

Thursday Morning, November 3, 2011

Applied Surface Science Division

Room: 102 - Session AS-ThM

Analysis of Insulators and Challenging Samples

Moderator: D.J. Gaspar, Pacific Northwest National Laboratory

8:00am **AS-ThM1 Imaging and Differentiation of Epicuticular Waxes on *Arabidopsis thaliana* Organs by TOF-SIMS**, *G.L. Fisher*, Physical Electronics, *P. Wong*, *C. Buschhaus*, *R. Jetter*, University of British Columbia, Canada

TOF-SIMS has emerged as an important tool for imaging mass spectrometry of biological samples due to its unique capability to detect molecular ion fragments and elemental ions at sub-micron spatial resolution and without the sample treatments required by e.g. the MALDI technique. For many biological specimens, the ability to image samples having a large degree of surface topography is also highly desired. The resulting elemental and molecular images provide important information regarding the composition of biointerfaces, for example between plant tissues and their natural environment. This TOF-SIMS study involves the differentiation and characterization of epicuticular waxes present at the surfaces of *Arabidopsis thaliana* organs including the flower, stem, adaxial (top) leaf surface and the abaxial (bottom) leaf surface.

High spatial resolution images obtained from a flower petal, an adaxial leaf surface, and an abaxial leaf surface revealing spores, trichomes and respiratory pores, respectively, demonstrate the capability of TOF-SIMS to image molecular ion fragments with a spatial resolution of < 0.3 microns. Total ion images, and molecular fragment ion images of epicuticular wax components, demonstrate the capability to image entire organ surfaces without topographical artifacts. High mass range spectra in both the positive and negative secondary ion polarities reveal that the epicuticular surface of each *Arabidopsis thaliana* organ is comprised of distinct wax components. Mass spectra acquired from specialized cells forming the 1 μm x 7 μm respiratory pores of the abaxial leaf surface indicate that, even within a single organ surface, the epicuticular wax composition may vary. The differences in wax composition on each of the interrogated organs of *Arabidopsis thaliana* will be presented and discussed. Structural assignments for characteristic mass spectrometric features related to the wax composition will also be presented and discussed.

8:20am **AS-ThM2 Aqueous SIMS – Towards in Situ Detection of Chemical Reaction Intermediates in Aqueous Solutions**, *Z. Zhu*, *L. Yang*, *X. Yu*, *M.J. Iedema*, *J.P. Cowin*, Pacific Northwest National Laboratory

This research provides the first in-situ detection of aqueous surfaces using time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS provides a molecular recognition capability with super-low detection limits, making it a great choice to detect short-lifetime chemical reaction intermediates in aqueous solutions. However, it is difficult to detect aqueous solutions by ToF-SIMS because ToF-SIMS is a high vacuum technique, and the vapor pressure of water is about 2-3 kPa at room temperature. We designed and fabricated a self-contained microfluidic module, allowing in-situ analysis of aqueous surfaces by ToF-SIMS. Microfluidic channels were prepared on top of a block of polydimethylsiloxane (PDMS) using a patterned silicon template with soft lithography techniques, and then a ~100nm thick silicon nitride film was placed on top of the microfluidic channels, on which a small hole with a diameter of ~2-3 microns could be drilled using a focused primary ion beam in a ToF-SIMS instrument. De-ionized water, heavy water, a 0.5% (weight ratio) formic acid aqueous solution, a 0.5% glycerol aqueous solution, and a 0.5% glutamic acid aqueous solution were successfully analyzed through the small hole using our ToF-SIMS instrument (IONTOF-V). The pressure in the analysis chamber was usually at ~5E-7 mbar during measurements, and this value was sufficient for ToF-SIMS analysis. Our device could be safely staying in vacuum for more than 8 hours, and 1 hour continuous SIMS measurements were practical. Molecular signals (M-H) from formic acid (HCO₂⁻), glycerol (C₃H₇O₃⁻), and glutamic acid (C₅H₈NO₄⁻) were clearly observed in the small hole, but not elsewhere. Based on current data, the detection limits of formic acid, glycerol, and glutamic acid were estimated to be <0.01% (weight ratio).

8:40am **AS-ThM3 Challenges of the XPS Analysis of the Ionic Liquid [BMIM][PF₆]**, *R.R. Harl*, *B.D. Booth*, *G.K. Jennings*, *B.R. Rogers*, Vanderbilt University

Room temperature ionic liquids (ILs) are ionic compounds that are liquids at ambient conditions due to a bulky, asymmetric organic ion that inhibits crystalline packing. The inhibition of crystalline packing results in ILs having a vapor pressure that is negligibly low. The properties of ILs make them candidates for applications such as nonvolatile solvents, electrolytes, and lubricants. The ionic liquid pair 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] is being investigated for use as a lubricant in micro-electrical mechanical systems (MEMS). Surface properties are important in tribological applications like lubrication and the negligible vapor pressure of the [BMIM][PF₆] ionic liquid makes it compatible with traditional surface analysis tools like x-ray photoelectron spectroscopy (XPS).

XPS analysis of ILs is challenging due to the ability of the ionic molecules within the ILs to freely move within the sample. Also, since the ILs are comprised of charged molecules, the motion of the molecules and their relative position within the sample may be affected by changes in surface charging brought about by photoelectron emission or by the electron and ion beams used to neutralize surface charging.

We will present results of our XPS analyses of [BMIM][PF₆] ionic liquid drop-cast onto a silicon substrate. We dropped enough of the IL to form an approximately 150 nm thick film to mimic a film that would be used for lubricating a MEMS device. However, the IL drop-cast in this manner did not form a continuous film, but rather beaded up on the silicon substrate. Under certain analysis conditions we can force the IL droplets to coalesce into a continuous film.

Preliminary results show that when the surface is positively charged the PF₆ molecule segregates to the liquid/vacuum interface. This observation is consistent with previous studies. When the IL surface is negatively charged the C1s peak shape changes from that indicative of the imidazole ring C-N bonding to that indicative of C-C bonding, most likely from the butyl chains of the BMIM molecules. This change in the C1s spectrum suggests the BMIM molecules are segregating to the liquid/vacuum interface. A corresponding drop in the F1s peak intensity suggests that the PF₆ molecules are moving deeper into the sample.

Along with the XPS results we will propose a mechanism by which the charge and/or energy provided by the x-ray, electron and ion beams induce the change from dispersed droplets to a continuous film. We will also provide insight into how these results could be used in developing or using ILs for MEMS lubricants.

9:00am **AS-ThM4 Working with Difficult Samples - Preparation, Damage, Charging and Data Analysis**, *D.R. Baer*, *M.H. Engelhard*, *A.S. Lea*, *P. Nachimuthu*, *Z. Zhu*, Pacific Northwest National Laboratory
INVITED

X-ray Photoelectron Spectroscopy (XPS) and other surface analysis methods (e.g. AES and SIMS) are playing increasingly important roles in the analysis of many materials ranging from ancient artifacts, geological minerals and even biological specimens to modern very complex nanostructured materials. Samples that need to be analyzed can be made up of components with a wide variety of physical and chemical properties that impact how they can be handled, prepared, mounted and analyzed without destroying the information that is sought from the analysis. During this presentation a variety of the methods and approaches needed to characterize a range of sample and analysis challenges that we have faced in the EMSL, a US Department of Energy user facility, will be discussed. Analysis challenges discussed will include: inexperienced users and their expectations; sample handling, preparation (including extraction of particles from aqueous solution) and mounting (including anaerobic transfer and freezing); identifying and dealing with damage; identifying and controlling impacts of charging (which are not always obvious); and analysis approaches used to extract information about the nanostructure of complex materials. The materials and materials systems to be discussed will include the impact of processing on catalyst surface composition and chemistry, the oxidation state of species adsorbed on mineral surfaces, the nature and properties of organic layers on inorganic substrates, and the nature of the surfaces and intentional as well as inadvertent coatings (shells) on nanoparticles. Some of the methodology and special capabilities developed in EMSL for controlling sample environments, the value of more rapid and enhanced data analysis, and the importance of procedural guides and standards will be noted. Although many of the topics discussed relate to a variety of surface analysis and other methods, the talk will focus on XPS and use TOF-SIMS to provide an example of challenges associated with

measurement of hydrogen. The importance of complementary measurements by a variety of methods (including XRD, TEM, APT, SEM and RBS) will be highlighted.

Aspects of the work have been supported by the Offices of Basic Energy Sciences and Biological and Environmental Research of the US DOE and by the National Institute of Environmental Health Science under grant NIH U19 ES019544. Portions of this work were conducted in the Environmental Molecular Sciences Laboratory (EMSL), a DOE user facility operated by Pacific Northwest National Laboratory for the Office of Biological and Environmental Research of the DOE.

10:40am **AS-ThM9 Transient Electron Emission from Insulators under Pulsed Electron Beam Injection.** *Y. Kimura, H. Koyama, H. Makino, H. Shinada*, Hitachi, Ltd., Japan, *Y. Mochizuki, H. Kazumi*, Hitachi High-Technologies Corp., Japan

Electron emissions from poorly conductive specimen stimulated by photon and electron injections result in charging phenomena. These can cause distortion of data in electron spectroscopy and image artifacts in scanning electron microscopy because surface potential which influence the motion of emitted electron is modified by charging and change time dependently. Therefore, time dependence of electron emission yields are important for understanding of radiation induced charging of resistive materials.

In this study, we present the transient characteristics of electron emission from SiO₂ using a new experimental facility (Pulsed Electron Microscope: PULSEM) built in the present work. Main feature of the PULSEM, as with electron beam testing system, is a beam blanking system attached below the condenser lens. The beam blanking pulses electron beam into the minimum number of 6 electrons under the condition of primary beam current $I_p = 20$ pA and beam-pulse-width $t_p = 50$ ns. The Everhart-Thornley detector with high response scintillator, afterglow time of which is 0.5 ns, and with a photomultiplier is synchronized to the beam blanking system. Transient SE signal as a function of the number of injected electrons is obtained.

Time-dependent electron emission yield (σ) with the resolution of 30 ns is investigated as a function of the primary electron dose which is controlled by pulse duration (Δt) as well as primary energy (E_p). Quasi static emission yield, which assumed to be intrinsic electron emission in the absence of charging, is obtained under low dose condition of below 60 electrons with $I_p = 20$ pA and $\Delta t = 500$ ns. The maximum yield (σ_m) and its corresponding energy (E_m) are 2.5 and 300 eV, respectively. With the increase in electron dose, σ approaches unity due to a charging effect. Finally, we will present total electron emission yield curves in the range of $E_p < 6$ keV and 50 ns $< \Delta t < 500$ ms.

11:00am **AS-ThM10 High Resolution XPS Chemical State Imaging of Fuel Cell Membranes.** *S.N. Raman, P.E. Larson, J. Moulder, J.S. Hammond, S. Alnabulsi*, Physical Electronics USA

Nafion based membranes are being developed for applications in fuel cells. These fuel cell membranes are multi-layer structures with a permeation membrane and two thin layers of noble metal in a polymer matrix acting as the anode and the cathode of the fuel cell. The cross-sectional chemical analysis of these membranes, both new and used, may be extremely useful in improving the performance of the fuel cells. In this study we will highlight new and advanced scanning XPS microprobe based techniques to provide cross-sectional line scans and high resolution chemical mapping of these membranes. The line scan and chemical mapping results elucidate the modifications of the membrane chemistry as a function of use.

11:20am **AS-ThM11 Gas-Cluster Ion Beam Secondary Ion Mass Spectrometry Characterization of Thin Films for Organic Electronics Applications.** *D.J. Gaspar*, Pacific Northwest National Laboratory, *S.R. Bryan*, Physical Electronics USA, *T. Miyayama*, ULVAC-PHI, Japan, *A.B. Padmaperuma, J.S. Swensen, E. Polikarpov*, Pacific Northwest National Laboratory

Organic light emitting devices (OLEDs) have the potential to dramatically change the way we light our living spaces. OLEDs offer the potential for high efficiency lighting from a large area source, with the possibility of transparent and flexible lighting as well. Currently, OLED displays are found commercially in cell phones and in televisions in limited production. One of the key barriers holding back widespread adoption of OLEDs for both lighting and other products is the challenge of generating long-lived devices, particularly for high-efficiency phosphorescent blue OLEDs (a necessary component of high-efficiency white OLEDs). Challenges in the design of stable materials are hampered by our relatively poor ability to measure degradation products in situ, or in ways that ensure we have not damaged the material in the measurement process. To this end, we have generated thin films of single blue phosphorescent OLED components, multilayer films, and working OLEDs before and after aging. These components including the well-studied bis[2-(4,6-difluorophenyl)pyridyl-N,C2']iridium (III) (FIrpic), 2,8-bis(diphenylphosphoryl)dibenzothiophene

(PO15), 4-(diphenylphosphoryl)-N,N-diphenylaniline (HM-A1) and di-[4-(N,N-ditolyamino)-phenyl]cyclohexane (TAPC). Based on previous experiments in our lab and literature reports, FIrpic and PO15 are known to undergo degradation reactions under conditions similar to those used in this series of experiments. Analysis of these films and systems by gas cluster ion beam secondary ion mass spectrometry (GCIB-SIMS) and other methods show degradation products, which permit the development of useful models for their degradation pathways. These results clearly demonstrate the utility of GCIB-SIMS in the characterization and analysis of OLED devices and materials, and should enable better design and screening of stable materials for high-efficiency OLEDs.

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