM). Annealing a flat amorphous PET film at 150 @super o@C produces a semicrystalline film which is rough on several length scales. We found good correlation of the height (3.5 nm) of small topographical features with the lamellar thickness determined by small angle X-ray scattering in previous studies. It was shown that larger agglomerates (large peaks) are multiples of small ones. The phenomenon is known as lamellar stacking. We hypothesize that the surface corrugation originates as follows: elevated (more crystalline) areas are created at the locations of crystallization nuclei. The polymer chains fold to create lamellar structures and pull "loose" ends out of amorphous regions. Subsequently, lamellar stacks grow using a similar mechanism forming the elevated regions and leaving recessed (less crystalline) ones behind Surprisingly, the density of the small topographical features is the same in the recessed and elevated regions, apparently indicating similar crystallinity, while interfacial force microscopy (IFM) data [J. Mater. Res. 12 (1998) 3565] show the elevated regions to be more crystalline. This apparent conflict results from the sensitivity of AFM phase imaging to only the outermost surface of the film compared to IFM, even for IFM indentation depths of a few nm. Therefore, the variations in the density of crystalline domains (lamellae) that are visible in AFM phase images represent a surface phenomenon that cannot be simply correlated with the state of sub-surface regions.

11:00am MC-ThM9 Morphology of Catalytically Formed Polyethylene on a Planar Model System for the Phillips (CrOx / SiO2) Catalyst, P.C. Thuene, J. Loos, P.J. Lemstra, Eindhoven University of Technology, The Netherlands; J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands, Netherlands

One of the neglected topics of polymerization catalysis is the so called nascent morphology of polyolefins which is the result of polymer formation below the melting temperature and simultaneous crystallization. Nascent polyolefins have special physical properties, which might be controlled and manipulated to enhance the processability of certain high performance polyolefins. Using a planar model system for the chromium on silica catalyst for ethylene polymerization we have obtained AFM images of polyethylene in the state of nascent morphology. By diluting the number of catalytically active sites on the model, individual islands of polymer, produced by single sites have been observed.

11:20am MC-ThM10 Nano-Mechanics of Polymer Surfaces, C. Steffan, H. Liu, **R.M. Winter**, South Dakota School of Mines and Technology

We report on the nano-mechanical properties (elastic modulus and time dependent phenomena) of polymer surfaces as they relate to polymer matrix composites. This work is prompted by the desire to engineer macroscopic polymer matrix composite properties by systematic variation of nano- and micro-scopic properties of the interphase. The interfacial force microscope, a scanning probe microscope, which utilizes a noncompliant force sensor is employed to characterize the surfaces. Forcedisplacement curves are obtained, from which, elastic modulus is determined using contact mechanics analysis. Creep and relaxation experiments are performed to characterize the time dependent phenomena of the polymeric surfaces. The surfaces are comprised of epoxy, amine curing agent, and amine coupling agent of systematically varied epoxy-amine equivalence ratios. These ideal interphases model the interphase found in polymer matrix-inorganic reinforcement composites and are used to reveal the relationship between chemistry and nano-mechanical properties. Fourier transform infrared spectroscopy is used to analyze the model interphase chemical composition as a function of amine-epoxy equivalence ratio. The FT-IR analysis and nano-mechanical results are correlated showing how elastic modulus and time dependent properties can be controlled by varying the chemistry and reaction conditions of the system. These data are compared to previously obtained elastic modulus profiles of the interphase in fiber reinforced epoxy matrix composites where the modulus was found to vary by 100% in a ~5 micron region surrounding the reinforcing fibers.

Surface Science Room 208 - Session SS1+MC-ThM

Oxide Applications and Oxidation

Moderator: E.I. Altman, Yale University

8:20am SS1+MC-ThM1 Synthesis and Characterization of Self-assembled Cu@sub2@O Quantum Dots on SrTiO@sub3@(001) Surface, Y. Liang, D.E. McCready, A.S. Lea, S.A. Chambers, S. Gan, Pacific Northwest National Laboratory

Self-assembled quantum dots have received much attention recently because their atom-like electronic and optical behavior can be tailored. One common problem with many quantum dots has been the poor chemical and thermal stability as most of them are made of conventional semiconductors. An alternative to this problem is to use oxide based quantum dots due to their superior stability. We have successfully synthesized self-assembled Cu@sub2@O quantum dots on SrTiO@sub3@ substrates using a molecular beam epitaxial method. The structure and chemical states of Cu@sub2@O quantum dots have been confirmed by xray diffraction and x-ray photoelectron spectroscopy (XPS). Reflection high energy electron diffraction (RHEED), atomic force mic roscopy (AFM), and high-resolution scanning Auger microscopy (SAM) show that formation of Cu@sub2@O quantum dots occurs after deposition of a few monolayers of Cu@sub2@O due to the large compressive lattice mismatches between Cu@sub2@O and SrTiO@sub3@. SAM reveals that the interdiffusion between Cu@sub2@O quantum dots and SrTiO@sub3@ is significantly less than many other quantum-dot systems. XPS further shows that the interfacial electronic structure of Cu@sub2@O/SrTiO@sub3@ exhibits the so-called the type-II heterojunction, i.e., the valance and conduction bands of Cu@sub2@O are both higher than that of SrTiO@sub3@. Consequently the photo-excited electrons and holes are spatially separated with holes being confined to Cu@sub2@O quantum dots and electrons confined to SrTiO@sub3@, a property important for photocatalysis and solar cell applications. We are currently using AFM-based surface potential measurements to elucidate the spatial charge separation behavior of this system upon photo-excitation at different wavelengths. @FootnoteText@ # Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

8:40am SS1+MC-ThM2 Correlation of Electronic Structure with Photoluminescence Properties in Oxidized Silicon Nanoclusters, J.A. Carlisle, I. Germanenko, Y. Pithawalla, M.S. El-Shall, Virginia Commonwealth University

The relationship between morphology, band-gap size, and photoluminescence data in surface-oxidized silicon nanoclusters is established using photon-yield measurements at the Advanced Light Source. After removal from the growth chamber, photoluminescence (PL) results indicate that as the clusters oxidize, the main PL peak moves from 1.83 eV to 1.94 eV in energy. The central focus of this work is to establish the origin of the PL peak, whether it arises due to quantum size effects or due to the formation of suboxides as the clusters oxidize. The changes in the morphology and bonding structure of the clusters were established using soft-x-ray fluorescence spectroscopy (SXF) and photon-yield nearedge x-ray absorption fine structure (NEXAFS) spectroscopy, which probe the element-specific density of occupied (SXF) and unoccupied (NEXAFS) electronic structure. Our finding is that the as-synthesized nanoclusters consist of a pure, crystalline Si core within a nearly pure SiO2 shell. Very few suboxides are present, and the oxidation process does not lead to an increase in the amount of suboxides present within the particles. As the nanoclusters oxidize, the radius of the crystalline core decreases in size. which gives rise to the change in the position of the PL signal.

9:00am SS1+MC-ThM3 The Behavior of Ultrathin Al@sub 2@O@sub 3@ Films in Very High Electric Fields: STM-induced Pitting and Dielectric Breakdown, N.P. Magtoto, C. Niu, J.A. Kelber, University of North Texas The behavior of ultrathin oxides under high electric fields is of critical importance to areas as diverse as microelectronics (gate oxides, magnetoresistance devices) and corrosion. We report the use of high electric fields applied via the STM to induce pits and dielectric breakdown in ultrathin @gamma@'-Al@sub 2@O@sub 3@ films (7 Å thick) grown on Ni@sub 3@Al(111) substrates in UHV. Voltage pulses (bias voltages of 1-6 V, either polarity) are applied to a specific location on the oxide surface with the feedback current loop operative to prevent tip/sample physical interaction. Subsequent imaging at 0.1 V bias voltage and 1 nA feedback current reveal the effects of high field on surface composition and topography. Results show that dielectric breakdown occurs at a field of 12.3±0.7 MV/cm. Breakdown is marked by the creation of an area ~20 nm high and 100 nm wide and the loss of the insulating nature of the oxide as deduced from I/V spectroscopy. Once the threshold breakdown voltage is reached, the STM tip retracts precipitously (~20-25nm) from the sample surface due to the onset of the leakage current. At fields ~ 60 % of breakdown, small pits in the oxide that are 0.4-0.8 nm deep can be created. Repeated application of this field within the pit will cause dielectric breakdown, even though the same field will not induce breakdown in regions away from the pit. The results provide direct evidence of the ability of localized defects to decrease the barrier to dielectric breakdown in an ordered oxide film.

9:20am SS1+MC-ThM4 Oxidation of Sn/Pt (111) Surface Alloys under UHV Conditions- Formation of Ultrathin SnOx Films on Pt(111), *M. Batzill, D. Beck, B.E. Koel*, University of Southern California

Platinum-tin systems are important as hydrocarbon reforming catalysts when supported on alumina. The tin may however exist in oxidic form and thus SnOx may be responsible for the altered catalytic properties of the Sn-Pt system compared to pure Pt, rather than alloying of Sn and Pt. In order to study ultrathin SnOx overlayers on Platinum we have oxidized both ordered Sn/Pt(111) surface alloys (the p(2x2) and the (sqr3 x sqr3)R30 alloy structure) using NO2 as an oxidant. The structure, chemical state and thermal stability of the oxide films have been examined by LEED, STM, XPS, AES and TPD. Oxidation of p(2x2) alloy results in a discontinuous monolayer thick SnOx film that decomposes at 760 K. Oxidation of the (sqr3 x sqr3)R30 in contrast forms a thermally more stable continuous overlayer that shows two ordered surface phases depending on the annealing temperature. These structures have been analyzed using LEED and STM. The chemical activity of these surfaces was probed by small hydrocarbon molecules and CO.

9:40am **SS1+MC-ThM5 Monte Carlo Simulation of Initial Al(111) Oxidation**, *D.E. Oner*, *R. Chakarova, I. Zori@aa c@, B. Kasemo*, Chalmers University of Technology, Sweden

In this work a Monte Carlo simulation technique is applied, exploring the influence of several models for O@sub 2@ dissociation on the initial Al(111) oxidation. The primary experimental data motivating this are the STM studies by Brune et al. (J. Chem. Phys. 99 (1993) 2128). The simulations are performed to gain more insight into the kinetics of the oxidation process. The Monte Carlo simulation is based on the lattice-gas approach using the Metropolis algorithm. The simulations assume alternatively "normal" dissociation (deposition of O atoms at adjacent surface sites), hot dimer dissociation (widely separated O atoms due to hot dissociation fragments) or abstraction (one of the separating O atoms performs a ballistic motion away from the surface). Further elements of the model are surface mobility, attractive forces between adsorbed O-atoms (i.e. adsorbate-adsorbate interaction), and in-diffusion of O atoms into the 2nd and deeper layers to form 2D and 3D oxide. Input data are, when available, taken from experiments or first-principles calculations. The results of this computational work are compared to the experimental results by Brune et al. The calculated surface configurations of chemisorbed O-atoms at 300 K in the low coverage regime, based on the hot dimer dissociation model, are in good agreement with the observed experimental STM data. The simulations of thermal annealing of chemisorbed oxygen islands are in fair agreement with the observed island kinetics by Trost et al. (J. Chem. Phys. 108 (1998) 1740). In the latter case, the O-O interaction strength is a crucial parameter. The present simulation model provides a useful platform for further simulations of Al oxidation. @FootnoteText@ Keywords: Monte Carlo simulation, surface oxidation, oxide nucleation and growth, hot chemisorption, metal oxidation, kinetics, aluminium.

10:00am SS1+MC-ThM6 Thin Epitaxial Oxide Films and Interfaces for Advanced Microlectronics and Magnetics, S.A. Chambers, Pacific Northwest National Laboratory INVITED

Metal oxides constitute an extremely diverse class of materials, with virtually all types of electronic and magnetic behavior represented. These materials thus possess many properties that make them unique and potentially important for future technologies. No other class of materials exhibits such a wide range of behavior: band gaps spanning the visible and UV; electronic properties ranging from superconducting to metallic to semiconducting to insulating; magnetic properties ranging from ferromagnetic to antiferroma gnetic; and dielectric properties ranging from low-k to ferroelectric and piezoelectric. In addition, metal oxides exhibit a wide range of crystal structures, including spinel, perovskite, and corundum. As a result, a variety of heteroepitaxial structures can be designed and synthesized. In this talk, I present recent results on three heteroepitaxial oxide systems that illustrate the fascinating interface physics and potential technological advantages of these materials: (1) SrTiO@sub 3@(001)/Si(001), (2) CoFe@sub 2@O@sub 4@(001)/MgO(001) and, (3) MgO(001)/Ag(001) and Pt(111)/@alpha@-Cr@sub 2@O@sub 3@(0001)/Pt(111)/@alpha@-Al@sub 2@O@sub 3@(0001). System 1 is of considerable interest as a high-k gate oxide in next-generation MOSFETs.@footnote 1@ System 2 is a model that permits us to investigate thin films of what appears to be a very promising high-magneticanisotropy, insulating ferrimagnet.@footnote 2@ System 3 allows us to examine the effects of polarizable metals on the optical, electronic and magnetic properties of ultrathin oxides that are within electronic screening lengths of the metal.@footnote 3@ Structural, electronic and magnetic properties of these systems, all grown by molecular beam epitaxy, will be presented. @FootnoteText@ @footnote 1@ R.A. KcKee et al., Phys. Rev. Lett. 72, 2741 (1994). @footnote 2@ Y. Suzuki et al., Appl. Phys. Lett. 68, 714 (1996). @footnote 3@ S. Altieri et al., Phys. Rev. B59, R2517 (1999).

10:40am **SS1+MC-ThM8 The Oxidation of Pd(100)**, *G. Zheng*, *E.I. Altman*, Yale University

Motivated by interest in Pd as a catalyst for oxidation reactions and the catalytic combustion of CH@sub 4@, the interaction of Pd(100) with O@sub 2@ was studied using LEED, STM, and TPD. Initial exposure of Pd(100) to O@sub 2@ at room temperature resulted in a (2x2) structure that saturated at an oxygen coverage of 0.25 ML (1 ML = 1 O/Surface Pd) following 30 L exposure. Further exposure to O@sub 2@ at room temperature resulted in a mixture of (2x2) and p(5x5) LEED patterns, which persisted until the oxygen coverage reached a saturation value of 0.68 ML. Increasing the exposure temperature to 475 K resulted in the p(5x5) structure in the oxygen coverage range of 0.60-0.80 ML, which transformed into a (@sr@5x@sr@5)R27° pattern beyond 0.80 ML. TPD experiments revealed four oxygen desorption features from Pd(100) following exposure to O@sub 2@, including peaks at 800 K, 700 K and 650 K, as well as a low temperature oxygen shoulder at 600 K. The highest temperature peak corresponds to the (2x2) chemisorption structure, and the other two peaks fall into the regime where p(5x5) and (@sr@5x@sr@5)R27° patterns appear. The three peaks saturated in sequence, and the low temperature shoulder showed up before saturation of the 650 K peak. These results indicate at least four distinct oxygen states on Pd(100). Upon annealing, the (@sr@5x@sr@5)R27° LEED pattern transformed into the (2x2) pattern without stepping through the p(5x5), and the p(5x5) structure converted into the (2x2) pattern. The temperature dependence of oxygen up-take was also studied. Oxygen was found to have the highest sticking coefficient on Pd(100) at 550 K. STM studies revealed the atomic structures of various oxygen phases on Pd(100), as well as their relative reactivity towards reduction by in-situ monitoring of the surface during exposure to CO and propylene.

11:00am SS1+MC-ThM9 Surface Characterization of Oxidative Corrosion of U-Nb Alloys, D. Kelly, Los Alamos National Laboratory; W.L. Manner, Union Carbide Corporation; J.A. Lillard, R.J. Hanrahan, Jr., M.T. Paffett, Los Alamos National Laboratory

We have studied the relative rates of oxidative corrosion of U-Nb alloys containing 2 to 8 wt. % Nb, using X-ray photoelectron spectroscopy (XPS) and depth profiling by sputtered neutrals mass spectroscopy (SNMS), The alloys have been characterized after exposure to dry and humidified air (up to 50% relative humidity) at temperatures from 25 to 125 @super o@C, and exposure to electrochemical solutions. XPS studies of U-6 wt. % Nb following oxidation at 300 K with oxygen indicate formation of a thin overlayer of stoichiometric UO@sub 2@ intermixed with Nb@sub 2@O@sub 5@. This same stoichiometry is exhibited upon oxygen treatment at 500 K, however, niobium is much less oxidized, forming a

mixture of NbO and Nb. SNMS depth profiling indicates that oxides formed using oxygen are thicker than those obtained using water. The formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to enhance corrosion resistance by preventing diffusion of oxygen and/or hydroxyl species into the oxide/metal interface region. Tube furnace oxidation of the U-Nb alloys produces oxide layers comprised of UO@sub 2@ and Nb@sub 2@O@sub 5@ under all experimental conditions used. The thickness of the oxides increased with treatment time and temperature, but decreased with increasing Nb alloy content. For example, a 48 hour treatment at 75 @super o@C and 50% relative humidity results in oxide thickness on U-2%Nb that are three times that on U-8%Nb. Electrochemical oxidation of U-Nb alloys facilely generated UO@sub 3@ and Nb@sub 2@O@sub 5@ oxide layers with thicknesses qualitatively similar to thermal oxidation results. U-Nb alloys electrochemically oxidized at low pH exhibit oxide layers with near-surface regions (50 ???) enhanced in Nb content, as compared to the bulk material. Surface UO@sub 3@ was not readily reduced upon exposure to molecular D@sub 2@; however, D atoms facilely reduced UO@sub 3@ to UO@sub 2@.

11:20am SS1+MC-ThM10 AFM Non-contact Imaging of Titaniumdioxid at Variable Temperatures, A. Bettac, P. Güthner, S. Molitor, A. Feltz, T. Berghaus, Omicron Vakuumphysik GmbH, Germany; A.W. Grant, S. Fain, University of Washington

True atomic resolution in AFM non-contact mode has been achieved on several samples. Here we present first images on a TiO@sub 2@ (110) single crystal at sample temperatures from as low as 50 K up to 400° C. A new instrument design allows to perform true atomic resolution AFM images in a temperature range from 25 K to 1000 K. The sample was prepared by several cycles of ion sputtering and annealing in UHV. After this treatment it is conducting enough to perform STM measurements for controlling the quality of surface preparation. Non-contact AFM images on the TiO@sub 2@ (110) crystal show atomic resolution across mono-atomic steps. The surface is mostly showing a 1x1 reconstruction. At the step edges, lines with 1x2 reconstruction are starting. These lines may be associated with the formation of Ti@sub 2@O@sub 3@ strings along the surface. The density of areas with 1x2 reconstruction is increased with the annealing temperature which can be explained by the desorbtion of oxygen during the annealing process. Atomic resolution images on the TiO@sub 2@ (110) crystal were achieved at low temperatures down to 50 K sample temperature and at high temperatures up to 400° C.

11:40am SS1+MC-ThM11 Plasma Oxidation as a Tool to Design Oxide Films at Low Temperatures, *R. Schennach*, Lamar University; *D.G. Naugle*, Texas A&M University; *H. McWhinney*, Prairie View A&M University; *D.L. Cocke*, Lamar University

Interfacial oxidation is an established approach to produce surface thin films for catalysts, corrosion, ware protective coatings and electronic structures. The three main oxidation methods: thermal, anodic and plasma, still lack adequate fundamental physical-chemical models that can allow film design, particularly on alloys. Plasma oxidation of a CuZr alloy is studied using XPS (X-ray Photoelectron Spectroscopy). The dependence of the resulting oxide film on alloy composition and sample temperature during plasma oxidation is investigated. In contrast to thermal and electrochemical oxidation heads to the formation of a zirconium oxide film, plasma oxidation leads to the formation of a copper oxide or metallic copper over layer depending on temperature and copper concentration in the bulk. It is shown that plasma oxidation can be used to design oxide films at room temperature, which require high temperatures using thermal oxidation.

Material Characterization Room 207 - Session MC-ThA

Evolving Technologies in Surface Analysis Moderator: E. Garfunkel, Rutgers University

2:00pm MC-ThA1 In-situ Control of Wet Chemical Etching of Patterned Bulk-GaAs using Real Time Spectroscopic Ellipsometry, *S.-J. Cho*, *P.G. Snyder*, University of Nebraska, Lincoln; *C.M. Herzinger*, *B. Johs*, J. A. Woollam Co.

High controllability and reproducibility of the etching process are regarded as key factors for the success of device fabrication. In-situ optical techniques such as real time spectroscopic ellipsometry (RTSE) may be used to control etch depth as well as determine etch rates. We have previously demonstrated control of etch depth through the cap and AlGaAs layers of an unpatterned GaAs/AlGaAs/GaAs heterostructure. In this work, in-situ monitoring and control of etch depth in patterned bulk GaAs was studied using RTSE. Patterning is necessary for monitoring etching in the bulk substrate (unlike etching in thin layers), since without it optical interference would not occur. Patterned (lines or squares) pieces of bulk GaAs wafer were etched in a citric acid-hydrogen peroxide-deionized water etch solution. The grating periods were 10, 20, or 40 µm. During the etching RTSE data were taken and simultaneously analyzed, and etching was stopped when the fitted etch depth reached a predetermined value (for example, 1.6 µm). The final etch depth was confirmed by ex-situ spectroscopic ellipsometry and SEM analyses. The etch rate of bulk GaAs was also determined based on the real time fit results. The model currently used for RTSE data analysis assumes spatial coherence of the light beam over an area large compared with the grating period, but does not explicitly include diffraction effects. This model appears to work well for grating periods in the range 20~40 µm. These and the previous results show that RTSE can be used to control etch depth in both thin layers and the substrate. Research supported by AFOSR Grant #49620-96-1-0480.

2:20pm MC-ThA2 In- and Ex-situ Characterization by Second-harmonic Generation of the RPECVD Oxidation and Nitridation of Silicon and Ex-situ Comparisons with Other Optical Techniques, G.D. Powell, R.S. Johnson, G. Lucovsky, D.E. Aspnes, North Carolina State University

We report azimuthal dependences of second-harmonic generation (SHG) spectra obtained in-situ and ex-situ from 800 to 900 nm of oxide, nitride, and oxynitride interfaces formed by Remote Plasma Enhanced Chemical Vapor Deposition (RPECVD) on singular and vicinal Si(111) substrates. Spectral dependences are linear over this limited spectral range that make it possible to compare slopes and intercepts among the different processes. SHG measurements were performed for both p-p and p-s polarization configurations. We found only slight variations for the terminations except for one parameter describing the electric field phase differences for the step for the nearest direction. We also observe significant differences, of the order of 10 meV, in ellipsometrically determined apparent critical point energies and broadening parameters under various processing conditions. Finally, we advance beyond a purely phenomenological model of a signal associated with the bond symmetries to a more physical model that directly connects the macroscopically measured far-field intensity to the dipole radiation from the anharmonic bonds.

2:40pm MC-ThA3 What Is Needed and What Is Practically Available for Small Area, Small Depth, Chemistry Sensitive Analysis in the Semiconductor Wafer Processing Industry, C.R. Brundle¹, Applied Materials INVITED

The continuing health of the semiconductor industry depends on the insatiable demand to reduce CD (critical dimensions), eg gate length and thickness, interconnect line dimensions, barrier layer thickness. For needed analytical methods, this translates into improved spatial resolution (area and depth). In addition, because of (a) the drive towards where everything is interface, (b) the introduction of many "non-traditional" materials (eg Cu, low k, high k), and (c) a general push towards even higher yields, the need for chemical state information has increased and will continue to increase. In this paper I review, from a wafer processing perspective, what analytical instrumentation is needed, compared to what is actually available. I also try to define the differences in instrumentation needs for "analytical laboratory" usage and "metrology usage." Though I will concentrate on

techniques which are thought of as surface sensitive (eg electron spectroscopies), there is no longer any practical reason to distinguish these from techniques which are not mainly thought of as surface sensitive (eg EDS, Raman). The reason is twofold. First, we need information over a range of depth. Second, such techniques can be, and have been, made more surface/interface/small area applicable than has been traditional. Finally, since our particular interests have to do with small particle defects during wafer processing, I will give examples to illustrate our current capabilities and our unmet needs.

3:20pm MC-ThA5 Dopant-Induced Contrast of Si Devices in PEEM, V.W.

Ballarotto, K. Siegrist, R.J. Phaneuf, E.D. Williams, University of Maryland Spatial variation of doping, such as in a pn junction, produces contrast in photoelectron emission microscopy (PEEM) that may be useful for dopant profiling, failure analysis, or as a processing diagnostic of Si. The contrast mechanism arises from reduction of the effective photothreshold when Si is heavily to degenerately doped. We report on a quantitative investigation of doping-induced contrast in PEEM images of Si devices. The calibration samples consist of p-type (B) stripes of different dopant concentrations and line separations, written on n-type (N@sub d@=10@super 14@ cm@super -3@) Si(001) substrates. Using a near-threshold light source, we find that the signal intensity increases monotonically with B concentration over a range of doping from 1x10@super 18@ to 6x10@super 20@ cm@super -3@. The measured intensity ratios are in good agreement with a calculation based on photoemission from the valence band. In addition, PEEM images of memory chip devices acquired through a 2000 Å SiO@sub 2@ layer and showing clear doping contrast will be shown. This depth sensitivity and the potential for improved doping contrast will be discussed in terms of the incident photon energy above threshold. This work is supported by Advance Research Development Activity (ARDA) grant number: 97-C-3048.

3:40pm MC-ThA6 Elemental Mapping of Sub-µm Particles and Structures by LASER-SNMS and TOF-SIMS, *F. Kollmer, R. Kamischke, R. Ostendorf,* Physikalisches Institut der Universitaet Muenster, Germany; *H. Bender,* Materials and Components Analysis Group IMEC; *A. Benninghoven,* Physikalisches Institut der Universitaet Muenster, Germany

Sputtering-based surface mass spectrometry as SIMS or Laser-SNMS combines high sensitivity with high lateral resolution, provided a high fraction of sputtered particles is ionized and a finely focused primary ion beam is applied. For sub-µm characterization the transformation probability of a surface atom into an ion should be optimized. The large fraction of sputtered neutrals and their efficient laser-postionization result in high Laser-SNMS sensitivities. The use of a time-of-flight (TOF) mass spectrometer guarantees parallel mass registration at high transmission. We report on recent results of TOF-SIMS and Laser-SNMS characterization of sub-µm particles. The analyzed particles include Al@sub 2@O@sub 3@, Fe@sub 2@O@sub 3@ and CeO@sub 2@ with diameters down to 15 nm. On the base of these results we compared both techniques one with the other and in addition with Scanning Auger Microscopy (SAM). The know how gained from these investigations was applied to supported metal catalysts and other sub-µm structures such as magnetic heads. By applying a combined TOF-SIMS/Laser-SNMS instrument, a direct comparison of both techniques was possible. The use of a 30 keV finely focused Ga@super +@ source and a time-of-flight instrument guarantees high lateral (@>=@80 nm) and mass resolution at high transmission. For nonresonant postionization an excimer-laser (193 and 248 nm) was applied. SAM characterization was carried out in a VG 350 F instrument. We determined useful yields, as a measure of sensitivity, for a variety of mono-elemental metal samples. The obtained useful yields in the order of 10@super -2@ (SNMS) and 10@super -3@ (SIMS) allow to analyze structures well below the spot size of the primary ion beam. We found higher elemental sensitivities for TOF-SIMS and especially Laser-SNMS compared to SAM. Quantification was possible by the use of SAM and Laser-SNMS, the latter additionally allows to estimate the total amount of material in a particle.

4:00pm MC-ThA7 Dose Quantity Effects on Nano-scaled Dot Size and Depth Profile of Gallium Implantation on Silicon by Finely Focused Ion Beam, L. Shen, L.C. Feldman, R.F. Haglund Jr., R.A. Weller, Vanderbilt University

In a FFIB(Finely Focused Ion Beam) System, the beam current is controlled by choosing the aperture, which determines the spot size on nanomaterials fabrication. The total beam dose is determined by beam current intensity, beam duration time and scan repeat rate. The total dose determines the ultimate feature size. We have investigated the total dose

¹ Featured Speaker - Science and Technology in the 21st Century Thursday Afternoon, October 5, 2000

effects on apparent spot size and depth profiles by controlling beam current intensity, beam dwell time and/or scan times. In particular we report the AFM apparent spot size for a single scan as a function of dwell time and compare to theoretical estimates. We also report apparent spot size as a function of number of scans. Achieving minimum spot size is critical for creating nano-scale feature size and depth profile.@footnote 1@ @FootnoteText@ @footnote 1@Supported in part by the National Science Foundation under grant DMR-9871234 and by the U.S. Army Research Office under contract DAAD-19-99-1-0283.

4:20pm MC-ThA8 Ion Channeling Effects on the FIB Milling of Crystalline Materials, B.W. Kempshall, S.M. Schwarz, University of Central Florida; B.I. Prenitzer, Lucent Technologies; L.A. Giannuzzi, University of Central Florida; R.B. Irwin, F.A. Stevie, Lucent Technologies

The focused ion beam (FIB) instrument is being used as a fundamental tool for the investigation of ion beam/material interactions. One particular topic of interest is the effects of ion channeling on the sputtering behavior of Si and Cu. Although applications involving the FIB milling of Si are straightforward, the FIB milling of Cu may be complicated by effects such as the development of milling induced topographical features. The difference in milling behavior between Si and Cu may be attributed to the inherent physical properties of materials that influence the sputtering yield. As ions channel deep into the target along preferred crystallographic directions, a corresponding decrease in sputtering yield is observed. In this presentation, the effects and the mechanism of Ga+ channeling in Cu is used to illustrate the relationship between the sputtering yield, the quality of FIB mill cuts, and the surface characteristics of FIB milled Cu for various crystallographic orientations. The correlation between the theoretical Lindhard-Onderdelinden axial channeling model and the observed ion channeling contrast in the FIB milling of Cu is investigated.

4:40pm MC-ThA9 XPS Analysis of Si Samples Prepared Using the FIB Lift-Out Technique, A.C. Ferryman, J.E. Fulghum, Kent State University; L.A. Giannuzzi, University of Central Florida; F.A. Stevie, Cirent Semiconductor

Si samples prepared using the FIB lift-out technique were analyzed using high spatial resolution XPS imaging and spectroscopy. Sample mounting and associated problems with sample location will be discussed. The analyzed samples were 5 x 20 micron cross-sections mounted on carbon-coated TEM grids. Results indicate that XPS data can be acquired from FIB lift-out samples. XPS provides new information about the effect of Ga surface residue on the Si surface.

5:00pm MC-ThA10 Determining Area Selectivity in Small-Area XPS Analysis@footnote 1@, D.R. Baer, M.H. Engelhard, Pacific Northwest National Laboratory

For many real world applications, the ability of new XPS instrumentation to examine small features can be a tremendous advantage. Most users and vendors define the spatial resolution of these instruments in a similar relatively simple and useful fashion involving resolution of a sharply defined edge or grid. However, it can be useful and is sometimes important to know the area of a sample that actually contributes to the XPS spectra measured. We have found that measurements on well defined "dots" of a material on a substrate provide a useful experimental approach for determining the area of a specimen that contributes to a small area XPS measurement. The method provides a way to verify instrument operation and set up conditions and the adequacy of specimen alignment procedures for small area analysis. Data collected from a Phi Quantum 2000 and a Kratos Axis 165 demonstrate that the method can provide information about signal generated from regions outside of an intended analysis area. The method also demonstrates that commonly used methods of defining resolution produce values that can be 2 or 3 times smaller than the diameter of the area truly analyzed by a spectrometer. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Geosciences Program, The measurements were made in the Environmental Molecular Sciences Laboratory, a DOE User facility operated for the USDOE by Battelle Memorial Institute.

Processing at the Nanoscale/NANO 6 Room 302 - Session NS+NANO6+MC-ThA

Near-field Optics and Photonics

Moderator: Y. Kuk, Seoul National University, Korea

2:00pm NS+NANO6+MC-ThA1 Optical Sieves - How to Get the Light through Subwavelength Holes, T.W. Ebbesen, Louis Pasteur University, France INVITED

Metallic films perforated with sub-wavelength holes (~150 nm) can transmit the light with an efficiency thousand times larger than what theory predicts for single holes. The efficency can even be larger than the fractional area of the holes, which means that even the light falling beside the holes emerges on the other side of the sample. This extraordinary transmission is due to the coupling of the incident light with the surface plasmons of the film. The transmission spectrum contains peaks attributed to surface-plasmon modes that depend on both the symmetry and the 2D lattice parameter of the surface corrugation. We have shown that this phenomenon can also be used to tune and enhance the transmission of single subwavelength aperture. These results have broad fundamental and practical implications and show that, with modern fabrication techniques, surface plasmons can be engineered and controlled to yield unique optical properties.

2:40pm NS+NANO6+MC-ThA3 Near-field Optical Measurements of Two Types of the Super-resolution Near-field Structures, *D.P. Tsai*, National Taiwan University, Taiwan; *W.C. Lin*, National Taiwan University

Two different types of super-resolution structures for the near-field optical storage were studied. Direct experimental observation of the near-field optical properties in the super resolution near-field structures of glass/SiN(170nm)/Sb(15nm)/SiN(20nm) and glass/ZnS-SiO2(20nm)/AgOx(15nm)/ZnS-SiO2(20nm) have been achieved by using a tapping-mode tuning-fork near-field scanning optical microscope. Both propagating and evanescent field intensities were found at the focused spots of the surfaces of the super resolution structures. The evanescent intensity may result from the localized surface plasmons excited at the antimony or silver oxide. Images of the near-field intensity gradients at different excited laser powers demonstrated that the area had the static evanescent intensity could be stably controlled. Direct observation of the focused spot sizes of the static evanescent field intensity and their changes controlled by the excited laser power have demonstrated the working mechanism of both two types of super-resolution structures.

3:00pm NS+NANO6+MC-ThA4 Near Field Surface Photovoltage Microscopy, R. Shikler, S. Saraf, Y. Rosenwaks, Tel-Aviv University, Israel Surface photovoltage (SPV) is a well-established technique for the characterization of semiconductors, which is based on analyzing illumination-induced changes in the semiconductor surface potential. The SPV and other related techniques like surface photovoltage spectroscopy (SPS), has been successfully used to study metal-semiconductor interfaces, surface states, bulk defects, and minority carrier lifetime and diffusion length. To date, all the SPV related technique have a common significant drawback: they do not have high spatial resolution. With the developments of scanning probe microscopy techniques in recent years, the way is payed to conduct SPV measurements with nanometer lateral resolution. In this talk we describe a novel technique called near-field photovoltage (NFPV) which measures the SPV using near-field optical force sensor. The key feature of the technique is that the excited semiconductor sample is in the optical near- field region of a pulled optical fiber that measures the contact potential difference (CPD) between the fiber and the sample using the Kelvin probe force microscopy (KPFM) method. In such a case the illumination spot size is determined by the diameter of the aperture at the end of the tip and is not limited by diffraction. In addition, the light propagation is evanescent i.e. the intensity of the light falls off exponentially with increase distance from the tip edge (perpendicular to the crystal surface). This in combination with the high spatial resolution of the KPFM makes it possible to obtain depth-sensitive two-dimensional photovoltage images in semiconductors, and other materials. The method is demonstrated by photovoltage measurements conducted on buried p-n junctions of III-V compound semiconductors. . When the sample was excited under far-field conditions, a decrease in the PV of the whole structure was observed due to a larger photovoltaic effect (band flattening) in the p-n junction. This is due to the fact that under super-bandgap illumination the band bending of the p-n junction decreases and causes a decrease of the structure work function. On the other hand, when the sample was excited and measured with the near-field optical force sensor,

an increase in the PV was observed due to band flattening only in the surface space charge region. Our results demonstrate the large surface sensitivity of the NFPV technique, and opens the way for a variety of ultrasurface sensitive SPV measurements and applications.

3:20pm NS+NANO6+MC-ThA5 Dual-Wavelength Scanning Near-Field Optical Microscopy, *P.R. LeBlanc, M. Gu, P. Grutter, D.G. Gray,* McGill University, Canada

We have developed a Dual-Wavelength Scanning Near-Field Optical Microscope to shed light onto the scanning process and investigate biological samples in air. We couple 442 and 325 nanometer light into a tapered optical fiber glued to a quartz tuning fork which serves as our 'shear-force' sensor. Light transmitted through the sample is detected in a confocal arrangement by two photomultipliers. We have achieved topographical and optical resolutions of 10 and 30 nanometers, respectively. The dual-wavelength nature of our microscope permits the discrimination of topographical and optical cross-talk. It also allows the distinction of far-field artifacts from near-field features. Our primary biological application of the microscopy focuses on the investigation of the lignin distribution in wood fibers. Lignin, a cross-linked phenolic polymer, is of paramount importance in the pulp and paper-making processes. Our instrument permits the discrimination between chemical species density and topographical variations of the sample. The ratio of the two wavelength channels provides a simple and accurate parameter to determine the local concentration of lignin. These studies agree with atomic force microscopy images of wood cells and ultraviolet studies of wood cell walls.

3:40pm NS+NANO6+MC-ThA6 Novel Scanning Near-field Optical Spectroscopy/Atomic Force Microscope Probes with High Polarisation Single/Double Slit and Cross Aperture Tips, *H.P. Zhou*, University of Glasgow, UK, United Kingdom; *G. Mills, L. Donaldson, J.M.R. Weaver*, University of Glasgow, UK

We have developed novel scanning near-field optical microscopy/atomic force microscope (SNOM/AFM) probes. These probes have high polarisation single/double slit and cross apertures situated at the hollow tip apex of a silicon nitride cantilever. Direct-write electron-beam lithography (EBL) and silicon micromachining are used in a reliable batch process. The apertures are defined by lithographic means, therefore, the size, shape and orientation of apertures are well controlled and reproducible. The integration of a conventional force microscope cantilever with the aperture allows reliable control of the aperture-sample distance. The cross aperture probe has two very narrow orthogonal slits which have a width of much smaller than a wavelength, and a length on the order of a wavelength. We have designed and constructed a SNOM system based on the cross aperture probes. A parallel-polarised (p polarised) beam passes through the vertical slit and illuminates a sample hold in the near field of the aperture. The reflected light from the sample with the incident polarisation is received by the same slit, while the perpendicular-polarised (s polarised) fluorescent component is received by the horizontal slit. Using this system. we have obtained near-field fluorescence imaging and have demonstrated spectrally resolved photoluminescence imaging with a spatial resolution of 50nm. The single and double slit apertures are vertically or horizontally oriented. The polarisation properties of the optical transmission from the slit aperture probes have been investigated as a function of the polarisation orientation. The polarisation behaviour of the slit probes is linearly polarised. The polarisation ratio ranged from 1:60 to 1:1000 for different ratios of length to width of slits.

4:00pm NS+NANO6+MC-ThA7 Optical Properties of Strained GalnP/InP Quantum Dots Studied with STM Based Electro-luminescence, *M.K.-J. Johansson*, *U. Hakanson*, *J. Johansson*, *M.-E. Pistol*, *L. Montelius*, *L. Samuelson*, Lund University, Sweden

The physics of nanometer scale structures has become a rapidly evolving field sparked by considerable interest from both science and technology. In the effort to assess the optical properties of individual nano-structures the use of scanning tunneling microscopy (STM) as the excitation source has received a lot of attention.@footnote 1@ Compared to more conventional techniques such as photoluminescence and cathodoluminescence the excited volume is very small and a further advantage is that the excitation energy can be greatly varied, from resonant conditions to above the impact ionization threshold. In addition STM provides very detailed information of the electronic structure and thus a manifold of data can be obtained within the same experiment. Here we will present measurements using a variable temperature UHV-STM combined with a scanning electron microscope. Furthermore, the system is equipped with an ex-situ laser source and

optical detection system allowing a combined study of STM based electroluminescence, laser induced photoluminescence and cathodoluminescence to be performed without the need to change experimental conditions and set-up. In this report we investigate the optical properties of capped InP quantum dots grown by metalorganic vapor phase epitaxy on a highly doped GaInP layer, lattice matched to GaAs grown on a GaAs(001) substrate. We discuss the mechanisms of inducing luminescence and the dependence on excitation energy using the InP quantum dots as a model system. @FootnoteText@ @footnote 1@See for instance, A. Gustafsson et al. J. Appl. Phys. Rev. 88, 1715 (1998) and references therein.

4:20pm NS+NANO6+MC-ThA8 Silicon Nanostructures via Intense Ultrafast Electronic Excitation, A.V. Hamza, M.W. Newman, University of California, Lawrence Livermore National Laboratory; T. Schenkel, University of California, Lawrence Berkeley National Laboratory; H.W.H. Lee, University of California, Lawrence Livermore National Laboratory; P. Thielen, University of California, Lawrence Livermore National laboratory; J.W. McDonald, D.H. Schneider, University of California, Lawrence Livermore

National Laboratory Due to the indirect nature of its band gap, bulk silicon is typically a poor photon emitter upon external excitation. However, as the crystal size approaches nanometer scales, the band gap widens due to quantum confinement and may become direct allowing for more efficient photon emission. Phase transformations induced by intense, ultrafast electronic excitation from slow, highly charged ions have produced nanometer-sized structures in silicon. Beams of highly charged ions of various charge state from 20+ to 69+ and various kinetic energies from 5 to 14 keV times charge have been utilized to induce this phase transformation in clean, silicon surfaces. The new phase is characterized by ex situ photoluminescence from the irradiated area after excitation with laser wavelengths from 379 -514 nm. Photoluminescence spectra from the exposed areas show emission centered at ~540 nm. This is consistent with emission observed from 1-2 nm silicon nanocrystals. A series of sharp lines at 565, 555, and 548 nm are present in the photoluminescence spectrum from areas exposed to Xe@super 44+@ which are characteristic of an excitonic series in nanometer-sized material.

4:40pm NS+NANO6+MC-ThA9 Microstructural and Optical Properties of Porous SiC, S. Zangooie, University of Nebraska, Lincoln; H. Arwin, Linkoping University, Sweden; J.A. Woollam, University of Nebraska, Lincoln

Electrochemical etching of crystalline SiC in hydrofluoric acid creates a high surface area material with room-temperature light-emitting properties stronger than those obtained from bulk SiC. The luminescence properties of porous SiC (PSC) open up application possibilities with, e.g., SiC-based integrated electronics. Applications of PSC demand a detailed understanding of microstructure and its relation to different fabrication parameters. In this work, ellipsometry and electron microscopy are used for characterization of 4H- and 6H-PSC. The dominant surface morphology consists of branched rosette-like structures surrounding sparsely located and circularly shaped holes with diameters of the order of 20 nm or less. The density of pores descending from the surface does not show clear dependence on the etching conditions. It is likely that pore initiation is favored at certain defect sites. Pores in PSC are found to initially propagate nearly parallel to the surface and gradually change direction and align with the c-axis. Consequently, well-defined columnar pores are formed. Thickness dependent anisotropy in pore propagation influences the etch rate, which varies nonlinearly with anodization time. Etching parameters such as hydrofluoric acid concentration and current density influence the rate of change of propagation direction. Pore sizes are found to increase with depth due to a decrease in acid concentration. A disordered phase is encountered at the interface between crystalline SiC and the pores. Spectrsocopic ellipsometry is used to study the microstructure, and we find that a simple effective medium approximation assuming mixtures of crystalline SiC and void does not result in good agreement with experimental data. To obtain good agreement with thickness and porosity, the disordered phase must be consideration. Anodization of SiC introduces remarkable changes to the optical properties due to depth-inhomogeneity and particle shape effects.

5:00pm NS+NANO6+MC-ThA10 Development of a Photon Detection STM for Inelastic Light Emission, D. Fujita, W.-L. Deng, T. Ohgi, K. Ishige, National Research Institute for Metals, Japan

Recently it has been demonstrated that the light emission induced by tunneling electrons can be detected with normal STM operation even with

atomic resolution. The possible processes are inelastic tunneling (IET) and hot-electron thermalization (HET). Generally speaking, in the case of IET, the tunneling electrons lose a part of the energy during the tunneling events to excite the state with some radiative decay processes. In the latter case, hot electrons lose the excess energy in the bulk. However, in order to get more detailed understanding of the luminescence process, much more precise measurements of these photons are required. For this purpose, we have developed a novel LT-UHV-STM system for the detection of light emission caused by the tunneling electrons. The emitted photons can be collected by the apex of a conductive and transparent optical fiber coated with a 100nm ITO (Indium-Tin-Oxide) film. Using a cooled photon detection system, single photon counting and spectroscopy with a very low noise level can be achieved. The system has been successfully applied to noble metal surfaces (Ag(111) and Cu(100)), and a direct-gap semiconductor surface (GaAs(110)) in UHV.

Surface Science

Room 208 - Session SS1+MC-ThA

Oxidation and Molecule-Oxide Interactions

Moderator: S.A. Joyce, Pacific Northwest National Laboratory

2:00pm SS1+MC-ThA1 Real Time TEM Observations of the Oxidation of Silicon, F.M. Ross, IBM Research Division INVITED

By making real-time observations of the progressive changes occurring at the silicon/oxide interface during oxidation, it is possible to examine the mechanism of the reaction and accurately measure the oxidation kinetics. In this presentation we will describe experiments carried out in a UHV transmission electron microscope which has been modified to allow images to be obtained before, during and after oxidation. By careful choice of imaging conditions we can follow the motion of the silicon/oxide interface in real time during oxidation, and in particular we can observe the configuration of interface steps. Our experiments show that passive oxidation, in which SiO@sub 2@ is formed, occurs in a layer-by-layer fashion with no flow of interface steps. Active oxidation is also a terrace reaction, although the SiO which is formed evaporates preferentially from surface steps. We will briefly discuss how the observation and analysis of step and terrace contrast is a powerful tool for examining the mechanism of other silicon surface reactions, such as epitaxial growth or silicide formation, as well as oxidation.

2:40pm SS1+MC-ThA3 Comparison of Electrochemical Corrosion Properties and Oxidation Kinetics of Ozone- and Oxygen-formed Aluminum Oxide Films, A. Kuznetsova, I. Popova, V. Zhukov, G. Zhou, J.C. Yang, J.T. Yates, Jr, University of Pittsburgh

Ozone, O@sub 3@, has been employed to produce an aluminum oxide layer (thickness about 20 Å), on Al(111)and also on polycrystalline Al surfaces. It has been found, by electrochemical impedance spectroscopy, that the impedance of such films is about 10 times higher than films grown to similar thickness with O@sub 2@.Transmission electron microscopy studies have shown that the average pore size of Al@sub 2@O@sub 3@ films grown with O@sub 3@ (20 Å) is smaller than in films grown with O@sub 2@ (100 Å). In addition, electron diffraction studies of amorphous film have shown that the density of oxide films grown with O@sub 3@ is 10% greater than for oxide films grown with O@sub 2@. Thus the enhanced corrosion passivation properties of O@sub 3@-grown aluminum oxide films may be caused by the reduction of defect site density when O@sub 3@ is used.

3:00pm SS1+MC-ThA4 Temperature Dependent Adsorption of Oxygen on TiO@sub 2@ (110): A Photoemission Study, H. Geisler, Xavier University of Louisiana; E.L.D. Hebenstreit, W. Hebenstreit, M. Li, U. Diebold, Tulane University; S.N. Thornburg, C.A. Ventrice, Jr., University of New Orleans; D.A. Hite, P.T. Sprunger, CAMD/ Louisiana State University

The Titanium dioxide (110) surface is one of the most thoroughly studied metal oxide systems. One of the primary reasons for this interest is the fact that TiO@sub 2@ is easily reduced by annealing in vacuum. During the annealing process, oxygen vacancies and titanium interstitial are created, which can increase the conductivity of the substrate sufficiently to allow characterization with electron and ion spectroscopies. In order to heal the surface region, the reduced crystals are exposed to oxygen adsorption on the electronic structure of reduced TiO@sub 2@ crystals, angular resolved photoelectron spectroscopy (UPS) measurements have been performed in conjunction with scanning tunneling microscopy (STM)

measurements. STM indicates that the adsorption of oxygen on TiO@sub 2@ (110) at temperatures above 400 °C or below 200 °C results in an unreconstructed surface. However, adsorption between 200 °C and 400 °C results in a rosette-like structure that represents an incomplete restructured TiO@sub 2@ (110) surface with coordinatively unsaturated surface atoms.@footnote 1@ UPS measurements of the vacuum-annealed, reduced TiO@sub 2@ surface show emission from a defect state centered at approximately 1 eV below the Fermi level. The onset of emission from the TiO@sub 2@ valence band occurs ~3 eV below the Fermi level. After dosing oxygen at room temperature the defect state disappears with only slight modifications to the valence band structure. On the other hand, UPS spectra from the defect state and strong modifications of the TiO@sub 2@ valence band emissions. @FootnoteText@@footnote 1@ M. Li, W. Hebenstreit, L. Gross, et al., Surf. Sci. 437, 173-190 (1999)

3:20pm SS1+MC-ThA5 Water Reactions at Plutonium Oxide: Surface Chemistry, J.D. Farr, R.K. Schulze, M.P. Neu, L.A. Morales, Los Alamos National Laboratory

We have examined the surface chemistry of water at both monolithic and high surface area plutonium oxide using Auger and X-ray photelectron spectroscopy (AES and XPS). This work investigates the chemical reactions at the Pu oxide surfaces, primarily to help address issues that are critical for plutonium stabilization and 50-year storage. Interactions between PuO@sub 2@ particles and the adsorbed water vapor play a dominant role in potential catalytic gas generation reactions. Understanding the chemistry at this interface, particularly with respect to reactions with water and water vapor is crucial for predicting the storage behavior of Pu oxide powders. XPS indicates that water adsorbs initially at active sites to form surface hydroxyls groups. Upon saturation of these sites and at substantially higher exposures, particularly with high surface area oxides, the water adsorbs in molecular form as part of the surface layer. Heating the oxide to 200°C in vacuum results in removal of the adsorbed water and partial removal (conversion) of the hydroxyl. Above 400°C the oxide surface continues to undergo a transformation and the removal of hydroxyl is largely complete at 600°C. The tenacious nature of these surface groups suggests that most of the active sites at the surface are irreversibly saturated at room temperature and up to a temperature in excess of 200°C, with some of them irreversibly saturated up to 600°C, or greater. The surface reaction will be discussed in the context of reaction energetics for the active sites at the PuO@sub 2@ surface.

3:40pm SS1+MC-ThA6 Studies of Water Plasma Treatments on Silicon Oxide Films, N.A. Alcantar, University of California, Santa Barbara; T.L. Kuhl, University of California, Davis; A. Stacy, J. Au, E.S. Aydil, J.N. Israelachvili, University of California, Santa Barbara

Chemically active oxide surfaces can react with polymers to enhance their surface properties. Surfaces covered with polyethylene glycol have been shown to reject biological attack and protein adhesion. We activate silicon dioxide (i.e., silica) films by exposing them to water vapor plasma. These activated films are then reacted with polyethylene glycol (PEG, OH-(CH@sub 2@-CH@sub 2@-O)@sub n@-H) to make them biocompatible. We have characterized silica films prepared by plasma enhanced chemical vapor deposition (PECVD) before and after water plasma activation. We found that water plasma treatments chemically and physically modify the silica surface. For instance, water plasma fully saturates the silica surface with hydroxyl groups, significantly reduces their surface roughness without affecting the thickness of the deposited films and increases their cohesion force. This surface modification was monitored by in situ real time attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Other characterization techniques such as ellipsometry, atomic force microscopy (AFM), surface forces apparatus (SFA) and contact angle measurements were utilized to fully establish the effects of this surface modification. The optimal water plasma parameters for creating smooth, chemically reactive silicon oxide films were also obtained.

4:00pm SS1+MC-ThA7 The Nature of Oxygen at Rocksalt and Spinel Oxide Surfaces, M.A. Langell, J.G Kim, S. Chapman, H.Y. Xu, University of Nebraska

The chemical environment of oxygen in mixed metal oxides with compositions M@subx@M'@sub(x-1)@O and M@subx@M'@sub(3x-1)@O@sub4@, (M, M' = Li, Mn, Fe, Ni, Co) has been studied by Auger electron spectroscopy, x-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy. While there is a single type of lattice oxygen in the bulk structure of simple rocksalt and spinel oxides, the nature of oxygen at the surface of the mixed-metal oxide materials is

considerably more complex. Photoemission from core oxygen states in these materials often shows multiple peaks and satellite structure which have been attributed to a range of intrinsic and extrinsic oxygen states. Mixed-metal oxides form an ideal set of systems to investigate the nature of the lattice oxygen through their ability to tailor cation oxidation state and site occupancy within the crystal structure and thus affect the chemical environment of the lattice oxygen. All of these 3d transition metal oxides show a single, intense O1s core photoemission peak at approximately 529.6 eV. However, a second peak is often observed at about 1-1.5 eV higher binding energy, depending upon the types and distribution of the cations, and the history of the substrate surfaces. Surface hydroxylation, cation clustering and final state effects in the photoemission mechanism can all contribute to the O1s photoemission process and will be discussed in view of the data obtained for the mixed-metal oxides.

4:20pm SS1+MC-ThA8 Direct Observation of Native Hydrogen Adatoms on Rutile TiO@sub 2@(110) Surface, *T. Fujino, K. Inudzuka, T. Okuno, M. Katayama, K. Oura,* Osaka University, Japan

Titanium dioxide (TiO@sub 2@) surface has received considerable attention because TiO@sub 2@ is the material of photocatalyst such as the photodecomposition of water. Over the past few years a considerable number of studies have been made on the analysis of rutile TiO@sub 2@(110) surface composition and structure. Most of these studies were conducted using microscopic techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). However, the information of hydrogen atoms adsorbed on TiO@sub 2@(110) surface seems to be lacking because it is difficult to detect the surface hydrogen using STM or AFM. In the present study, we have investigated the structure and composition of the rutile TiO@sub 2@(110) using coaxial impact collision ion scattering spectroscopy (CAICISS), time-of-flight elastic recoil detection analysis (TOF-ERDA) and low energy electron diffraction (LEED). CAICISS and TOF-ERDA have been proved to be useful techniques for in situ observation of surface structure and composition, in particular, for the determination of the amount of surface hydrogen atoms. When the sample was introduced into ultra high vacuum (UHV) chamber without any treatments, a large quantity of hydrogen and oxygen atoms adsorb on the surface. These atoms can be attributed to water molecules. After annealing the sample at 800°C in UHV, the clean surface of TiO@sub 2@(110) with the LEED pattern of a sharp 1x1 spots was obtained. It was found from the CAICISS measurement that this surface formed bulk terminated structure, known as bridging oxygen rows model. However, it was also found from the TOF-ERDA measurement that the hydrogen atoms still resided on the surface. These hydrogen atoms are not components of water molecules but directly chemisorb on the TiO@sub 2@(110)1x1 surface. Thus, native hydrogen adatoms on the TiO@sub 2@ surface was directly observed and evidenced. Detailed results will be discussed in the presentation.

4:40pm SS1+MC-ThA9 Work Function Changes and Surface Chemistry of Oxygen and Hydrogen on Indium Tin Oxide, J.A. Chaney, P.E. Pehrsson, Naval Research Laboratory

Indium tin oxide (ITO) is used as a transparent, semiconducting substrate for many device applications. However, there is an inadequate understanding of ITO surface properties, its interaction with gaseous species, and the physical/electronic changes imposed by its surface chemistry. The surface physics and chemistry of oxygen plasma treated ITO were investigated under ultra high vacuum conditions. The work function (@PHI@) of ITO was determined by a vibrating Kelvin probe calibrated with a graphite standard. Sample composition, electronic structure and chemistry were examined by Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). Commercial ITO films were heated in-vacuo to remove physisorbed species and then exposed in-situ to oxygen or deuterium activated with a hot metal filament. Oxidation increased the work function from 5.2 to 5.6 eV, but @PHI@ then decayed to <5.2 eV, possibly due to oxygen diffusion into the bulk along defects and grain boundaries. The AES oxygen level was stable after oxidation, and the ELS spectrum consistently showed a strong feature at 0.7 eV for oxidized samples. Deuteration visibly metallized the film and sharply reduced the surface oxygen level. The ELS feature simultaneously disappeared, and the work function decreased to 4.6 eV. The HREELS of clean ITO revealed substantial C-H contamination, which persisted after heating to ~300°C. Even substantial oxygen treatment did not remove the hydrogen signal, suggesting that C-H permeates the ITO film.

5:00pm SS1+MC-ThA10 Adsorption of Atomic Hydrogen on Both Polar Surfaces of ZnO, *Th. Becker, M. Kunat, Ch. Boas, U. Burghaus, C. Wöll,* Ruhr-University Bochum, Germany

The interaction of atomic hydrogen with Zn-ZnO and O-ZnO surfaces has been investigated by LEED, He atom scattering, He atom reflectivity measurements (as a function of H exposure and surface temperature, T@sub s@), and XPS. Furthermore, measurements of adsorption probabilities of CO on the two polar surfaces of ZnO are presented (see [1] for CO/O-ZnO) as well as the effect of pre-exposed atomic hydrogen on the adsorption dynamics of CO. He atom diffraction measurements indicate the formation of a well ordered H overlayer structure. The strong attenuation of the specular He atom reflectivity by hydrogen exposure indicates, however, a second competing reaction pathway; since extensive exposure to atomic hydrogen leads to a high degree of disorder on the surface. Values for the heat of adsorption for H were estimated from He-atom reflectivity curves, measured as a function of T@sub s@. The shape of the coverage dependent adsorption probability curves, S(@theta@@sub CO@), of CO are for both surfaces consistent with a precursor mediated adsorption; adsorbate assisted adsorption dominates the adsorption. The He atom reflectivity measurements point to the influence of an intrinsic precursor state. A comparison of He atom reflectivity with S(@theta@@sub CO@) curves, respectively, showed that CO initially populates defect sites. The coadsorption of H and CO can be explained by a site blocking mechanism; leading to an estimate of @theta@@sub H@. [1] Th. Becker, Ch. Boas, U. Burghaus, Ch. Wöll, Phys. Rev. B 61(7) (2000) 4538.

Material Characterization Room 207 - Session MC+NS-FrM

Characterization of Interfaces and Thin Films Moderator: L.A. Giannuzzi, University of Central Florida

8:20am MC+NS-FrM1 RBS, AFM, and AES Characterization of Pt Films Deposited by Ion Assisted CVD, B. Rogers, K.A. Telari, H. Fang, L. Shen, R.A. Weller, Vanderbilt University; D. Braski, Oak Ridge National Laboratory The semiconductor industry has used focussed ion beam (FIB) systems for several years to create site specific transmission electron microscopy (TEM) and secondary electron microscopy (SEM) cross sections, repair lithography masks, and to reroute electrical current by cutting and creating current carrying paths for circuit testing. The FIB systems' capability to both etch and deposit material in defined areas makes them good candidates for use as flexible processing systems for the development of specialized circuits. For example, metal patterns deposited in a FIB system could be used to form electrical connections and sensors on micro-electromechanical systems (MEMs) devices. Properties of the deposited material as well as the process by which it is deposited must be well characterized in order for the material to be successfully used in this type of development program. This work presents results from characterization of the ion assisted chemical deposition of Pt from vapor trimethyl(methylcyclopentadienyl)platinum [C@sub 9@H@sub 16@Pt]. Films were deposited in squares ranging from 50 μ m on a side to 400 μ m on a side. Process parameters, including precursor temperature, dwell time, and ion beam current were varied to investigate their affect on the composition of the deposited films. A specially designed sample holder and Be mask enabled Rutherford backscattering spectrometry (RBS) determination and comparison of the Pt areal densities in these small features. Atomic force microscopy was used to determine the thickness and surface morphology of the deposited films. Scanning Auger electron microscopy was used to analyze the films for oxygen and carbon. Results show that the films contain a large amount of carbon and gallium in addition to the desired platinum. The presentation will conclude with a discussion of the effects of process parameters on the films' composition and possible pathways to maximize the platinum content of the films.

8:40am MC+NS-FrM2 Material and Interface Characterization of Locally Deposited Dielectrics and Metals Fabricated with a Focused Ion Beam (FIB), H.D. Wanzenboeck, H. Langfischer, E. Bertagnolli, H. Stoeri, M. Gritsch, H. Hutter, Vienna University of Technology, Austria

A chemical vapor deposition process was performed under vacuum conditions utilizing a focused ion beam (FIB) tool confining the deposition on a selected area in the µm down to the deep sub-µm range. The direct fabrication by FIB offers a versatile approach for rapid development and instant testing of novel microelectronic devices. The electrical properties of devices are influenced by the bulk attributes of the material. For complex multilayer structures the interface between 2 materials is of crucial importance. A focused Ga ion beam with diameter down to 5 nm was applied to induce decomposition of selected metalorganic species and siliconorganic compounds adsorbed on the sample surface. Deposition of metals was achieved by using metalcarbonyls such as W(CO)6 as precursors. Dielectrics such as siliconoxides were deposited by coadsorption of siloxane and pure oxygene. For siliconoxide the mixture ratio of the volatile precursor gases was found to be decisive for the chemical composition and electrical properties. For material characterization multilayer structuresof dielectric and metal have been investigated. Auger-Spectroscopy revealed a correlation between the chemical composition of the FIB-deposited layers their electric characteristics and the process parameters chosen. Images of the X-section of the surface and interface deposited layers showed a homogeneous bulk density and a satisfactory surface roughness. Although the interface between FIB-deposited metal and dielectric layer is clearly visible in the secondary electron image depth profiling by secondary ion mass spectroscopy (SIMS) suggests an altered layer due to atomic mixing by the ion beam in a typical range up to 100 nm. The refined comprehension allowed to optimize the process parameters foraer improved material properties.

9:00am MC+NS-FrM3 Three-Dimensional Material Characterization using Focused Ion Beams (FIB), *R.J. Young*, FEI Company INVITED The focused ion beam (FIB) system is integral to the manufacture of semiconductor and data storage devices. Systems are now found throughout the manufacturing process, from the research laboratory to the production line. The ability of the FIB to image at high resolution, and to locally sputter and add material, provides capabilities not obtainable with optical and scanning electron microscope (SEM) techniques alone. FIB techniques include cross-sectioning, gas-assisted etching and deposition, circuit editing, ion channeling imaging, secondary ion mass spectroscopy (SIMS), and transmission electron microscope (TEM) thin film preparation. In addition, combining together the FIB and SEM in a single instrument (a "dual beam") produces an extremely powerful and flexible materials characterization system, providing unique three-dimensional subsurface metrology and analysis capabilities. In particular, the electron beam can be used to image the face of the cross section as it is being milled by the ion beam. This greatly aids in the location of very small defect sites. Further, the use of in-situ delineation etching allows the whole process of sample preparation to final imaging to be carried out in a single instrument. It should also be noted that SEM and FIB images and analysis techniques are in many ways complementary, the different contrast mechanism in each case giving additional information about the sample. Many of the FIB and dual beam techniques used in the analysis and sample preparation of microelectronic devices apply equally to other disciplines. In particular, the ability to locate, expose and then analyze submicron or unique defects has a wide applicability within material and biological sciences. This paper reviews the capabilities of focused ion beam systems, illustrating these with a number of case studies.

9:40am MC+NS-FrM5 Visualizing Interfacial Structure at Non-Common-Atom Heterojunctions with Cross-Sectional Scanning Tunneling Microscopy@footnote 1@, J. Steinshnider, M. Weimer, Texas A&M University; R. Kaspi, Air Force Research Laboratory; G.W. Turner, Lincoln Laboratory, M.I.T.

We describe how scanning tunneling microscopy (STM) may be used to image the interfacial bonding across the nearly-lattice-matched, noncommon-atom GaSb / InAs heterojunction with atomic-scale precision. An ideal, compositionally-abrupt GaSb / InAs interface introduces new bonds either InSb-like or GaAs-like - whose natural lengths differ from those in the surrounding host materials. These bond length differences are readily distinguished following (110) cleavage of the heterojunction, which locally relieves the out-of-plane compressive or tensile strain otherwise accommodated by a lattice-mismatched interface. The method is equally applicable to AISb / InAs and suggests how it might be possible to determine the interfacial structure of such non-common-atom heteroiunctions from atomic-resolution STM data.@FootnoteText@@footnote 1@Work supported by the National Science Foundation, Division of Materials Research, and the Air Force **Research Laboratory**

10:00am MC+NS-FrM6 Atomic Resolved Spectroscopic Study of AlGaAs/GaAs/InGaAs by Cross-sectional Scanning Tunneling Microscope, J. Yu, L. Liu, J. Li, J. W. Lyding, University of Illinois

An atomic resolved cross-sectional STM spectroscopic study has been performed on UHV-cleaved AlGaAs/GaAs/InGaAs heterostructures. Current imaging tunneling spectroscopy (CITS) results demonstrate significant electronic structure contrast between the column III and V sublattices as well as for the different compositional regions. The resulting images reveal surface structures not always evident in topographic images. Using a pattern recognition algorithm derived from the VERI analysis developed at Sandia,@footnote 1@ the image pixels can be grouped into classes according to similar electronic structure. This technique can be applied to automatically identify the spatial distribution of various elements during semiconductor growth. A detailed analysis and physical explanation of the spectra will be presented. @FootnoteText@@footnote 1@Bouchard, A. M., Osbourn, G. C., and Swartzentruber, B. S., Surf. Sci. 321, 276 (1994).

10:20am MC+NS-FrM7 Scanning Spreading Resistance Microscopy of MOCVD Grown InP Structures, *St.J. Dixon-Warren, S. Ingrey,* Nortel Networks, Canada

Scanning spreading resistance microscopy (SSRM) is a new probe microscopy technique that provides localized resistance profiling over a semiconductor surface. The technique, which is based on contact-mode atomic force microscopy (AFM), provides information on the two dimensional distribution of charge carriers and on the position of pn junctions in semiconductor structures. We have used SSRM to examine the cleaved edge of a number of MOCVD grown InP structures, including multiquantum well layers and buried heterojunction laser structures. Information on the spatial distribution of dopants in the InP epitaxial layers was obtained. The effect of the applied tip voltage was investigated. We

found that the active region of the laser structure, where the band gap is lowest, could be identified in the voltage dependence of the SSRM images. The effect of scanning rate, surface preparation and tip choice will also be discussed.

10:40am MC+NS-FrM8 XPS Analysis of Interfacial WO@sub x@ using Linear Least Squares and Standard Curve Fitting Routines, *D.K. Fillmore*, Micron Technology, Inc.

X-ray photoelectron spectroscopy (XPS) has proven itself extremely useful in determining the chemical states of various materials. These chemical state identifications are primarily inferred from characteristic peak shapes and energy shifts along with the correlating presence of other elements and a previous knowledge of typical chemical compounds. When several chemical species are present in a particular sample, standard curve fitting routines are employed to extract the individual spectral components from multi-component spectra. This entails significant care in assigning each of the individual component peak energies, relative intensities and characteristic widths. The problem is exacerbated when ion sputtering is employed which results in sputtering-induced decomposition of components. From the curve-resolved data, atomic concentrations of individual components in a multi-component sample may be obtained. By making certain assumptions in specific circumstances, linear least squares (LLS) analysis routines may be able to quickly extract similar atomic concentration data from multi-component spectra without explicitly identifying individual spectral component peaks. This paper will discuss and compare analyses of interfacial WO@sub x@ found between a surface SiO@sub 2@ layer and underlying elemental W using both LLS and standard curve fitting analysis routines. Specific advantages and disadvantages of each approach will be covered.

11:00am MC+NS-FrM9 Investigations into the Chemical Nature of the Interfaces of Cu and Ta with SiN, J.F. Bernard, E. Adem, S. Avanzino, M.-V. Ngo, Advanced Micro Devices

Surface chemistry is typically related to film properties such as adhesion, wetability, etc. For Cu interconnects the surface mobility of of Cu ions can affect electromigration and line-to-line leakage in damascene structures.@footnote 1@ The surface treatment of Cu after CMP planarization will effect the chemical nature of the interface with the capping material as well as the interface of any liners with the cap. The chemical nature of the interface of Cu with SiN has been determined through XPS and AES compositional and chemical state depth profile analyses. The effect of plasma treatments on the Cu surface and resulting interfaces with the SiN capping layer is detailed. A mechanism for the Cu° catalyzed generation of the observed interfacial non-N bonded Si resulting from a silane based SiN deposition is proposed. Additionally, the interface of SiN with Ta is investigated to explore the effects of Cu treatments on the liner/cap interface. The basic outgassing behaviors of Cu and Ta are also discussed relative to the effects observed at the interface with the SiN capping layer. @FootnoteText@ @footnote 1@ Noguchi, J., "TDDB Improvement in Cu Metallization under Bias Stress"; International Relaiabilty Physics Symposium 2000.

11:20am MC+NS-FrM10 On the Organic Content and Outgassing Behavior of Organometallic-based CVD-TiN Films, J.F. Bernard, E. Adem, Advanced Micro Devices

The drive to smaller IC geometries has led to an increasing use of organometallic precursor based chemical vapor depositions of TiN barrier films. The CVD-TiN process yields more uniform step coverage in high aspect ratio features. The CVD process also presents challenges in generating a consistently high quality TiN film. At lower temperatures both organometallic and metal halide precursors yield a lower density film with high resistivity and low N conents. A N-based treatment process has been widely employed to i)reduce the organic component and ii)increase the N content of the films resulting from the use of TDMAT or TDEAT organometallics. The remaining C in the film has been shown to be present as a cabide of Ti. The chemical state of this remaining C has been further examined through the use of depth profiling, FT/IR, and wet chemical etching techniques. Deviations in the plasma treatment or the as deposited thickness can have a significant effect on the film quality. The affinity for O exhibited by uncapped PVD-TiN is higher still for untreated CVD films. The evolved gas profiles for a low resistivity film are dominated by H/H@sub2@ outgassings. Films with a deviation in plasma conditions exhibited higher resistivity beyond spec limits and outgassings dominated by OH.

Processing at the Nanoscale/NANO 6 Room 302 - Session NS+NANO6+MC-FrM

Nanoscale Spectroscopy

Moderator: L.J. Whitman, Naval Research Laboratory

8:20am NS+NANO6+MC-FrM1 Identification of Atom Species on Semiconductor Surface Using Noncontact AFM, Y. Sugawara, Osaka University, Japan INVITED

Recently, the noncontact atomic force microscope (AFM) using frequency modulation (FM) technique achieved true atomic resolution imaging. In order to apply the noncontact AFM as a powerful scientific tool for resolving the atomic features in variety of fields such as materials and biological sciences, it is very important to clarify the imaging mechanisms of the noncontact AFM. The imaging mechanism of the noncontact AFM was not establish clearly, however the investigation concerning the imaging mechanism has been making progress gradually on various surfaces. In this paper, we experimentally investigated the force interaction between silicon tip and Si(111)@sr@3x@sr@3-Ag surface by using the noncontact AFM. In case of reactive silicon tip, the AFM images showed the strong distance dependence dominated by the chemical-bonding interaction due to onset of the orbital hybridization very close to surface. On the other hand, in case of the adsorbed silver atom tip, the AFM images showed no distance dependence, and the individual silver atom on the top most layer of the surface could be resolved, corresponding to the true topography.@footnote 1@ This tip-sample force interaction seems to be dominated by physical bonding interaction such as the van der Waals force between the silver atom on the tip and the silver atom on the surface. These experimental results suggest that the noncontact AFM images drastically change depending on the atom species on the tip apex. It should be emphasized that there is a possibility to identify or recognize atom species on a sample surface using the noncontact AFM, if we can control an atomic species at the tip apex. @FootnoteText@@footnote 1@K.Yokoyama, T.Ochi, Y.Sugawara and S.Morita: Phys. Rev. Lett., 83 (24) 5023, 1999.

9:00am NS+NANO6+MC-FrM3 Dynamic Polarization Imaging using Heterodyned Electrostatic Forces, *D.R. Oliver*, *A. Pu*, *D.J. Thomson*, *G.E. Bridges*, University of Manitoba, Canada

Electric fields at the surface of dielectric materials will produce dipoles related to the polarizability of the material. In this paper we will present a technique that measures the polarization induced by a conducting probe near a surface. The images obtained are derived from the electrostatic forces between the probe and surface. In favourable geometries, the spatial resolution approaches the probe diameter. This measurement technique can be extended to frequencies well above the mechanical resonant fr equency of the probe cantilever by utilizing amplitude modulation heterodyning. Using heterodyning, both time- and frequency-domain forms of this technique can be realized. We expect this technique to be useable up to frequencies of at least 20 GHz and time resolution of 100 ps. We present calculations of the forces generated assuming simple probe geometries and also thermal noise. Experimental results presented compare favourably with these calculations.

9:20am NS+NANO6+MC-FrM4 Atomic Scale Chemical Identification on Si(111)@sr@3x@sr@3-Ag by Atom Probe-Scanning Tunneling Microscope, T. Shimizu, H. Tokumoto, JRCAT-NAIR, Japan

A scanning probe microscope (SPM) can determine atomic arrangement of various surfaces. It is, however, difficult to identify the chemical species of the atoms and molecules with the SPM. In order to know the atomic arrangement and its chemical species, there are several trials by combining the SPM with chemical analysis technique such as time-of-flight (TOF) mass spectroscopy and XPS. Spence has first demonstrated the possibility of TOF technique for chemical analysis. Then we have shown the usefulness of the TOF combined system in several cases. Furthermore a group in Delft Univ. has just tried to construct a TOF combined system. Nishikawa's group has already constructed a different kind of TOF. Here we shall present our challenge to atom-by-atom chemical analysis on solid surfaces by combining an Atom Probe of single atom sensitivity with the SPM ability of single atom manipulation (AP-STM). We have already demonstrated the following facts: (1) More than hundred Si atoms transferred from Si surfaces to a W-tip are detected; (2) The transferred Si atoms intermix with the tip material and form silicide; (3) Highly doped arsenic can segregate to the surface layers during annealing, form strange triangular step structure on Si(001) and the ratio of Si to As can be quantitatively determined. In this study, we will demonstrate the single atom identification on

Si(111)@sr@3x@sr@3-Ag, whose atomic structure is supported by the Honeycomb Chained Trimer (HCT) model. The model is as follows. The topmost layer is formed by Ag atoms with the HCT arrangement. Below the Ag HCT layer, there is a Si trimer layer. From this model, it is believed that STM bright spots with sample plus voltage correspond to neither Ag nor Si atoms on the surface, but to the center of the triangle formed by three Ag atoms. To confirm the model directly, we are trying to identify the atomic position of Ag by extracting atoms from the surface and detecting the chemical species of extracted atoms.

9:40am NS+NANO6+MC-FrM5 Tunneling Spectroscopy of Passivated Gold Nanocrystals, *R.B. Wyrwas*, *A.Y. Ogbazghi, T.P. Bigioni, L.E. Harrell,* Georgia Institute of Technology; *T.G. Schaaff,* Oak Ridge National Laboratory; *R.L. Whetten, P.N. First,* Georgia Institute of Technology

Scanning tunneling spectroscopy (STS) and microscopy (STM) have been used to study the electronic structure of small (< 2 nm diameter) alkanethiol-passivated gold nanocrystals. The nanocrystals were prepared via chemical methods, and their mass distribution was characterized by time-of-flight mass spectrometry. STM/STS measurements were done at room temperature, 77 K, and 8 K, with isolated nanocrystals immobilized on Au(111) surfaces by a xylenedithiol self-assembled monolayer (SAM). A histogram of nanocrystal heights measured by STM shows several peaks. These correlate well with distinct peaks in the mass spectrum. STS dl/dV spectra vary with nanocrystal size, and show prominent features due to their quantized density-of-states. Spectra acquired repeatedly over a single nanocrystal evolve in time slowly, possibly due to configurational changes of the nanocrystal or its passivation layer.

10:00am NS+NANO6+MC-FrM6 Scanning Probe Microscopy Study of Engineered Ferroelectric Domain Structures, *G. Rosenman, A. Agronin, Y. Rosenwaks, M. Lesnih, P. Urenski,* Tel-Aviv University, Israel

Ferroelectric domain engineering has recently become an attractive and perspective tool for diverse nonlinear optical applications based on the quasi-phasematching method (QPM). The QPM occurs by the use of specifically tailored ferroelectric domain configurations with alternate direction of spontaneous polarization. Various types of engineered domain structures (periodic, aperiodic and quasi-periodic) allow an effective generation of coherent light in spectral regions where conventional lasers are not available. In this work we have studied engineered domain configurations (fabricated by electrical poling method in ferroelectric KTiOPO4 crystals) using different scanning probe techniques like: piezoresponse imaging, Kelvin probe force microscopy, and conventional topography imaging. The different AFM methods image the periodically poled domains and domain walls with high spatial resolution. A detailed electrostatic analysis of the data, and the contrast between ferroelectric domains with opposite polarity is presented.

10:20am NS+NANO6+MC-FrM7 Imaging of Single Molecules by Low Energy Electron Point Source Microscopy, A. Eisele, B. Völkel, Universität Heidelberg, Germany; S. Rehbein, Universität Göttingen, Germany; B. Jäger, Universität Heidelberg, Germany; H.J. Kreuzer, Dalhousie University, Canada; A. Gölzhäuser, M. Grunze, Universität Heidelberg, Germany

Low Energy Electron Point Source Microscopy (LEEPS)@footnote 1,2@ has been used for taking in-line holograms of single DNA strands and carbon nanotubes. These two molecules were chosen to elucidate the extend to which the hologram images are determined by structural and electronic properties of the sample. The holograms were analyzed by reconstruction via the Kirchhoff-Helmholtz integral transformation.@footnote 3@ The resulting image is suggested to represent the scattering centers of the molecule, i.e. yielding its atomic structure. However, various effects can impose a limit to the resolution: vibrations between tip and sample, electronic charge deposition on the sample, non-ideal electron coherence, distortion of the electrical field near the sample molecule. It is discussed to which extend such artefacts are visible in the experimental data and whether they constrain the applicability of the Kirchhoff-Helmholtz transform. A comparison between the transformed images of DNA strands and carbon nanotubes shows differences that can be explained by properties of the molecules. @FootnoteText@ @footnote 1@ H.-W. Fink, W. Stocker and H. Schmid, Phys. Rev. Lett. 65, 1204 (1990). @footnote 2@ A. Gölzhäuser, B. Völkel, B. Jäger, M. Zharnikov, H.J. Kreuzer, M. Grunze, J. Vac. Sci. Technol. A16(5), 3025 (1998). @footnote 3@ H. J. Kreuzer, K. Nakumura, A. Wiezbicki, H.-W. Fink, and H. Schmid, Ultramicroscopy 45, 381 (1992).

10:40am NS+NANO6+MC-FrM8 Atomically-resolved Observation of Single Surface States and Trapped Electrons at Semiconductor Surfaces using Photovoltage Imaging with STM, S. Aloni, I. Nevo, G. Haase, Weizmann Institute, Israel

Atomically-resolved, super- and sub-band-gap photon surface photovoltage (SPV) imaging was used to study surface states and a trapped exciton at semiconductor surfaces. Super-band-gap radiation that flattens the electronic bands gives rise to SPV that reflects the local band bending in the dark. On the other hand, a sub-band-gap photon can excite a localized electron in a surface state into the conduction band, and produce an SPV that reflects the new charge distribution. By studying the effect of the tip on the local band bending, we can learn about the nature of a single localized surface state on an otherwise surface-state-free surface. It turns out that a single adsorbate or a single atom-size defect, can sometimes screen efficiently a strong external electric field. When a filled deep surface state, such as As-vacancy defect on the surface-state-free GaAs(110) surface, was excited by 1064 nm (sub-band-gap) illumination, a trapped electron state was imaged: It's induced SPV feature had a slight positive value at a radius of ~20 AA, and a negative portion 5-50 AA further away, as expected for a localized positive charge with a wide (bias-dependent radius of 25-70 AA) electron-density distribution around it. An observed six-point star shape of the SPV feature is explained by the contribution of the surface atoms to the potential well shape.

Surface Science Room 209 - Session SS+MC-FrM

Characterization of Oxides and Thin Films Moderator: J.A. Kelber, University of North Texas

8:20am SS+MC-FrM1 Characterisation and Microreactor Studies of Nanofabricated Model Pt/Ceria Catalysts, C. Werdinius, Chalmers University of Technology, Sweden; O. Hjortsberg, Volvo Technological Development Corporation, Sweden; L. Österlund, B. Kasemo, Chalmers University of Technology, Sweden

In modern automotive catalysts, ceria is an important component for transient storage and release, respectively, of oxygen during lean and rich conditions. In order to study the detailed kinetics of the oxygen storage, well-characterised samples are required. Model catalysts (1 cm@super 2@ sample area) of platinum particles on ceria were nano-fabricated by a novel method called "colloidal lithography".@footnote 1@ Its principal feature is the ability of fast parallel fabrication of almost mono-sized, evenly distributed nano-particles. The manufacturing consists of the following steps; (i) deposit a ceria film on a silicon wafer, (ii) deposit a Pt film of desired thickness, (iii) deposit an array of colloidal particles of desired size and spatial separation, (iv) remove all Pt not shadowed by the particles, using Ar-ion beam etching, (v) remove the particles. The final step leaves an array of Pt particles with size and separation reflecting the colloidal particle size and separation. Samples with different Pt-particle densities and particle sizes (40 and 110 nm) were made, and characterised by several surface analytical techniques, including SEM and XPS. Preliminary results of pulsed CO oxidation experiments in a specially designed microreactor are presented, along with vacuum CO TPD measurements. @FootnoteText@ @footnote 1@ P. Hanarp, D. Sutherland, J. Gold, and B. Kasemo, Nanostructured Materials 12, 429-432 (1999).

8:40am SS+MC-FrM2 Characterization of Hf and Zr Oxides, Silicides and Silicates, Formed on the (0001) Surfaces of HfB@sub 2@ and ZrB@sub 2@, by AES, XPS, LEED and STM, *R. Singh*, University of Illinois at Chicago; *Y. Paderno*, Academy of Sciences of Ukraine; *T. Tanaka*, National Institute for Research in Inorganic Materials, Japan; *M. Trenary*, University of Illinois at Chicago

Transition metal (TM) diborides have comparable and often higher degrees of hardness, chemical inertness and thermal stability than their nitride and carbide counterparts. Therefore, TM-diborides are attractive for the same type of applications as nitrides and carbides such as for hard coatings and diffusion barriers. In order to explore their usefulness as diffusion barriers and gate dielectrics, a series of experiments with silicon were performed. Silicon was deposited by the UHV-CVD of silane gas on clean and oxygen covered HfB@sub 2@ and ZrB@sub 2@(0001) surfaces. On the clean surfaces, HfSi@sub 2@ and ZrSi@sub 2@ were formed. A p(2x2)R30° LEED pattern was observed. The structure of Si on the surfaces was also investigated with STM. On the oxygen covered surfaces, silicates were formed. Oxidation of the crystals leads to the formation of HfO@sub 2@ and ZrO@sub2@, which both exhibited a (3x3) LEED pattern at a high

exposure (5 L) and a p(2x2)R30 pattern at a low exposure (0.5 L). Information gained from exposure of oxygen to ZrB@sub 2@ was crucial in interpreting the O 1s region in HfB@sub2@, which partially overlaps with the Hf 4s peak.

9:00am SS+MC-FrM3 Controlled Coordination and Oxidation State of Copper and Manganese Cations in Complex Nickel-Copper-Cobalt-Manganese Oxide Thin Films, D.A. KuKuruznyak, M.-H. Lee, K.A. Omland, M.C. Gregg, F.S. Ohuchi, University of Washington

Ionic configuration and cation distribution of the nickel-copper manganite spinels have profound effects on their electrical conduction. As these materials are being widely used for thermistor applications, it is important to find a way of controlling the oxidation states of transition metal cations in these mixed oxides. We have therefore undertaken our research developing a unique method fabricating thermistor composition by chemical solution deposition where cations with unusual coordination and unusual oxidation state can be obtained. Organometallic films deposited on silicon and glass substrates by spin-coating of a liquid precursor solution were decomposed in air at 550°C followed by furnace-annealing at temperatures ranging from 600° to 800°C to obtain single-phase cubic spinel of chemical composition Ni@sub 0.48@Co@sub 0.24@Cu@sub 0.6@Mn@sub 1.68@O@sub 4-x@. XPS, FTIR, and Mossbauer spectroscopy have been used to study oxidation states of transition metal ions. Octahedrally coordinated Cu@super +1@ observed from the specimens (prepared below 700°C) showed unusually large negative binding energy shifts in Cu(2p) peak relative to metallic Cu, of which origin was attributed to the difference in the Madelung potentials. Annealing at higher temperatures causes oxidation of copper to Cu@super 2+@ and reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. The annealing temperature can precisely control oxidation state distribution of copper and manganese cations.

9:20am SS+MC-FrM4 Behavior of Lightly Doped-electrons on the Electronic Structure of SrTiO@sub 3@: An Angle-resolved Photoemission Study, Y. Aiura, H. Bando, I. Hase, Electrotechnical Laboratory, Japan; T. Yasue, Tsukuba University, Japan; T. Saitoh, D.A. Dessau, University of Colorado

Behavior of lightly doped-electrons on the electronic structure of SrTiO@sub 3@ has been studied using angle-resolved photoemission spectroscopy (ARPES). Two states in the band gap region of SrTiO@sub 3@ (in-gap states) are observed; a state with a sharp Fermi cut-off (metallic state) and a broad state centered at ~1.5eV below the Fermi level (~1.5eV state). In order to study the origin of the metallic state, we have calculated the energy-band of non-doped (stoichiometric) SrTiO@sub 3@ and lightly electron-doped SrTiO@sub 3@ based on the full-potential linearized augmented plane wave (FLAPW) method. From comparison between the calculated results and the experimental ones from ARPES, it was shown that the metallic state can be quite well explained by the rigid-band behavior based on one-electron band theory. For the ~1.5eV state, on the other hand. ARPES spectra showed that there is no visible empirical energy dispersion and that its spectral intensity is very sensitive to the surface condition. These experimental results means that the ~1.5eV state is not caused by the bulk electronic structure, but the surface one due to the surface defects.

9:40am SS+MC-FrM5 Reactions of Acetaldehyde over UO@sub2@(111) Single Crystal Surfaces: Evidence of Benzene Formation, S.V. Chong, H. Idriss, The University of Auckland, New Zealand

The reactions of aldehydes on metal oxide surfaces have exposed some of the most exquisite chemistry compared to their alcohol and carboxylic acid counterparts. Due to the intermediate oxidation state of the carbonyl carbon on an aldehyde, reactions such as the Cannizzaro reaction (forming alcohol and carboxylate) and Tishchenko reaction (forming ester) have been observed on various metal oxide surfaces. Furthermore, condensation reactions have also been observed on aldehydes possessing alpha-H atom(s) over stoichiometric metal oxide surfaces, while surface defect sites are able to reductively couple two aldehyde adsorbates to yield alkene. Herein, we present the reactions of acetaldehyde over the stoichiometric, electron irradiated, and H@sub2@ reduced surfaces of UO@sub2@(111) single crystal. TPD results over the three surfaces show evidence of benzene formation, and it appears that electron irradiation slightly increases the conversion to benzene, while H@sub2@ reduction doubles it. Thus, the amount of benzene yield might be a novel way to quantify the extent of surface defects. No C@sub4@ hydrocarbon (crotonaldehyde nor butadiene) traces were observed, indicating that the

formation of benzene through aldol condensation pathways might be ruled out.

10:00am SS+MC-FrM6 Synchrotron-based XPS Study of 1-Decanethiol Chemisorbed on Au(111), Y.W. Yang, Synchrotron Radiation Research Center, Taiwan; L.J. Fan, National Tsing Hua University, Taiwan; L.J. Lai, Synchrotron Radiation Research Center, Taiwan

Self-assembled monolayers have been the subject of intense research due to their potential applications in areas of lubrications, corrosion inhibitions, gas sensors, etc. We combined TDS and synchrotron-based, high resolution core level spectroscopy to study the chemisorption of 1-decanethiol monolayer on Au(111) surface with the molecular films prepared from both gas-phase dosing and solution immersion. On heating to temperatures higher than 400 K. decanethiolate starts to decompose, forming 1-decene via @beta@-hydrogen elimination, and leaves atomic sulfur on the surface. For thin films produced by both methods, S2p core level exhibits a single, well-characterized spin-orbit doublet with S2p@sub 2/3@ at 162.1 eV, indicating identical chemical interaction between sulfur and gold atoms in the films. However, C 1s core level starts from 284.0 eV at low coverage, develops a high-binding shoulder at intermediate coverage and eventually becomes a single peak at 285.0 eV for the high coverage prepared from solution phase. Angle-resolved XPS measurements of substrate core level signal provide a direct measure of the film thickness. The increases of C 1s binding energy is found to be associated with the incomplete final-state relaxation of the carbon atoms due to the thickness increase of the film as the carbon chains tilt toward the surface normal. Moreover, the implication of observing only a well-defined doublet of S 2p signal will be discussed in relation to the sulfur dimer model.

10:20am SS+MC-FrM7 STM Studies of Pyrrole-sdsorbed Si(111)-7*7 Surfaces, Z.L. Yuan, National University of Singapore, Singapore

The Si(111)-7*7 surfaces is particularly appropriate in Si surface chemistry, because it contains dangling bonds on several different sites within the surface unit cell, and also STM has been used to provide direct and local information on an atomic scale.@footnote 1@ In the present work, the topographic and spectroscopic analysis of pyrrole adsorption on Si(111)-7*7 surfaces at room temperature under different pyrrole exposures is investigated by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). No significant changes in the surface reconstruction are observed, some adatoms become dark, however this is not due to the vacancies of Si adatoms, because these adatom are visible under the higher sample bias, the disappearance of adatoms is the result of changes in electronic structure upon reaction with pyrrole. the preservation of the 7*7 reconstruction suggests that the reaction with pyrrole has primarily saturated existing dangling bonds on Si(111)-7*7 surfaces. The adsorption is site selective, the faulted center adatoms are most favored for adsorption among the adatoms. The rest atoms also react with pyrrole from STS observation. Based on our STM/STS and HREELS data, a possible adsorption mechanism of pyrrole chemsorption on Si(111)-7*7 surfaces is also discussed. @FootnoteText@ @footnote 1@R. Wolkow and Ph Avouris, Phys. Rev. Lett. 1988, 60:1049; Phys. Rev. B,1989, 39:5091; J. Yoshinobu et al, Phys. Rev. B 1992, 46:9520; Jpn. J. Appl. Phys. 1993, 32:1171; M. N. Piancastelli et al, Phy. Rev. B 1993, 48:17892, R. A. Wolkow, Annau. Rev. Phys. Chem. 1999, 50:413.

10:40am SS+MC-FrM8 Characterization of Bound Ultrathin Perfluoropolyether-Functionalized Polysiloxane Films on Silicon Oxide Surfaces, F. Parsapour, Colorado State University; D.G. Castner, University of Washington; D.W. Grainger, Colorado State University

Current technological demands for magnetic recording media lubrication include a reduction in the head-disk gap, elimination of stiction, and fabrication of a low adhesion protective surface which can withstand thermal and mechanical stresses associated with hard disk drive operation. Perfluoropolyethers (PFPE) are the most commonly used lubricants in the magnetic recording media. These polymers are typically applied thin films to the hard drive overcoat to which they are generally physisorbed. As a result, they are subject to thermal degradation and "spin-off", ultimately resulting in tribological failure modes. Direct attachment of PFPE films is potentially interesting as a foundation for improved friction and wear performance. We have previously reported fabrication of ultrathin films of polysiloxanes functionalized with perfluoropolyether side chains chemisorbed to surfaces and exhibiting structural anisotropy due to separation of various polymer-grafted components normal to the interface. We now report analogous polymer monolayers but with the important chemical and functional distinction of surface bonding to silicon oxide through alkylsilane anchoring groups. These copolymers were synthesized

in a single step through the respective PFPE functional and alkylsilane anchor group coupling reactions. Monolayer films were formed on silicon oxide surfaces through the dip-coating method, resulting in hydrophobic immobilized films ~3 nm thick. XPS measurements support a stratified three-layer film chemistry within the monolayer, and an outer interface enriched with the PFPE moiety. AFM experiments show a high degree of coverage of the oxide surface by the copolymer film, and a relatively uniform surface. LFM measurements exhibit low frictional forces in the areas covered by the monolayer film. Force-displacement curves obtained in a fluid environment reveal a low adhesion surface compared to films prepared from copolymers without the PFPE functional group.

11:00am SS+MC-FrM9 Aerial Oxidation of Self-assembled Monolayers studied by SIMS, AFM and Contact Angle Measurement, N.J. Brewer, G.J. Leggett, University of Manchester Institute of Science and Technology, UK For many applications, the long term stability of self-assembled monolayers (SAMs) is a critical issue. We have undertaken a systematic study of SAM oxidation using secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM) and contact angle measurements. Samples were left in an ambient environment for specific periods of time and then surface analytical techniques were used to observe any changes in the SAMs. SAMs were formed from long and short chain methyl, carboxylic acid and hydroxyl terminated alkanethiols. By using SIMS, we were able to monitor the rate of oxidation. We found that DDT, a long chain methyl terminated SAM, oxidised in seven hours, but the long chain carboxylic terminated SAM was unoxidised after seven hours. This shows that long chain carboxylic acid terminated SAMs exhibit increased stability in air. AFM was used to record the friction coefficients of the SAMs over a period of hours. The change in the coefficient of friction was slow and it was little changed after times when SIMS showed complete conversion of thiolates to sulfonates had occurred. This suggests that although the sulfur-gold bond is broken, the interchain forces still hold the structure together. The collapse of the system is gradual and this is reflected in the slow change in the friction coefficients. Advancing water contact angle measurements exhibited a sharp change in contact angle for carboxylic acid and hydroxyl terminated SAMs due to adsorption of contaminants, but a small change for the methyl terminated SAMs. It is concluded that SAMs may oxidise reasonably rapidly on exposure to air, but that the degradation of their structures and properties is much slower.

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