Monday Morning, October 28, 2013

Applied Surface Science
Room: 204 - Session AS+BI-MoM

Organic Depth Profiling
Moderator: K.G. Lloyd, DuPont, D. Moon, DGIST

8:20am **AS+BI-MoM1 Combining Gas Cluster Ion Beam (GCIB) and Angle-Resolved XPS (ARXPS) Depth-Profiling**, *P. Cumpson, A. Barlow, N. Sano, J. Portoles*, Newcastle University, UK
Over the last decade there have been progressive developments in analytical sputter sources within the surface analysis community[1]. These sources (moving from monoatomic ions, to polyatomic ions, to large gas cluster ions) have progressively reduced damage, but importantly gradually reduced the thickness of the damaged layer. With argon GCIB sources at low-to-medium energy-per-atom this depth *should now be smaller than the inelastic mean free path (IMFP)* for analysis by XPS for normal monochromated lab x-ray sources. This offers the prospect of *seeing through the damage* to produce XPS depth-profiles of polymer and other organic materials that are damage-free for the first time. Angle-Resolved XPS[2] has the potential to give information at each step in the sputter-depth profile so that the undamaged profile can be faithfully reconstructed.

We have a new XPS instrument that combines an argon GCIB source with a parallel-acquisition Angle-Resolved XPS analyser, meaning that we can acquire Angle-Resolved XPS spectra simultaneously from analytical points without tilting the specimen. This combination of GCIB and parallel-acquisition ARXPS is unique as yet, so far as we know. This instrument allows us to take angle-resolved spectra at each step of a GCIB sputter-depth profile, and reconstruct the surface concentration as a function of depth. Instrument performance has been reliable and very effective since the instrument was installed in January 2013.

We have developed numerical algorithms to "unfold" damage from GCIB/ARXPS depth-profiles. These are stable and virtually automatic. X-ray damage can be an important limiting factor[3] in the case of some specific polymer types, but we present some strategies to overcome this. Otherwise the almost automatic nature of GCIB/ARXPS depth-profiling (i.e. involving no time from an expert in interpretation of damage artefacts) suggests this combination of GCIB and ARXPS is a powerful technique for the surface analysis community, especially where (such as in organic electronics) electronic information is sought as function of depth, or cases where we start with very little *a priori* certainty about the structure of samples (as is often the case in analysing biological materials).

[1] S. Rabbani, A. M. Barber, J. S. Fletcher, N. P. Lockyer, and J. C. Vickerman, Anal. Chem. 83, 3793 (2011).

[2] PJ Cumpson, J Elec spectrosc 73 (1), 25-52 (1995)

[3] X-ray enhanced sputter rates in argon cluster ion sputter-depth profiling of polymers. P. J. Cumpson, J. F. Portoles, N. Sano and A. J. Barlow, J. Vac. Sci. Technol. B 31, 021208 (2013).

8:40am **AS+BI-MoM2 XPS Analysis of Oxygen Plasma Modified Polyethylene Surfaces**, *S.S. Alnabulsi*, Physical Electronics Inc., *N. De Geyter, R. Morent,* Ghent University, Belgium, *J.F. Moulder*, Physical Electronics Inc.
Plasma modification of polymers is of great interest for surface preparation to enhance the covalent binding of functional groups and the surface adhesion in biomedical applications. The depth of the plasma treatment is expected to be limited to the top few nanometers, and in this this study, we are investigating the extent of oxygen incorporation through plasma surface modification of a polyethylene surface while varying treatment parameters, and examining the effects of aging on the stability of the modified layer.

Obtaining quantitative chemical state information of the extent of the plasma modification as a function of depth and determining the extent of the depletion region is accomplished through the application of XPS depth profiling utilizing two complimentary methods; the first is with the application of an angle dependent profile to probe the outer most layers of the modified surface, and the second is a sputter depth profile with C_{60} cluster ion beam.

We will present complimentary XPS results of angle dependent profiles and C_{60} sputter depth profile analyses of plasma modified polyethylene to reveal changes in the composition of the modified surface layers, which may explain the effects of varying the plasma treatment parameters, and the effects of sample aging on the shelf life of these modified polymers.

9:00am **AS+BI-MoM3 XPS Valence Band Profiling of Polymer Mixtures with Argon Cluster Ions**, *P. Mack, A.E. Wright*, Thermo Fisher Scientific, UK
Modern food packaging materials can be complex mixtures of polymers, with a wide range of surface properties, compositions and structures. X-ray Photoelectron Spectroscopy (XPS) is typically the technique of choice for analyzing polymeric surfaces, combining chemical selectivity and surface specificity. Core level XPS spectroscopy, however, is not always sensitive to compositional changes in complex mixtures of polymers. A commonly cited example of this would be in the analysis of blends of polypropylene and polyethylene. Each of the individual polymers in this case has an almost identical C1s spectrum, meaning the polymeric mixtures cannot be quantified using the core level data.

The valence region of the XPS spectrum, however, has been shown to be sensitive to compositional changes in polymeric mixtures even when the core level spectra are not. The XPS valence band of polyethylene and polypropylene, for example, are significantly different and using reference data for each of the individual polymers, it is possible to quantify mixtures of the two.

There has also been an increasing requirement for compositional profiling of these complex materials. Profiling with monatomic argon can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials, but it has been shown recently that the use of argon cluster beams for depth profiling can preserve chemical information during analysis of organic materials. This talk will present data from cluster profiling studies of polymer blends, using XPS valence band analysis to quantify the polymeric mixtures during the profile.

9:20am **AS+BI-MoM4 Successful XPS Sputter Depth Profiling of Organic Materials Using Massive Argon Cluster Ions**, *S.J. Hutton*, Kratos Analytical Limited, UK, *J. Walton,* The University of Manchester, UK, *W. Boxford, C.J. Blomfield, J.D.P. Counsell, S.C. Page*, Kratos Analytical Limited, UK
Several XPS vendors currently offer massive Argon gas cluster ion sources as accessories for sputter depth profiling of organic materials. These sources utilise Argon cluster ions formed via adiabatic isentropic expansion of Argon gas into a vacuum followed by subsequent electron impact ionisation and cluster size selection. In ideal cases the aforementioned massive cluster ions efficiently sputter the surface of organic materials revealing undamaged subsurface structure for analysis.

Advanced software controlled ion sources and flexible sample handing equipment allow a wide range of experimental conditions to be routinely employed during sputter depth profiling with these massive Argon clusters. In this study we investigate these parameters including: incident ion energy; cluster size distribution; ion angle of incidence; and sample condition (temperature, rotation). A range of organic materials are analysed and optimum sputter depth profiling conditions determined.

9:40am **AS+BI-MoM5 3D Characterization of Multi-Layer Polymer Films by XPS and TOF-SIMS**, *S. Iida, T. Miyayama,* ULVAC-PHI, Inc., Japan, *G.L. Fisher, J.S. Hammond, S.R. Bryan*, Physical Electronics Inc.
The recent introduction of Gas Cluster Ion Beams (GCIB) and FIB-TOF has provided new possibilities for 3D characterization of organic materials. The use of GCIB as a sputter beam for both XPS and TOF-SIMS has made it possible to acquire molecular depth profiles on a wide variety of polymers. The purpose of this study was to compare XPS and TOF-SIMS depth profiling to FIB-TOF analysis of a model Polystyrene (PS)/PS+Nylon/Nylon/PS+Nylon/PS multi-layer structure. Total thickness of the muli-layer stack is 10 um. XPS depth profiling provided quantitative analysis that could be used to calibrate the TOF-SIMS data. Both TOF-SIMS depth profiling and FIB-TOF can provide 3D characterization of the polymer stack. The TOF-SIMS data provided imaging of the heterogeneous distributions found in each of the PS+Nylon layers as well as trace molecular components found throughout the multi-layer stack. Advantages and disadvantages of both approaches to 3D analysis will be discussed using data from this polymer multi-layer model system.

10:00am **AS+BI-MoM6 In Situ TOF-SIMS and SFM Measurements Providing Real 3D Chemical Information**, *E. Niehuis, S. Kayser, R. Möllers,* ION-TOF GmbH, Germany, *L. Bernard, H.-J. Hug,* EMPA, Switzerland, *N. Havercroft,* ION-TOF USA, Inc., *R. Dianoux, A. Scheidemann*, NanoScan AG, Switzerland
Advances in analytical instrumentation and nanometrology have been the key to the remarkable progress in nanoscience and nanotechnology research over the last two decades. Detailed knowledge of the chemical composition,

physical properties and the three dimensional structure of materials and devices at the nanometer scale is required in all phases of the development from exploratory research to concept and prototyping and finally manufacturing.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a very sensitive surface analytical technique. It provides detailed elemental and molecular information about surfaces, thin layers, interfaces, and full three-dimensional analysis of the sample.

In recent years bismuth clusters have become the standard analysis species for all imaging applications providing a lateral resolution of down to 80 nm. 3D chemical information can be derived by a well-controlled removal of surface layers with an additional sputter beam in a so-called dual beam experiment. Inherent to all 3D TOF-SIMS data is a z-axis with a native time scale instead of a length scale. A starting topography of the initial sample surface as well as an evolving topography due to different erosions rates of the compounds cannot be identified by the technique and yields to relevant distortions.

Scanning force microscopy (SFM), has become the most versatile scanning probe microscopy (SPM) technique since its first application in 1986. In a scanning force microscope, a microscopic tip is scanned over the surface of interest and probes the local properties at each pixel of the scan region. A SFM cannot only map topography up to atomic resolution; it can also map other sample properties with nanometer scale resolution such as local mechanical properties, materials contrast, or electric and magnetic stray fields emanating from the surface.

We have developed a TOF-SIMS / SFM instrument which combines both complementary techniques in a single UHV chamber. The core piece of the new instrument is a high precision, five axes piezo stage which allows fast and accurate navigation between the TOF-SIMS and the SFM analysis position. The combination makes it possible to acquire SFM data before, after and in between TOF-SIMS acquisitions at exactly the same sample position.

In this paper we will present first measurements illustrating the strength of this novel instrument and its potential for a wide range of applications including sputter induced effects on the surface morphology of organic surfaces.

10:40am AS+BI-MoM8 Time of Flight Secondary Ion Mass Spectroscopy (ToF SIMS) Analysis of Stress Tolerant Polymer (STP) in GenGard Corrosion Inhibitors, *G. Zorn, M. Karadge, M.M. Morra,* GE Global Research, *J. Davis, C.C. Pierce, J.I. Melzer,* GE Power & Water

GE Power & Water GenGard technology is GE's most advanced and effective water treatment technology for open recirculating cooling systems. It can be applied across a broad pH spectrum and provide superior results, even under the most stressed system conditions. The patented GenGard technology includes a new Stress Tolerant Polymer (STP) in combination with phosphate-based steel corrosion inhibitors. The GenGard technology, when used, develops complex multilayered structures that incorporate metal, ceramic and polymer, where the STP is designed to maintain phosphate-based corrosion inhibitors' solubility. For optimal performance it is important to understand the structure, morphology and composition of different layers. However, characterizing these nano scale films is very challenging, as they can be sensitive to preparation technique and damage. Moreover, surface roughness and homogeneity of the layers should be considered.

This work is focused on the ToF SIMS study of the multilayered structures formed by the GenGard technology, with an emphasis on the STP analysis and its distribution within the inhibition layers. ToF-SIMS is capable of high detection sensitivity (ppb), very high surface specificity (analysis of the top 1-3 surface layers during date acquisition, high mass resolution ($\Delta m/m$ greater than 8000), and is able to detect high mass molecular fragments associated with the STP. ToF SIMS allows rapid data collection while analyzing through multilayers, and provides high interfacial resolution during a depth profile measurement.

ToF SIMS depth profiling of the structures formed by the GenGard technology showed a calcium phosphate / iron oxide two layer structures on the base metal. This structure was further confirmed by Transmission Electron Microscopy (TEM) equipped with Energy Dispersive X-Ray Spectrometer (EDS). The STP that is added in ppm levels was identified in the ToF-SIMS by three high mass $Na_xS_yO_z$ fragments at m/z=229,245 and 261 amu. In order to eliminate the possibility that these fragments are associated with surface contamination, Ion Chromatography (IC) was performed. After identifying the STP characteristic tags, ToF SIMS depth profiling of the inhibition layers allows showing that the STP is incorporated within the entire inhibition layers at the initial steps (after 7 days) but later it starts to migrate to the surfaces of these films as they grow with time. This ToF SIMS study combined with TEM and IC provides a detailed picture of the complex structures and compositions as well as the kinetic behavior of the inhibition films formed by the GenGard technology.

11:00am AS+BI-MoM9 Argon Gas Cluster Beam Etching of Organic Contaminants on Graphene and HOPG, *BJ. Tyler*, *A.J. Pollard, I.S. Gilmore*, National Physical Laboratory, UK

Under ambient conditions, the surface of graphene is contaminated with a range of organic compounds. These compounds include both those that derive from the production of the graphene, such as photo-resists and transfer agents, and adventitious organic compounds that adsorb rapidly to the high energy graphene surface. The ability to remove and control this contamination layer without damaging the graphene is crucial to reproducible production of graphene devices as well as in fundamental studies of graphene properties. In this study, we have investigated cleaning of HOPG and graphene surfaces via heating in vacuum and sputtering with Argon Gas Clusters. Common adventitious organic contaminants have been identified via temperature programmed SIMS experiments and include fatty acids and their fatty acid amides, as well as PAHs and siloxanes. While contamination with siloxanes can be avoided with careful handling, adsorption of fatty acids and amides is virtually instantaneous upon exposure to the ambient environment. Damage to the graphene layer via the sputtering process has been assessed via micro-Raman analysis. Formation of defects due to sputtering with Argon Gas Clusters is dependent on the cluster size, impact energy and ion fluence. An impact energy of less than 1eV per atom in the cluster is needed to minimize defect formation. Optimized conditions for sputter profiling these organic overlayers without damaging the underlying graphene will be presented.

11:20am AS+BI-MoM10 Why is Low Energy Cesium so Efficient for Depth-profiling Organics?, *L. Houssiau*, University of Namur, Belgium
INVITED

Organic materials are known to be very sensitive to ion bombardment, mostly owing to free radical creation upon etching, leading to many chemical reactions like hydrogen abstraction, double bond creation and crosslinking. Most organics eventually degrade into a graphitized material, with no memory left of the initial material's chemistry. However, this picture has dramatically evolved over the last decade thanks to breakthrough developments in the field of molecular depth profiling. It started with the use of polyatomic ion sources (SF_5^+, C_{60}^+), followed by massive Ar_n^+ clusters which are now considered as standards for molecular depth profiling. Those cluster sources exhibit a sputtering yield high enough to sputter molecular damages away. Our group has followed a thoroughly different approach since 2007, when we showed that, surprisingly, low energy (~250 eV) Cs^+ ions could also be used to depth profile polymers. We have extended the study to many different organic materials, including amino acid thin films, analyzed in the energy range 150-1000 eV. So far, it appears that most organics are amenable to depth-profiling with this method, making it a complementary approach to cluster ion beams. We will review our understanding on how low energy Cs^+ ions prevent material degradation. Cs^+ ions are neutralized as soon as they hit the surface, for electrostatic reasons, leaving implanted Cs atoms in the subsurface region. Cs being an extremely reactive element quickly reacts with free radicals generated by ion impact, preventing cross-linking reactions, thus allowing molecular depth profiling. This reaction goes along with a strong negative ionization, as an electron is transferred from the alkali to the molecule. Indeed, negative molecular ion detection in ToF-SIMS experiments is much increased with respect to inert ions. Our model is supported by XPS data, showing changes in the charge state of various molecules (amino acids, polymers) irradiated with Cs^+ ions. Moreover, the existence of neutral cesium at the surface was detected by optical emission spectroscopy measurements. We will present our most recent data on Phenylalanine delta layers embedded in a Tyrosine matrix, on which a depth resolution below 5 nm was observed. We will also discuss the decisive influence of the analysis beam (i.e. Ga^+ or Bi_3^+) in a ToF-SIMS dual beam experiment. Besides its fundamental interest, low energy Cs^+ sputtering appears to be an efficient tool to depth profile both organics and inorganics. Its major assets are a high negative ion signal combined with an excellent depth resolution.

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