Wednesday Afternoon, November 2, 2005

Applied Surface Science
Room 206 - Session AS-WeA

SIMS Cluster Probe Beams and General Topics

Moderator: I.S. Gilmore, National Physical Laboratory, Australia

2:00pm **AS-WeA1 Analysis of a Model System for Reactions of Organic Molecules on Atmospheric Particles: SAMS and Ozone**, ***D.J. Gaspar,*** Pacific Northwest National Laboratory*; T.M. McIntire,* University of California, Irvine*; A.S. Lea, N. Jaitly,* Pacific Northwest National Laboratory*; Y. Dubowski,* Technion-Israel Institute of Technology*; B.J. Finlayson-Pitts,* University of California, Irvine

Self-assembled monolayers (SAMS) provide a useful model system for the study of reactions of organic molecules. The preparation, use and analysis of SAMS are prone to variability and artifacts that can confound measurements that are do not provide molecular information on the state of the surface. Time of flight secondary ion mass spectrometry, on the other hand, provides a direct probe of the SAM surface chemistry. In this work, we describe our efforts to extract useful information regarding the reaction of ozone with saturated and unsaturated organic monolayers covalently bound to silicon dioxide surfaces under atmospherically relevant conditions. We have used a combination of imaging TOF-SIMS and spectral analysis aided by principal component analysis (PCA) to extract chemical information about the reaction of two model SAMS with ozone. The TOF-SIMS data provide the molecular information necessary to accurately interpret data obtained using other methods and described herein, including atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning Auger microscopy (AES). We show that the organic monolayer is removed from the Si substrate by ozone for an unsaturated 1-octene (C8=) monolayer, while it remains intact for a saturated dodecane (C12) monolayer. The implications of these observations for the atmospheric chemistry of organic molecules are discussed.

2:20pm **AS-WeA2 Formation and Volatilization of Small Molecules From a PTFE Matrix Upon MeV Alpha Particle Irradiation Examined by ToF-SIMS, SEM, and RGA**, ***G.L. Fisher,*** *R.E. Lakis, C.C. Davis, C.J. Wetteland,* Los Alamos National Laboratory*; C.W. Szakal, N. Winograd,* Pennsylvania State University

The chemical structure and morphology at the surface of @alpha@-irradiated polytetrafluoroethylene (PTFE) has been examined and compared to unirradiated PTFE. The samples were irradiated to doses of 10@super 7@ to 10@super 11@ Rad using 5.5 MeV [@super 4@He]@super 2+@ from a tandem accelerator beam line. Static time-of-flight SIMS (ToF-SIMS), using a 20 keV C@sub 60@@super +@ source, was employed to probe chemical changes versus irradiation. Chemical images and high resolution spectra in both positive and negative polarity were collected and analyzed to reveal the effects of @alpha@ particle radiation on the chemical structure. Where appropriate, comparison is made to static ToF-SIMS data collected using a 15 keV Ga@super +@ primary ion source. Residual gas analysis (RGA) was utilized to monitor the evolution of volatile species during vacuum irradiation of the samples. Secondary electron microscopy (SEM) was used to observe the morphological variation of samples with increasing @alpha@ particle dose. The data show that PTFE nominally retains its chemical structure and morphology at @alpha@ doses @<=@10@super 9@ Rad; however, at @alpha@ doses @>=@10@super 10@ Rad the PTFE matrix suffers severe chemical degradation, morphological roughening, and material loss. Chemical degradation is evidenced in the ToF-SIMS spectra by fragmentation, unsaturation, and speciation of molecules in the PTFE matrix. ToF-SIMS images support the assertion that chemical degradation is the result of @alpha@ particle irradiation and show morphological roughening of the sample with increased @alpha@ dose. High resolution SEM images more clearly illustrate morphological roughening and the mass loss that accompanies high doses of @alpha@ particles. Finally, RGA confirms the supposition that the product of chemical degradation in the PTFE matrix with continuing irradiation is evolution of volatile species resulting in morphological roughening and mass loss.

2:40pm **AS-WeA3 Depth Profiling Analysis by Secondary Ion Mass Spectrometry: Historical Perspective and Current State-of-the-Art**, ***C.W. Magee,*** Evans East **INVITED**

Secondary ion mass spectrometry has been used for in-depth characterization of materials and process for over 30 years. This talk will first touch briefly on history of SIMS depth profiling and then will review current state-of-the-art examples in semiconductors materials as well as in other areas as diverse from IC chips as potato chip bags and, yes, even the kitchen sink. Semiconductor areas will include, among others: profiling of ion implants with energies of a few hundred eV to a few million eV, along with high precision dose determination; and analyses of dopants and matrix elements in areas only a few 10's of um@super 2@. In addition, the talk will illustrate the utility of backside polishing for sample preparation.

3:20pm **AS-WeA5 SIMS Depth Profiling of Deuterium Labeled Polymers in Polymer Films and Multilayers**, ***S.E. Harton,*** *F.A. Stevie, D.P. Griffis, H. Ade,* North Carolina State University

Thin planar polymer films are model systems for probing physical phenomena related to molecular confinement at polymer surfaces and polymer-polymer interfaces. Secondary Ion Mass Spectrometry (SIMS) can provide real-space depth profiles of tracer labeled polymers directly with sufficient depth resolution for optimal analysis of these systems. Three different bilayer systems have been used to investigate various physical phenomena at polymer-polymer interfaces, including reactive compatibilization and interfacial segregation. Deuterated polystyrene (dPS) has been employed as the tracer polymer and has been imbedded in a matrix of either unlabeled polystyrene (PS) or poly(cyclohexyl methacrylate) (PCHMA). Using selective solvents and a direct casting method, these doped films have been placed on either poly(methyl methacrylate) (PMMA) or poly(2-vinyl pyridine) (P2VP) and thermally annealed. X-ray specular reflectivity measurements confirm ultra-sharp interfaces between the two polymers using this preparation method, allowing for maximum depth resolution during SIMS analysis. Varied analysis conditions for a magnetic sector instrument (CAMECA IMS-6f) were used to optimize the depth resolution and sensitivity while minimizing matrix effects and sample charging. For all systems Cs+ and O2+ have been used as the primary ion source, with detection of negative and positive secondary ions, respectively. Impact energy and primary ion species have been shown to affect matrix ion count rate for the various films studied. Conditions required to achieve constant matrix secondary ion yield across the heterogeneous interface are discussed.

3:40pm **AS-WeA6 Adjacent Electron Beam Method for SIMS Analysis of Insulators at High Depth Resolution Conditions Using a Magnetic Sector Instrument**, *C. Gu, Z. Zhu,* ***F.A. Stevie,*** *D.P. Griffis,* North Carolina State University

The adjacent electron beam charge neutralization method@footnote 1@ provides sufficient and self regulating charge neutralization for positive secondary ion SIMS analysis of both bulk and thick layer insulators using a magnetic sector instrument. This charge neutralization method has been extended to low primary ion impact energies, thus providing the ability to obtain high depth resolution SIMS analysis of both bulk and thick film insulating materials at high mass resolution. Results have been achieved with O@sub 2@@super +@ impact energy of 1.25keV and electron impact energy of 2.75keV. All prior analyses had been made using 5.5keV for O@sub 2@@super +@ and 6.5keV electron energy. Charge neutralization has been achieved for SiO@sub 2@, AlN, and AlGaN samples. Profiles have been obtained through at least two micrometers of insulator under the low impact energy conditions. While being able to profile through thick films is important, the real significance in these results is the ability to provide high depth resolution SIMS analysis of insulating materials. Electron impact charge neutralization using the adjacent electron beam method has been achieved with the following metal coatings: Al, Au, Ru, and Ir. Results will be presented demonstrating this method for both bulk and thick film insulating materials and current understanding of the mechanisms involved in this method of self regulating charge neutralization will be discussed. @FootnoteText@ @footnote 1@ A. L. Pivovarov, F. A. Stevie, and D. P. Griffis, SIMS XIV Proceedings, Applied Surface Science 231-232, 786-790 (2004).

4:00pm **AS-WeA7 The Atomic Motions behind Cluster Bombardment Secondary Ion Mass Spectrometry**, ***B.J. Garrison,*** Penn State University **INVITED**

The advent of cluster ion sources for Secondary Ion Mass Spectrometry (SIMS) has opened new applications for this technique. In particular, the C@super 60+@ ion beam appears to be quite promising as a source for imaging and depth profiling of molecular substrates. From a fundamental point of view, the obvious question is what are the atomic motions that result from the cluster vs. atomic bombardment? Using molecular dynamics computer simulations we have begun to elucidate the basics mechanisms of ejection or sputtering due to C@super 60@ bombardment of solids. Systems investigated to date include a clean Ag substrate,@footnote 1@ a thin film of benzene on Ag@footnote 2@ and

water ice. The various systems investigated to date will be discussed along with relevant experimental data. @FootnoteText@ @footnote 1@ Enhancement of Sputtering Yields due to C@super 60@ vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Analytical Chemistry, 75, 4402-4407 (2003)@footnote 2@ Microscopic Insights into the Sputtering of Ag{111} Induced by C60 and Ga Bombardment of Ag{111}, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, J. Phys. Chem. B, 108, 7831-7838 (2004) .

4:40pm **AS-WeA9 Comparison of TOF-SIMS and XPS Analysis Using a C@sub 60@ Ion Sputter Cleaning***, **N. Sanada**, T. Miyayama, J.S. Hammond,* ULVAC-PHI, Inc., Japan*; J.F. Moulder, S.R. Bryan,* Physical Electronics

The analysis of chemical layers buried in the near surface region from 1 to 100 nm is of great interest to polymer and biomaterials scientists. However, it has been a great challenge to get chemical information from this region of some materials because of chemical damage observed following ion beam sputtering. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for sputter cleaning and depth profiling to minimize chemical damage for organic and inorganic materials.@footnote 1@ Extremely low sputtering degradation of many organic materials such as polytetrafluoroethylene,@footnote 1@ polyesters, gelatins, and multilayer latex materials@footnote 2@ were observed by XPS. The effects of different C@sub 60@ ion beam accelerating voltages and impact angles on accumulation of residual carbon and chemical damage were examined with XPS using standard samples of polyethyleneterephthalate (PET) and SiO@sub 2@. The quantities of carbon residue in the SiO@sub 2@ film reduced as the increasing accelerating voltages. The impact angle of the ion beam also affected the carbon residue in the film.@footnote 3@ Based on these experiments, an optimized protocol for using a C@sub 60@ ion beam with XPS was developed. We will discuss TOF-SIMS analysis of polymers after sputter cleaning with a C@sub 60@ ion beam under the protocol optimized with XPS. For many polymers, the high energy resolution XPS spectra following C@sub 60@ ion beam exposure showed a constant elemental and functional group stochiometry. The higher sensitivity of TOF-SIMS analysis of these materials allows an examination of more subtle changes induced by the C@sub 60@ ion beam not observed in the XPS analysis. @FootnoteText@ @footnote 1@ N. Sanada et al., Surf. Interface Anal., 36 (2004) 280.@footnote 2@ D. Sakai, et al., J. Surf. Anal. (Tokyo), submitted.@footnote 3@ N. Sanada, et al., AVS 51st. Int. Symp. As-TuM5.

5:00pm **AS-WeA10 TOF-SIMS Imaging of OLED Devices using a Au Cluster Ion Beam***, **S.R. Bryan**,* Physical Electronics*; J.S. Hammond, N. Sekiya, A. Yamamoto,* ULVAC-PHI, Inc.

Organic light emitting diode (OLED) technology is a growing research area which may lead to next generation display and lighting commercial products. OLED is based on the use of multi-layers of thin molecular or polymer materials which emit light directly when a voltage is applied. The total thickness of the multi-layer film structure is usually less than 500nm. The organic layers can be doped with specific enhancing molecules to get the desired brightness and color. This new cutting edge technology based on patterned organics requires analytical techniques that can characterize the organic structure of the devices with submicron spatial resolution and good depth resolution. TOF-SIMS offers one of the only techniques that can provide the needed spatial resolution with molecular specificity. One of the most important commercial developments in TOF-SIMS instrumentation in recent years has been the introduction of cluster ion beams for enhancement of organic molecular secondary ion yields. Although Ga+ LMIG sources, which have been used in TOF-SIMS since 1990, has sufficient spatial resolution for most applications, the secondary ion yield of organic molecules from Ga+ sputtering is insufficient for many applications. Development of the Au LMIG emitter, which allows TOF-SIMS analysis with Au+, Au2+ or Au3+, extends the capabilities of TOF-SIMS to image patterned organic materials. The capabilities of imaging with the Au LMIG emitter will be compared to the Ga emitter for characterization of OLED devices. Spatial resolution, damage cross-sections, and ultimate detection limits will be compared between Ga, Au, Au2, and Au3 for typical molecules used in OLED devices.

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