

Wednesday Morning, November 1, 2017

Applied Surface Science Division

Room: 13 - Session AS+BI+MI+NS+SA+SS-WeM

Beyond Traditional Surface Analysis: Pushing the Limits

Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

8:00am **AS+BI+MI+NS+SA+SS-WeM1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol.** *Yao Fu, X.F. Yu, F. Zhang, Z.H. Zhu*, Pacific Northwest National Laboratory, *J.M. Chen*, Fudan University, *X.Y. Yu*, Pacific Northwest National Laboratory
Pyruvic acid are found in fogs, aerosols and clouds. The sunlight driven reaction pathways of pyruvic acid in the aqueous phase are more elusive compared to its well-known gas phase chemistry. Aqueous solutions containing pyruvic acid in a microchannel after different UV photolysis times up to 8 hours have been studied by in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the photochemical aging products at the solution surface. Compared with previous results using bulk approaches (i.e., NMR, ESI-MS), our unique liquid surface molecular imaging enables the observation of photochemical products of pyruvic acid at the aqueous solution surface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(\text{H}_2\text{O})_n\text{H}^+$, $(\text{H}_2\text{O})_n\text{OH}^-$) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS three-dimensional chemical mapping permits visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant shown in the chemical spatial mapping with increased photolysis time. In situ molecular imaging of the pyruvic acid aqueous solution surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20am **AS+BI+MI+NS+SA+SS-WeM2 XPS Depth Profiling of SrTiO₃ and HfO₂ with Small Argon Clusters.** *Christopher Deeks*, Thermo Fisher Scientific, UK, *M. Baker*, University of Surrey, UK, *P. Mack*, Thermo Fisher Scientific, UK

Metal oxides are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate (SrTiO₃) and hafnium oxide (HfO₂) due to their specific band gaps and high dielectric constants. SrTiO₃ is being studied for use in photocatalysis, energy storage and electronic sensors, whilst HfO₂ is widely employed for optical coatings and optoelectronic device applications. Both materials are regularly deposited as thin films and doped to optimise their properties for the application. An accurate determination of thin film composition is paramount to the understanding and optimisation of device performance.

In this work, thin films of SrTiO₃ and HfO₂ have been deposited onto silicon substrates and XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar⁺ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (MAGCIS) profiles were recorded using 8 keV Ar₁₀₀₀⁺ and 8 keV Ar₁₅₀⁺ for SrTiO₃ and HfO₂ respectively. For HfO₂ the optimum results were found when the MAGCIS ion beam was incident upon the sample at a glancing angle. These MAGCIS conditions yielded excellent retention of the original SrTiO₃ and HfO₂ stoichiometry during the profile, with no evidence of preferential sputtering or ion beam induced reduction. Using 500 eV Ar⁺, however, resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra of Ti in SrTiO₃ and Hf and HfO₂. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar₁₀₀₀⁺ was only 2.5 times lower than that for 500 eV Ar⁺. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

8:40am **AS+BI+MI+NS+SA+SS-WeM3 Surface Analysis of Intact Biomolecules: the Bigger They Are the Harder They Fly.** *Nina Ogrinc Potocnik, R. Heeren*, Maastricht University, The Netherlands **INVITED**
Secondary ion mass spectrometry (SIMS), as the oldest MSI techniques, gained popularity for analysis of biological samples due to its ability to obtain chemical and spatial information at unmatched lateral resolutions. The use of focused ion beams for desorption and ionization of surface molecules in SIMS affords for this notable spatial resolution over, for example, laser-based MS approaches such as Matrix Assisted Laser Desorption Ionisation

(MALDI). However, the excessive energy of the primary ions limits the method to the detection of elements, fragmented molecules and small intact molecular species. This consequently points at the method's major drawback, which is the difficulty to ionize and detect larger, intact molecular species such as peptides and proteins with great sensitivity. Over the last years, SIMS has been pushing the boundaries by redirecting focus into biomedical applications. Tissue sections and cell imaging has become common practice in research labs all over the world. Now, abundant lipids and small peptides can be studied with different sample surface modifications, where the upper most layer of the surface is sputter coated with a thin layer of metal ((MetA) SIMS – metal –assisted SIMS) or covered with the matrix (ME-SIMS). In both cases the sputtering efficiency and the secondary molecular yield have increased. Here, we studied how ME-SIMS can influence the ionization efficiency of desorbed intact molecules in comparison to MALDI.

First, we imaged mammalian tissue sections that were subjected to a variety of different matrices using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. The same or consecutive sections were subsequently analyzed by FTICR-SIMS, to accurately identify the enhanced molecular species of interest specifically intact lipids and metabolites, and by the PHI nano-TOF II for high lateral resolution images and confident identification of said species with tandem MS. Second, *de-novo* peptide sequencing was performed on endogenous neuropeptides directly from a pituitary gland. Careful sample preparation and the capability of using a 1 Da mass isolation window of the precursor ion followed by a collision-induced dissociation (CID) at 1.5 keV in an activation cell with argon gas enables the molecules to be fragmented in a specific pattern. Neuropeptides up to *m/z* 2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

9:20am **AS+BI+MI+NS+SA+SS-WeM5 Hydrogen/Deuterium Exchange Using Vapor Phase D₂O to Enhance SIMS Characterizations.** *Paul Vlasak*, The Dow Chemical Company

Hydrogen/Deuterium exchange of labile hydrogens is a well-known water solution-based phenomenon that has in recent years seen extensive use in the area of protein characterization. This presentation will demonstrate a method to accomplish vapor phase hydrogen/deuterium exchange of solid sample surfaces prior to analysis by SIMS. In many cases, it is not desirable to expose the sample to liquid solvent due to the possibility of dissolving and rearranging or removing surface species of interest. In contrast, the effect of vapor phase D₂O exposure is similar to typical exposures of the sample to humid room air.

The described method is simple and inexpensive in comparison with synthetic isotopic labeling studies. However, it is expected that only the sufficiently labile and sterically accessible H atoms can be tagged, typically those bound to N, O, or S. Possible benefits of this method include isomer differentiation, elucidation of fragmentation pathways, fundamental studies of ionization, differentiation of sterically or otherwise protected vs. unprotected functional groups, and determination of water diffusion or permeability in solid materials.

9:40am **AS+BI+MI+NS+SA+SS-WeM6 Fragmentation and Backscattering of Large Ar_n⁺ Clusters as a Probe of Polymer Glass Transition.** *C. Poleunis*, Université Catholique de Louvain, Belgium, *V. Cristaudo*, Université Catholique de Louvain, Belgium, *Arnaud Delcorte*, Université Catholique de Louvain, Belgium

Gas cluster ion beams (GCIB) have become the standard sources for molecular depth-profiling of organic materials with secondary ion mass spectrometry (SIMS) [1] and X-ray photoelectron spectroscopy (XPS). Since 2009, a number of experimental and theoretical studies were devoted to the investigation of the effects of energy, nuclearity and incidence angle of the Ar clusters on the energy deposition, fragmentation and molecular emission induced in organic solids [2-4]. Recently, Mochiji et al. reported that the backscattered Ar_n⁺ clusters observed in the SIMS spectra of pure metal surfaces provide information on the mechanical properties of the surfaces analysed by GCIB [5]. They correlated the ratio of Ar₂⁺ to the sum of Ar_n⁺ clusters intensities with the impulsive stress caused by the impact, a parameter directly linked to the elastic modulus of the material.

Here, the intensity variations of the backscattered Ar_n⁺ clusters are studied as a function of temperature for a series of thermoplastic polymers: high molecular weight polydisperse polyisobutylene and polybutadiene, polystyrene (Standard; M_w = 4000) and polymethyl methacrylate (Standards; M_w = 2000 and 150000). For all these polymers, our results show a transition of the intensity ratio Ar₂⁺/(Ar₂⁺+Ar₃⁺) when the temperature is scanned from

-120 °C to +125 °C. This transition generally spans over a few tens of degrees and the temperature of the inflexion point of each curve is very close to the glass transition temperature (T_g) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (a few nanometers as indicated by molecular dynamics simulations [4]), the presented analysis could provide a new method to specifically evaluate the surface T_g of polymers, with the same lateral resolution as the gas cluster beam. The results are discussed from the point of view of the structure and mechanics of polymers.

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11:00am **AS+BI+MI+NS+SA+SS-WeM10 Evolution of the Bi Cluster LMIS as a Universal Source for High Performance SIMS Analysis, Felix Kollmer***, ION-TOF GmbH, Germany **INVITED**

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF₆ beam in order to avoid charging effects on insulators. By coincidence they discovered that “the SF₆ beam is doing an excellent job of producing secondary ions ... it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces “[1].

In the following years the bombardment of organic surfaces with clusters was investigated by many research groups. The lateral resolution of the applied beams was rather low since the focus at this time was clearly on the fundamentals of the ion solid interaction and the secondary ion generation. However, as early as 1991 Benguerba applied an Au cluster liquid metal ion source (LMIS) for a fundamental study of phenylalanine [2].

At the beginning of the millennium Au cluster LMIS became commercially available for TOF-SIMS instrumentation. This led to a wider application in the SIMS community and to a further improved performance. However, the cluster sources remained an additional option for the SIMS instruments especially since the low cluster currents did not allow the replacement of the reference Ga LMIS for many applications.

With the introduction of a LMIS operated with Bi this changed fundamentally [3]. Roughly 50% of the beam consists of clusters and 50% are emitted as mono-atomic Bi species. This ensures a large flexibility for the analysis of inorganic as well as organic surfaces. Moreover, an uncompromised performance in terms of lateral and mass resolution is achieved, even with cluster beams, and a lateral resolution in the sub 20 nm range has been demonstrated with Bi₃⁺⁺ species [4].

Today, the Bi LMIS is used as the standard analysis source on more than 250 TOF-SIMS instruments for all kinds of applications. In combination with a massive cluster beam that is applied for the erosion of the sample (e.g. Ar_n) even depth profiling or 3D analysis of organic samples is possible.

In this contribution, we will have a retrospective look at the development of high performance cluster SIMS. Besides fundamental capabilities of the Bi LMIS and the secondary ion generation we will discuss milestones of the application as well.

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- [4] Kollmer, F. et. al. (2013) *Surface and Interface Analysis* 45 (1), pp. 312–314

11:40am **AS+BI+MI+NS+SA+SS-WeM12 Evaluating the Benefits of Cs Cluster Analysis in ToF-SIMS and Cs/Xe Co-sputtering for Depth Profiling Layered Thin Films, James Ohlhausen, P.T. Vianco, M.T. Brumbach, R. Chow**, Sandia National Laboratories

Depth profiling with Cs to create MCs⁺ clusters can produce semi-quantitative results by greatly reducing the matrix effects observed in common M⁺ analysis. Additionally, alkali metal clusters enhance negative ion detection in the form of positive Cs clusters, such as MCs⁺ and MCs₂⁺. In his review article, Wittmaack¹ discussed the many ways that Cs is used in SIMS analyses to provide this enhancement which includes using Cs as the sputtering species and/or analytical probe and using directed Cs vapor. Unfortunately, high Cs surface concentrations can lead to suppression of Cs cluster formation. Xenon and Cs can be co-sputtered in a ToF-SIMS system

to adjust the relative amounts of Cs and Xe in the co-sputtered beam to control Cs surface concentration and optimize Cs cluster formation². Cs/Xe co-sputtered depth profiling has been shown to work well in materials systems such as Au thin film on Si³ and Pd-Rh thin film⁴.

The present paper discusses the use of Cs/Xe co-sputtering to investigate an Au/Pd/Ni electroplated layered system. Gold and to some extent Pd have low positive ionization yields, so typical ToF-SIMS data from these metals can be difficult to interpret. However, Cs/Xe co-sputtering has been found to generate high yield MCs⁺ clusters in Au and Pd, thus enabling this analysis. This Au/Pd/Ni metal stack were analyzed in a pristine (as received) condition, after accelerated aging and after exposure to a (very high temperature) solder reflow process. The elemental and molecular sensitivities as well as quantitative results stemming from this analysis will be investigated. The manner whereby these results support the use of Au/Pd/Ni stack in an engineering application will be shown. In particular, interlayer diffusion, trace contaminants and interfacial contamination will be examined. Comparisons will be made to Auger and XRF to assess quantitation and sensitivity and to illustrate the advantage of this SIMS technique.

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- 2) E. Niehus, T. Grehl, in: J.C. Vickerman, D. Briggs (Eds.), *ToF-SIMS*, IMPublications, Chichester, West Sussex, UK, 2001, p. 753.
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12:00pm **AS+BI+MI+NS+SA+SS-WeM13 Real-Time Monitoring Electrochemical Reaction Intermediates using In Situ Time-of-Flight Secondary Ion Mass Spectrometry, Jun-Gang Wang**, East China University of Science and Technology; Pacific Northwest National Laboratory (PNNL), Y. Zhang, X.Y. Yu, Z.H. Zhu, PNNL

In situ monitoring of electrochemical reactions is traditionally performed by cyclic voltammetry[1], plasmonic spectroelectrochemistry[2, 3], and surface probing techniques such as scanning electrochemical microscopy and scanning ion conductive microscope.[4] However, it has been extremely difficult to obtain direct molecular evidence of the electrochemical reaction intermediates using these traditional techniques. Thus, the debate of reaction mechanisms has long been an issue. Recently, mass spectrometric techniques have been coupled with electrochemistry to provide the molecular information of intermediates of redox reactions.[5] The advantage of mass spectrometric techniques is that capture of molecular ions can provide direct molecular information of key chemical species, such as reaction intermediates. A novel approach, based on coupling of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrochemistry has been developed in Pacific Northwest National Laboratory and it has been used for in situ analysis of reaction intermediates in electro-oxidation of ascorbic acid at the electrode–electrolyte interface.[6] Herein, the electrochemical oxidation of acetaminophen was chosen as a model system, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen.[7] This reaction was real-time monitored using in situ ToF-SIMS. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. The NAPQI subsequently conjugated with glutathione and cysteine was molecularly confirmed. We demonstrated the proof of principle for the use of ToF-SIMS for real-time monitoring of electrochemical reaction with high chemical specificity. Our results demonstrate that the coupling of ToF-SIMS and electrochemistry has great potential to molecularly elucidate reaction mechanisms in the oxidative metabolism, pharmaceutical intoxicification, and cell toxicology.

References

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