Monday Afternoon, November 10, 2014

Applied Surface Science
Room: 316 - Session AS+BI+MC+SS-MoA

The Liquid Interface & Depth Profiling and Sputtering with Cluster Ion Beams
Moderator: Ian Gilmore, National Physical Laboratory, Michaeleen Pacholski, The Dow Chemical Company

2:00pm **AS+BI+MC+SS-MoA1 Quantifying the Impact of Curvature, Convection and Complexity on Dynamic Interfacial Tension of Fluid-fluid Interfaces**, *Lynn Walker*, Carnegie Mellon University **INVITED**
The ability to control and predict the adsorption of species at fluid-fluid interfaces is a central issue in many materials processing problems. In most processing steps, this adsorption is dynamic and part of a larger transport problem that requires understanding of local fluid flow, bulk diffusion, interfacial curvature and the details of the adsorption and desorption kinetics. We have been developing tools and a protocol to allow the details of transport of surface active species to interfaces to be quantified. Several examples of the characterization of complex fluid-fluid interfaces will be discussed. The dynamics of adsorption of single and multicomponent surfactant mixtures at oil-water and air-water interfaces has been characterized using a microtensiometer. The use of microscale interfaces allows the transport processes involved in adsorption to be analyzed and both diffusion and kinetic parameters characterized. Microscale interfaces with high curvature allow the impact of curvature to be characterized on the dynamic interfacial tension (IFT) and mechanics of the interface. The scale of the device allows the bulk solution in contact with the interface to be changed rapidly. We are able to remove the bulk surfactant at different points in during the dynamics of adsorption by rinsing the interface and continuously replacing the bulk fluid with surfactant-free aqueous phase to investigate the reversibility of adsorption. For a bulky nonionic surfactant, a critical interfacial tension arises that links the transport dynamics to the onset of partial reversibility in the system. By measuring the mechanical properties of pre-rinsed and rinsed interfaces, we also find a critical interfacial tension that leads changes in the elasticity of the interfaces. The impact of changes in interfacial coverage on coalescence and competitive adsorption are characterized to demonstrate the connection between structure of complex interfaces and interfacial behavior.

2:40pm **AS+BI+MC+SS-MoA3 *In Situ* Probing of Liquid Surfaces and Interfaces by Time-of-Flight Secondary Ion Mass Spectrometry**, *Xiao-Ying Yu*, Pacific Northwest National Laboratory
The surfaces of aqueous phases and films can have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface to enable direct observation of liquid surfaces and liquid-solid interactions. The unique aspect of our approach is that 1) the detection window is an aperture of 2-3 micrometers in diameter, which allows direct imaging of the liquid surface, and 2) surface tension is used to hold the liquid within the aperture. The microfluidic reactor is composed of a silicon nitride (SiN) membrane and polydimethylsiloxane (PDMS) . Its application in time-of-flight secondary ion mass spectrometry (ToF-SIMS) as an analytical tool was evaluated using a variety of aqueous solutions and complex liquid mixtures, some of which contain nanoparticles. Most recently, we demonstrated *in situ* probing of the electrode-electrolyte solution interface (or solid-electrolyte interface, SEI) using a new electrochemical probe based on our original invention. It provides the first direct observation of the surface and diffused layer of SEI in a liquid with chemical speciation using ToF-SIMS. Moreover, we extended the microfluidic reactor for biofilm growth and mammalian cell cultures and real-time correlative characterization by more than one spectroscopy and microscopy technique. Results from our latest development will also be presented in additional to published ones, showcasing new directions and applications using this novel approach based on microfluidics and combined vacuum and ambient spectroscopy and microscopy multimodal imaging.

3:00pm **AS+BI+MC+SS-MoA4 Mass Spectrometric Characterization of Droplet Surfaces at Ambient Pressure**, *Kaveh Jorabchi*, Georgetown University
Mass spectrometric methods provide excellent selectivity and sensitivity for chemical characterization of samples. For these methods, ionization constitutes a key step where chemical information from the sample is encoded into populations of gas-phase ions. Investigations on electrospray ionization have shown that the ionization efficiency has a positive bias with respect to surface affinity of analytes in droplets, opening a new avenue for liquid surface analysis. This ionization bias stems from higher ion production rates for surface active analytes. To this end, we have developed a new method to monitor gas-phase ion formation rates from charged nano-droplets. A pulsed nano-spray is used to emit a cloud of charged nano-droplets within an atmospheric-pressure mobility cell. The droplets are guided by a pulsed electric field through the mobility cell, undergoing desolvation and ion production prior to detection by a time-of-flight mass spectrometer. Each chemical species within the droplets creates an ion cloud. The arrival times of the ions at the mass spectrometer are recorded by varying the on-time of the pulsed electric field within the mobility cell, enabling ion cloud size measurements. We demonstrate that the ion cloud sizes are correlated with ion production rates, reflecting interfacial propensity of the analytes. These measurements are consistent with the ion evaporation mechanism from charged nano-droplets, providing a method for liquid surface analysis based on gas-phase ion formation rates.

3:40pm **AS+BI+MC+SS-MoA6 Organic Depth Profiling Alchemy: Can We Transmute Data into Meaning?**, *Alexander Shard*, National Physical Laboratory, UK **INVITED**
Argon cluster sources suitable for depth profiling organic materials have developed rapidly and are now widely available and routinely used to analyse materials ranging from organic electronic devices to biological samples. This fantastic progress allows detailed insight into the chemistry and structure of organic materials with depth resolutions below 10 nm over many micrometres. When combined with 2D surface chemical imaging, detailed 3D reconstructions can be obtained allowing the label-free visualisation of chemical distributions which were previously impossible to obtain. However, because detailed understanding of the processes involved is still developing, it is necessary to view such data with scepticism when a quantitative answer is required. Conversely, the ability to perform nearly damage-free profiles of organic materials allows us to answer fundamental questions about surface analytical methods provided that the sample analysed has a known structure and composition.

The recurring questions in organic depth profiling and 3D imaging relate to the depth scale and the translation of a signal into a concentration, or amount of material. At NPL, we have developed reference materials which are designed to address these questions and in this talk an overview of developments in quantitative organic depth profiling will be provided. The use of XPS is shown to provide accurate compositions, as expected. However, there are some practical issues to be understood involving X-ray and electron damage and sample heating. Additionally, XPS suffers from low sensitivity, specificity and lateral resolution compared to SIMS. Whilst SIMS is fast, specific, sensitive and has high lateral resolution it suffers from the lack of an adequate means of converting data into compositions. Here, reference materials have been constructed which enable the most important effects of the sample on SIMS data to be described. These effects are outlined and include an apparent depth of origin difference for secondary ions, surface transient behaviour and the matrix effect. It is also shown how it is possible to use the matrix effect to assess the nanoscale phase separation of materials.

4:20pm **AS+BI+MC+SS-MoA8 Argon Clusters - A Novel Solution for the Depth Profiling of Metal Alloys and Inorganic Materials**, *Jonathan Counsell, H.L. Brannon, S.J. Coultas, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK
Depth profiles are routinely used to gain information regarding elemental concentration and chemical composition of complex heterogeneous materials. Ion bombardment removes successive layers, exposing bulk material. The difference in the chemical composition of the surface relative to the sub-surface or bulk is often significant to the mechanical or electrical performance of the material.

Here we will discuss the use of Argon clusters for depth profiling a range of inorganic and alloyed materials. Traditionally, depth profiling inorganic materials employed Ar^+ as the bombardment ion. Unfortunately, monatomic Ar^+ can cause significant damage to the bulk structure of the material and can preferentially remove lighter and less well bound elements leading to misleading results. Recent studies show Argon cluster ions greatly diminish the effects of preferential sputtering with simple metal oxides such as titania.[1] Here we wish to broaden this application to a wider variety of materials including precious metal/non-precious metal binary alloys for novel electrode surfaces and ternary and quaternary chalcogenides. We show that with gentler ions, where the energy per atom can be as low as 5-40 eV, it is possible to greatly reduce bulk damage and the preferential removal of weakly bound elements in complex materials.[2]

References:

[1] J. D. P. Counsell, A. J. Roberts, W. Boxford, C. Moffitt and K. Takahashi, *J. Surf. Anal.,* **20** [3], 2014, 211–215

[2] A. Etin, G. E. Shter, R. Brener, S. Baltianski and G. S. Grader., *J. Am. Ceram. Soc.,* **90** [12], 2007, 3800–3803.

4:40pm AS+BI+MC+SS-MoA9 Low Temperature Plasma for Crater Edge Depth Profiling of Crosslinking Organic Multilayers: Comparison with C$_{60}$ and Argon Cluster Sputter Sources, *Shin Muramoto*, National Institute of Standards and Technology (NIST), *D. Rading,* ION-TOF GmbH, Germany, *B. Bush, G. Gillen,* National Institute of Standards and Technology (NIST), *D.G. Castner*, University of Washington

A model organic layer system consisting of three 1 nm delta layers of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) separated by three 30 nm layers of tris(8-hydroxyquinolinato)aluminum (Alq3) was used to evaluate the effectiveness of helium low temperature plasma (LTP) etching for the preparation of crater edge surfaces for subsequent compositional depth profile analysis. The quality of the depth profile was determined by comparing the depth resolutions of the BCP delta layers obtained from the plasma-etched craters with those obtained using ToF-SIMS dual-beam depth profiling equipped with C$_{60}^{2+}$ and argon cluster (Ar$_{1000\ to\ 2500}$) sputter sources. Using the full width at half maximum (FWHM) of each delta peak, the depth resolutions of the second and third delta layers were measured to be 6.9 nm and 6.0 nm for the plasma-etched crater, respectively, which were very close to the depth resolutions of 6.2 nm and 5.8 nm obtained from the argon cluster depth profile. In comparison, the use of a 1/e decay length to approximate the depth resolution gave results that identified the artifacts caused by ion bombardment in SIMS depth profiling. The 1/e decay length for the trailing edge of each delta were 2.0 nm and 1.8 nm for the plasma-etched crater, respectively, while the argon cluster depth profile gave decay lengths of 3.5 nm and 3.4 nm, owing to the longer tails produced by artifacts and possibly by slower sputter rate through the delta layers. For the C$_{60}^{2+}$ depth profile, the need to rescale the axis as a result of a strong nonlinear sputter rate gave artificially improved depth resolutions, where FWHM of the delta peaks were 5.6 nm and 7.3 nm, respectively, and 1/e decay lengths were 1.7 nm and 2.3 nm, respectively. Although some artifacts such as contaminant deposition remain, low temperature plasma was shown to be a viable option for creating crater edges for compositional depth profiling without artifacts seen in ToF-SIMS depth profiling.

5:00pm AS+BI+MC+SS-MoA10 Desorption/Ionization induced by Neutral Cluster Impact as a Versatile Tool for the Investigation of Sensitive and Complex Biosamples, *A. Portz,* Justus Liebig University, Germany, *M. Baur,* University of Applied Sciences, Germany, *C.R. Gebhardt,* Bruker Daltonik GmbH, Germany, *Michael Durr*, Justus Liebig University, Germany

Desorption and ionization induced by neutral clusters (DINeC) can be employed as a soft and matrix-free method for transferring surface-adsorbed biomolecules into the gas phase. Using neutral clusters with polar constituents such as SO$_2$, the impacting clusters do not only provide the energy necessary for desorption but also serve as a transient matrix in which the desorbing molecule is dissolved during the desorption process. As a consequence, desorption and ionization of oligopeptides and smaller proteins can proceed at comparably low energies of the impacting clusters and without any fragmentation [1]. Using a combination of DINeC and ion trap mass spectrometry, femtomol sensitivity was achieved for standard oligopeptides such as angiotensin II or bradykinin [2]; good ion-to-neutral ratio was observed [3].

In this contribution, we show that the signal of the intact molecules (M+H)$^+$ is predominant even in the case of phospho- and glycopeptides, and typical fragments were observed only in low abundance. The origin of these fragments was investigated by comparison with ESI measurements of the original solution as well as of samples which have undergone a similar treatment as for the preparation of the DINeC samples. In that way, we could show that fragmentation takes place already during sample preparation and DINeC is suitable to directly measure such changes of the samples.

Samples with a multitude of components as obtained from realistic biotechnological processes such as tryptic digest of proteins were also successfully analyzed. Peptide mass fingerprint analysis was applied for the evaluation of the respective spectra with very good sequence coverage and protein score. When compared to ESI or MALDI, a substantial number of the unique peptides which were identified with DINeC were not detected with the other methods. Notably, even in the presence of a large excess of salt in the original solution clear spectra of the intact biomolecules were detected. The results are correlated to the very properties of the DINeC process. The method was furthermore successfully applied to a variety of different classes of molecules such as lipids, dye molecules, and pesticides.

References:

[1] C. R. Gebhardt, et. al., Angew. Chem. Int. Ed. **48**, 4162 (2009).

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5:20pm AS+BI+MC+SS-MoA11 C$_{60}$ and Argon Gas Cluster Ion Sputter Depth Profiling for Quantitative Inorganic Thin Film Analysis, *Saad Alnabulsi, G.L. Fisher, S.R. Bryan, J.S. Hammond, J.F. Moulder*, Physical Electronics Inc.

A successful sputter depth profile accurately identifies layer thickness and composition of materials as a function of depth within film structures. In the case of inorganic thin films, monoatomic argon ion beam depth profiling continues to be the preferred choice despite issues with preferential sputtering, material migration, and chemical reduction that may occur during the sputter process to alter the apparent profile of the analyzed material[1][2].

The introduction of C$_{60}$ cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years provided the capability of successful depth profiling of polymer and organic materials while preserving the stoichiometry and chemical structure below the surface[3][4].

Currently, there is great interest in establishing the viability of these cluster ion sources as an alternative to monoatomic argon ion beam sources for analyzing inorganic semiconductor and glass films, with anticipated improvement in the quantitative accuracy of inorganic depth profile results [5][6].

The purpose of this study is to present a comparative evaluation of quantitative XPS analysis to demonstrate the benefits and limitations of monatomic argon, C$_{60}$, and argon gas cluster ion beam sputtering for compositional inorganic depth profiling.

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[6] D. Kobayashi, Y. Yamamoto, T. Isemura. *Sur. and Inter. Anal.* **45** 113 (2013).

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