Monday Morning, November 15, 2004

Applied Surface Science
Room 210A - Session AS-MoM

SIMS I - Cluster Probe Beams and General Topics

Moderator: I. Gilmore, National Physical Laboratory, UK

8:20am **AS-MoM1 Application of TOF-SIMS to Environmentally Relevant Surface and Interfaces*, D.J. Gaspar*,** *A. Laskin,* Pacific Northwest National Laboratory*; B.J. Finlayson-Pitts,* University of California, Irvine*; B.M. Sass,* Battelle Memorial Institute

TOF-SIMS analysis is an invaluable tool for analysis of environmentally relevant samples. The molecular identity and distribution of surface species can be essential in understanding environmental samples. In the Environmental and Molecular Sciences Laboratory, we have applied TOF-SIMS analysis to problems in atmospheric and environmental chemistry. Some examples presented here include: identification and measurement of fatty acids on aerosol particles, measurement of extent of reaction between NaCl and hydroxyl radicals,@footnote 1@@super ,@ @footnote 2@ investigation of the interaction between glass and gaseous nitric acid,@footnote 3@ and determination of heavy metal distributions in weathered, pressure-treated wood. In the first example, fatty acids were identified on field collected atmospheric aerosols as a function of time. Next, hydroxyl radicals were found to reacted with NaCl particles in the laboratory to produce basic species, while in the third example, the reaction products of gaseous nitric acid and borosilicate glass were determined to segregate on the glass surface in precipitates according to solubility. Finally, the distribution of copper, chromium and arsenic, as well as other metals, were measured in pressure treated wood after extended weathering. Each of these examples demonstrates the utility of TOF-SIMS in identifying species and determining distributions on environmentally relevant surfaces. @FootnoteText@ @footnote 1@ D.J. Gaspar, A. Laskin, W. Wang, S.W. Hunt, and B.J. Finlayson-Pitts. Applied Surface Science, in press, 2004.@footnote 2@ A. Laskin, D.J. Gaspar, W.H. Wang, S.W. Hunt, J.P. Cowin, S.D. Colson, B.J. Finlayson-Pitts. Science, 301 (2003) 340-344,"@footnote 3@ Y. Dubowski, A. L. Sumner, E. J. Menke, D. J. Gaspar, J. T. Newberg, R. C. Hoffman, R. M. Penner, J. C. Hemminger and B. J. Finlayson-Pitts. Physical Chemistry Chemical Physics, in press, 2004.

8:40am **AS-MoM2 Cluster Primary Ion Beam Secondary Ion Mass Spectrometry for 2 and 3 Dimensional SIMS Analysis*, G. Gillen*,** *P. Chi, A.J. Fahey, C.M. Mahoney, M.S. Wagner,* National Institute of Standards and Technology **INVITED**

The use of novel monoatomic and cluster primary ion beams for Secondary Ion Mass Spectrometry (SIMS) has several potential advantages for surface analysis. Cluster ion sputtering results in a reduced penetration depth for the constituent atoms of the cluster, which should improve SIMS depth resolution and minimizes the sputter depth over which the build up of the primary beam gives non-linear sputter and ion yield enhancements (the so-called transient region). Cluster bombardment may also reduce sputter-induced topography created during ion beam analysis of metal films. For organic surface characterization, cluster primary ion beam offers large improvements in sensitivity and, in selected cases, immunity to primary-beam-induced degradation of the sample. At NIST we are working on the application of novel primary ion beam SIMS for practical surface analysis. Several types of prototype ion sources are currently being evaluated for this application including; SF5+ , C8- and C60+. A variety of materials have been analyzed using these new ion sources including low energy ion implants of arsenic and phosphorous in silicon, boron delta-doped layers, surface metals, metal films, organic films and polymers. Recent key findings include the observation of improved depth resolution for semiconductor analysis and a reduction in beam-induced topography for metal films. Our most recent efforts have been focused on extending the cluster SIMS technique for the molecular depth profiling of organic thin films. Combined with secondary ion imaging we will demonstrate the unique capability of cluster SIMS to provide true 3 dimensional molecular surface analysis.

9:20am **AS-MoM4 Fundamentals and Applications of a New Bi-cluster Liquid Metal Ion Source*, F. Kollmer*,** *P. Hoerster, R. Moellers, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

In recent years Au cluster primary ions emitted from a LMIS (liquid metal ion source) have been successfully applied for the analysis of organic surfaces by TOF-SIMS. Compared to monoatomic primary ion bombardment the use of Au clusters leads to a considerable enhancement of the secondary ion yield up to several orders of magnitude. As the corresponding increase in the damage cross section is much smaller, the ion formation efficiency as a cumulative measure of the sensitivity of the analysis process, also increases significantly. In particular the Au cluster source combines the fundamental benefits of cluster ion bombardment with a high brightness source allowing to push the lateral resolution in organic imaging down to the 100-nm range. In this contribution fundamental as well as practical aspects of a newly developed Bi-cluster liquid metal ion source are addressed and compared with the capabilities of a Au cluster source. The Bi-cluster source offers excellent prospects for organic surface analysis since a large fraction of the primary ion current is emitted as singly and doubly charged clusters (up to Bi@sub 7@@super 2+@). Even at low emission currents stable operation is achieved which is advantageous with respect to the lifetime of the source and the spot size of the primary ion beam.

9:40am **AS-MoM5 TOF-SIMS Studies using a Newly Developed C@sub 60@@super +@ Primary Ion Gun: Fundamental Aspects and Applications*, R. Moellers*,** *F. Kollmer, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

Recently it was shown that cluster primary ion bombardment leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub-µm range. C@sub 60@ is currently discussed to be the most efficient projectile for organic surface analysis and first results have been published announcing depth profiling capabilities of C@sub 60@@super +@ primary ions on organic materials. We have integrated a newly developed C@sub 60@ ion gun into the TOF.SIMS 5. The gun can be operated both as sputter gun and as analysis gun with a primary ion energy of up to 20 keV using doubly charged C@sub 60@ particles. The new setup allows the direct comparison between different primary ions such as C@sub 60@@super +@, Au@sub 1@@super +@, Au@sub 3@@super +@ as well as the combination of metal cluster ions and C@sub 60@ in dual beam depth profiling. C@sub 60@@super +@ primary ions were used to extend our systematic investigation on the influence of different primary ion species, including metal cluster ions as well as monoatomic primary ions, on secondary ion parameters such as yield Y, damage cross section @sigma@ and efficiency E = Y/@sigma@. Those parameters have been evaluated for a variety of different sample materials and sample preparations allowing a classification of the merits of C@sub 60@ in different fields of application. Beside these fundamental aspects of cluster ion beam bombardment, the use of C@sub 60@@super +@ beyond the static limit on different samples will be highlighted.

10:00am **AS-MoM6 ToF-SIMS Quantitation of PDMS at the Surface of a Dehydrated Commercial Hydrogel Material*, J.A. Gardella, Jr.,*** State University of New York at Buffalo

The method of standard additions was performed in order to determine the amount of PDMS present at the surface of a dehydrated hydrogel material. Known amounts of a PDMS monomer were added to the surface and allowed to equilibrate. Peak ratios of 73Da (C3H9Si+):69Da(C4H5O+) and 147Da(C5H15Si2O+):113Da(C6H9O2+) were plotted against ng of PDMS added to the surface. A linear fit was applied to the data and the amount of PDMS present at the native surface was determined.

10:20am **AS-MoM7 SIMS Trace Uranium Measurements in HfO Films with the ims-1270*, A.J. Fahey*,** National Institute of Standards and Technology

The presence of radioactive elements, such as U, even at trace levels can make it impractical or impossible to use some materials in semiconductor applications because of randomly induced logic-errors from the decay of the radioactive element. Efforts have been put forth to determine the trace concentration of uranium in a HfO film deposited on Si. This measurement is complicated by the fact that high mass resolution is needed to resolve @super 178@HfSiO@sub 2@ from @super 238@U. In addition, high sensitivity is required in order to measure trace quantities of uranium in the film. The ims-1270 at the National Institute of Standards and Technology has been used for this purpose. Large magnetic sector SIMS instruments are not generally used by the semiconductor SIMS community because of their size and cost. However, they can address some very specific problems that cannot be addressed by smaller instruments that do not have the mass resolution or the transmission. A mass resolution of ~5000 is easily achieved with the ims-1270, while maintaining nearly full transmission. This condition can be used to separate the interference at U. An apparent concentration of U between ~1-10 ppm was measured is the available films. The measurement method, the data and attempted quantification of the measured concentration will be discussed.

10:40am **AS-MoM8 Improved Analysis of Bulk Insulators using Magnetic Sector SIMS with O@sub 2@@super +@ Primary Beam and Electron Beam Adjacent to Analysis Area***, F.A. Stevie, C. Gu, A. Pivovarov, R. Garcia, D.P. Griffis,* North Carolina State University

The application of a new method(1) for magnetic sector SIMS analysis of thick film and bulk insulators using O@sub 2@@super +@ primary beam with electron beam adjacent to the area of interest has been extended. Excellent results have been obtained for a wide range of bulk insulators, including SiO@sub2@, LiNbO@sub 3@, Al@sub 2@O@sub3@, AlN, and a low-K dielectric. Quantification of impurities in bulk insulators has also been demonstrated as evidenced by depth profiles of B implanted in silica, Ti in LiNbO@sub 3@, and Be in Al@sub 2@O@sub 3@. The 1E15 atoms/cm@super 3@ detection limit obtained for the Be in Al@sub 2@O@sub 3@ cannot be achieved using quadrupole analyzers because of the inability to filter the Al@super 3+@ mass interference. Profiles several micrometers deep have been routinely achieved. Accurate concentrations for several elements have also been obtained on NIST standard glasses. The analysis of the low-k dielectric was significant because direct electron bombardment results in decomposition of this material. While the efficacy of this method is indisputable, the apparently self compensating mechanism is not understood. It is clear that a conductive coating encompassing the sputtered area is required and that the electron beam must impact within approximately 100@micron@m of the analyzed area. While it is not clear which if any of these charge compensation mechanisms predominate, the most probable mechanisms contributing to positive charge compensation include secondary and/or backscattered electrons and electron beam induced conductivity (EBIC). Efforts to understand the charge neutralization mechanism for this method continue. (1) A. L. Pivovarov, F. A. Stevie, D. P. Griffis, Appl. Surf. Sci. (2004) in press

11:00am **AS-MoM9 Ionization of Al Atoms Emitted from Al Metal***, **X. Chen,*** University of California, Riverside*; Z. Sroubek,* Czech Academy of Sciences, Czech Republic*; J. Yarmoff,* University of California, Riverside

Ion-surface charge exchange is a central process in many surface analysis techniques, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). Recently, we achieved a better understanding of homogeneous charge exchange between metal ions and metal surfaces, which gives a general insight for all the above techniques and is especially critical in analysis of SIMS data. Atomically clean and modified Al (100) surfaces in ultra-high vacuum were bombarded by 2 and 5 keV Xe@super +@ ions. The absolute ionization probability of energetic (> 500 eV) recoiled particles was measured with time-of-flight, and then used to calibrate the energy and angular distributions of low energy (10-600 eV) sputtered ions collected with an electrostatic analyzer. The independent particle model of non-adiabatic surface-atom charge-exchange, which has typically been used to analyze single scattering events, is shown to accurately describe all of the experimental data from a few eV (typical sputtering energy) to the keV (typical scattering and recoiling energy) range. Extensions of this work to other clean metal surfaces, such as Fe, which has a d-band, will be discussed. Also, we plan to perform homogeneous scattering experiments with a novel liquid metal ion source (LMIS), to determine absolute homogeneous ionization probabilities for well-defined trajectories.

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