Wednesday Morning, October 21, 2015

Applied Surface Science
Room: 212D - Session AS-WeM

Practical Surface Analysis II: Influence of Sample Preparation and Novel Sample Prep Techniques

Moderator: Gregory Herman, Oregon State University, Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **AS-WeM1 ASSD 30th Anniversary Lecture: A Historical Perspective of the Materials Challenges and Instrumentation Solutions Available for Practical X-ray Photoelectron and Auger Electron Spectroscopy**, ***John Moulder***, Physical Electronics USA **INVITED**

During the first 30 years of the Applied Surface Science Division's (ASSD) existence the changing world around us has driven the need for new materials for a wide range of applications including: higher performance coatings, structural materials, electronics, data storage devices, display and printing technology, energy storage devices, and many more. For most of these materials systems the composition of a surface, interface, thin film or nanostructure plays a critical role in the performance of the material. During the same period of time, analysts have endeavored to characterize these new materials and instrument manufacturers have endeavored to provide the analytical capabilities required by the analyst to answer critical questions about the materials being studied.

When the ASSD was formed in the 1985 the second generation of XPS and AES based surface analysis instrumentation was emerging and surface analysts were characterizing structural materials, catalysts, thin film coatings, semiconductor devices, magnetic storage media, and more. Common challenges faced by the analyst included quantification, insulator analysis, micro area analysis, the desire for more chemical information, the desire for 2D and 3D information, and keeping up with the demand for more data.

This presentation will provide a historical perspective on the evolution of both the materials challenges faced by surface analysts and the XPS and AES instrumentation that became commercially available to address these challenges. Finally we will comment on where we are today and possible future directions.

8:40am **AS-WeM3 Using Argon clusters for Improved XPS Information**, ***Jonathan Counsell***, *S.J. Coultas, C.J. Blomfield, D. Surman, C. Moffitt*, Kratos Analytical Limited, UK

A thin layer of carbonaceous material is commonly found on the surface of air exposed samples - this layer is generally known as adventitious carbon. Adventitious carbon is generally comprised of a variety of relatively short chain, perhaps polymeric hydrocarbons species with small amounts of both singly and doubly bound oxygen functionality. Even brief exposures to atmosphere will produce a thin overlayer. During XPS analysis this overlayer has the unfortunate effect of attenuating the signal from the material underneath decreasing the signal strength and intensity. Furthermore, the presence of Carbon and Oxygen also add complexity to the peak fitting and assignment of high resolution spectra of these elements. For analysts it is seen as a hindrance when wanting to know the "real" surface chemistry

In recent times Argon cluster ions have been used to depth profile soft materials. The cluster ion sputters away sample material however the collision mechanism limits the propagation of damage into the sample bulk. This new method has been widely exploited with polymeric thin-films and biomaterials[1]. Here we will discuss the use of Argon cluster ions as a novel way to remove adventitious carbon to improve the information obtainable through analysis. Improvements in both sensitivity and detection limit will be discussed as well as improved spectral resolution. We will also demonstrate how Argon cluster cleaning can improve the spatial resolution of XP imaging. A variety of systems will be discussed to demonstrate the broadness of the application. A comparison with low energy monatomic Argon cleaning is also made including discussion ion incorporation and lattice damage.

[1] P. Cumpson, J. F. Portoles, N. Sano, and A. J. Barlow, *J. Vac. Sci. Technol. B* 31(2), 2013.

9:00am **AS-WeM4 *In Situ* Chemical Imaging of Environmental Liquid Surfaces and Interfaces Using Microfluidics and Dynamic ToF-SIMS: Toward Multimodal and Mesoscale Imaging**, ***Xiao-Ying Yu***, *Z. Zhu*, Pacific Northwest National Laboratory

The surfaces of aqueous phases and films 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, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The unique aspects of this R&D 100 award winner include the following: 1) the detection window is an aperture of 2-3 mm in diameter allowing direct imaging of the liquid surface, 2) surface tension is used to hold the liquid within the aperture, and 3) SALVI is portable among multiple analytical platforms. SALVI is composed of a silicon nitride (SiN) membrane as the detection area and a microchannel made of polydimethylsiloxane (PDMS). Its applications ToF-SIMS as an analytical tool were evaluated using a variety of aqueous solutions and complex liquid mixtures, some of which contain nanoparticles. SALVI was also used to investigate the solvent structure of switchable ionic liquids. Recently, we demonstrated *in situ* probing of the electrode-electrolyte solution interface (or solid-electrolyte interface, SEI) using a new electrochemical SALVI. It provides the first direct observation of the surface and diffused layer of SEI in a liquid with chemical speciation using dynamic ToF-SIMS. Moreover, SALVI was extended for studying biofilm growth and single mammalian cells using correlative imaging by more than one spectroscopy and microscopy technique, each offering different spatial and temporal scales. That is, collecting data on different information level from an identical area in the same sample ideally could lead to a more holistic view of the hierarchical structural organization of complex systems in the real world. Selected results from our latest development will be presented, showcasing new directions and applications of multimodal imaging of environmental surfaces and interfaces and studying chemistry from the bottom up, all based on microfluidics. SALVI, a portable microfluidic reactor, sets the analytical foundation toward chemical imaging of complex phenomena occurring in multiple time and length scales, or the mesoscale, underpinning chemical changes at the molecular level.

9:20am **AS-WeM5 A VAMAS Inter-laboratory Study of the Measurement of Chemistry and Thickness of Nanoparticle Coatings**, ***David Cant***, *N.A. Belsey, C. Minelli, A. Shard*, National Physical Laboratory, UK

Nanoparticles with a coating or shell are widely studied in both academic and industrial research. X-ray Photoelectron Spectroscopy (XPS) and Low/Medium Energy Ion Scattering (LEIS/MEIS) have potential for accurate measurement of chemistry and thickness of nanoparticle coatings, but the accuracy of these measurements is dependent upon correct modelling for analysis and reproducibility of sample preparation. There is as yet no uniform approach to these issues; to address this, VAMAS project A19 – an interlaboratory study involving 24 participants in 12 countries – has been undertaken with the following objectives:

• Assessment of inter-laboratory variability in measuring nanoparticle coating thickness

• Comparison of sample preparation techniques.

• Testing variability of procedures for quantitative analysis.

Samples were prepared from commercial gold colloid and incubated with a short peptide. Each participant received one pre-deposited sample on Si wafer, and one solution (and Si wafer) for their own in-house deposition. Participants were requested to return their samples to help identify the effect of differences in sample deposition between pre-deposited and in-house samples.

Thickness values reported by participants performing XPS were compared to values calculated from reported atomic concentrations using the *T*(NP) method [1,2]. A significant difference was observed between thicknesses determined for the pre-prepared sample and those determined for samples deposited by the participants in-house. Thicknesses determined for the in-house samples were larger than those determined for the pre-deposited samples. This was attributed to increased hydrocarbon presence observed in the C 1s spectra – likely caused by uneven sample deposition allowing detection of substrate contamination. In some cases, both pre-deposited and in-house samples exhibited abnormally low calculated thicknesses, potentially due to damaging of the coating by the x-ray beam.

The results of this study will assist in the development of a new ISO standard on the measurement of surface chemistry and thickness of

nanoparticle coatings. The study will also provide information relevant to the ISO standard for reporting information related to the history, preparation, handling and mounting of nanomaterials prior to analysis, currently in development under ISO TC201. The production of guidelines for the measurement of nanoparticle coatings and sample preparation will be of great use in commercial applications of coated nanoparticles.

References

[1] Shard, A.G., Journal of Physical Chemistry C, 2012. 116(31): 16806-16813

[2] Belsey, N. A., Shard, A. G., Minelli, C. Biointerphases, 2015. 10, 019012

11:00am **AS-WeM10 A Quantitative Quest: Single Cell Analysis by LG-SIMS**, ***Christopher Szakal***, National Institute of Standards and Technology (NIST)

Large geometry secondary ion mass spectrometry (LG-SIMS) has been used extensively for particle analyses and geochemical analyses, owing to its ability to maintain adequate mass resolution while operating at high secondary ion transmission. Efforts will be presented that extend the knowledge acquired in these application areas to single cell analyses of elemental species. To be useful, LG-SIMS results likely need to be quantitative for the amounts of a given element per cell and/or in ratios of different elements within each cell. Approaching this level of detail requires the establishment of the natural variability of such data from cell-to-cell, the reproducibility of the measurement technique, and whether the data is relevant to pertinent questions about the cellular population. Progress will be shown towards achieving these aims for single bacterial cells, including sample preparation necessary for such measurements, technique-specific considerations, and analytical figures of merit for LG-SIMS elemental ratios. Prospective application areas will be presented, along with potential pitfalls of such an approach.

11:20am **AS-WeM11 Ambient Mass Spectrometry Imaging of Live Cells and Tissues**, *J.K. Kim,* ***DaeWon Moon***, DGIST, Republic of Korea

Currently, mass spectrometry imaging is based on Secondary Ion Mass Spectrometry (SIMS) and Matrix-Assisted Laser Desorption and Ionization (MALDI). Generally specimens for SIMS and MALDI are prepared by cryo-section and drying, which modifies the intrinsic biology due to sample preparations and subsequently does not allow dynamic response studies of biosystems to various chemical and physical stimuli. Most of recently developed ambient mass spectrometry have the spatial resolution in the range of ~50 μm, lacking in celluar and subcellular imaging of cells and tissues.

To investigate the intrinsic biology and dynamic responses of live cells and tissues in the cellular level, we developed an ambient imaging mass spectrometry system with ~5 μm spatial resolution. The ambient imaging mass spectrometry is based on low temperature plasma-surface reaction and desorption and ionization of surface products using near IR (808 nm) laser. Mass imaging is based on the movement of the sample stage. To enhance the laser desorption and ionization, Au nanorods of 10 nm diameter and 40 nm length were used. To further enhancement of sensitivy and possibly membrane specificity, liposome conjugated Au nanorods were used. An orbitrap mass spectrometer with a differential pumping and a pumping load adjustment is used as a mass analyzer.

Colonies of HCT-8 cells and hypothalamus tissues were mass imaged. Hypothalamus tissues were prepared with vibrotome, which allow sectioning of a hypothalamus tissue without freezing. Approximately 40 mass peaks from ~80 amu upto ~ 350 amu were observed with mass imaging. Single cells were observed clearly form a colony of HCT-8 cells and a hypothalamus tissue. Indentification of imaged mass peaks are in progress with mass reference data and mass-mass analysis.

11:40am **AS-WeM12 Intricacies of Sample Preparation for ToF-SIMS Analysis of Biological Specimens**, ***John Fletcher***, Chalmers University of Technology, Sweden **INVITED**

Biological and medical research is a popular and expanding area of application for time-of-flight secondary ion mass spectrometry (ToF-SIMS). The ability to perform such analyses has greatly benefited in recent years from the introduction of new ion beams that generate more signal from intact molecular ions that are generally more chemically characteristic and so aid in the interpretation of the complex spectra generated from biological specimen. The introduction of polyatomic ion beams such as C_{60} heralded the dawn 3D molecular imaging with ToF-SIMS and most recently gas cluster ion beams such as Ar_{4000} have shown dramatic improvements for the detection of intact lipid species from tissue.

However, such advances are meaningless if the information from the analysis is erroneous due to artefacts introduced during the preparation of chemically complex, and delicate, biological samples such as cells and tissue sections. Analysis of samples in a frozen hydrated state is often considered to be the best approach for maintaining the integrity of the sample but is not always possible or practical. In this presentation the implications of different preparation approaches are presented and discussed and methods for removing artefacts due to imperfect sample preparation are presented.

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