Applied Surface Science Division
Room: 102 - Session AS-MoA

Quantitative Surface Chemical Analysis and Technique Development - Part II

Moderator: M.S. Wagner, The Procter & Gamble Company

2:00pm **AS-MoA1 Surface-based Model Systems of Biomolecular Hydrogels - From Supramolecular Organization and Dynamics to Biological Function**, *N.S. Baranova, S. Attili,* CIC biomaGUNE, Spain, ***R.P. Richter***, CIC biomaGUNE & MPI for Intelligent Systems, Spain **INVITED**

Nature has evolved complex materials that are exquisitely designed to perform specific functions. Certain proteins and glycans self-organize *in vivo* into soft and dynamic, strongly hydrated gel-like matrices. Illustrative examples of such biomolecular hydrogels are cartilage and mucus. Although biomolecular hydrogels are ubiquitous in living organisms and fulfill fundamental biological tasks, we have today a very limited understanding of their internal organization, and how they function. The main reason is that this type of assemblies is difficult to study with conventional biochemical methods.

In order to interrogate biomolecular hydrogels directly on the supramolecular level, we have developed an unconventional approach that draws on knowledge from several scientific disciplines. Exploiting surface science tools, such as supported lipid bilayers, we tailor-make model systems by directed self-assembly of purified components on solid supports. With a toolbox of surface-sensitive analytical techniques, including quartz crystal microbalance, ellipsometry, atomic force microscopy and microinterferometry, these model systems can be investigated quantitatively and in great detail. From the experimental data, combined with polymer theory, we develop a better understanding of the relationship between the supramolecular organization and dynamics of biomolecular hydrogels, their physico-chemical properties and their biological function. To illustrate this concept, I will present some of our recent work on the "sweet" jelly-like matrix that forms around the mammalian egg during ovulation (the so-called cumulus cell-oocyte complex matrix) and that is crucial for fertility, and on the proteoglycan-meshwork that contributes to the load-bearing and lubricating properties cartilage.

2:40pm **AS-MoA3 Soft Cluster-Induced Desorption and Ionization of Biomolecules – Influence of Surface Load and Sample Morphology on Desorption Efficiency**, *M. Baur, B.-J. Lee,* HS Esslingen, Germany, *C.R. Gebhardt,* Bruker Daltonik, Germany, *H. Schroder, K.-L. Kompa,* MPI for Quantum Optics, Germany, ***M. Durr***, HS Esslingen, Germany

Neutral cluster-induced desorption and ionization is a very soft method for transferring surface-adsorbed biomolecules into the gas phase [1]. Using neutral SO_2 clusters seeded in a He beam, the method makes use of the dipole moment of the cluster's constituents which allows both for solvation and charge transfer processes in the cluster [2]. Thus the cluster provides not only the energy for the desorption process but also serves as a transient matrix. As a consequence, desorption and ionization of oligopeptides and proteins is observed at low energies of the impacting clusters and without any fragmentation of the biomolecules.

Here we show that cluster-induced desorption and ionization of biomolecules can be efficiently applied for a wide range of surface concentrations and configurations, i.e. from µm-thick films down to surfaces prepared with submonolayer surface concentration of biomolecules. Highest signal intensity in the respective mass spectra was observed from thick films, indicating an efficient desorption mechanism from bulk-like material. In the submonolayer regime, the ion signal of the desorbed biomolecules was found to depend nonlinearly on surface concentration of the wet-chemically applied biomolecules. The behavior is traced back to the formation of multilayered islands of biomolecules on the surface, as observed by means of SEM and AFM, and a dominant contribution to the ion signal from these islands even at low coverage. With the current set-up and preparation scheme, the lower detection limit was shown to be 10^{-13} mol.

[1] C. R. Gebhardt, A. Tomsic, H. Schröder, M. Dürr, and K.L. Kompa, Angew. Chem. Int. Ed. **48**, 2009, 4162.

[2] C. R. Gebhardt, H. Schröder, K. L. Kompa, Nature **400**, 1999, 544.

3:00pm **AS-MoA4 Sensitive Elemental Analysis of Materials via Femtosecond Ablation Time of Flight Mass Spectrometry**, ***J.F. Moore***, MassThink, *S. Milasinovic, Y. Cui, J.S. Penzak, Y. Liu, R.J. Gordon, L. Hanley*, University of Illinois at Chicago

A new instrument is described which is capable of delivering ~70 fs pulses of 800 nm light to a 100 µm focus; this instrument can ablate small volumes (100-1000 μm^3) of material from a sample (e.g. a 10 µm spot to a depth of 3 µm) and analyze the ions formed in the ablation process by time of flight and quadrupole mass spectrometry. Some novel features of this instrument include (1) a variable pressure source that allows collisional cooling of ions from the ablation plume, (2) the ability to use fs pulse pairs as well as temporally shaped laser pulses with a variable delay line to provide control over the ablation and ion formation process, and (3) a high velocity sample stage combined with a rapid data acquisition system that allows rapid scanning of materials at kHz repetition rate (of ablation events). Results from the ablation of elemental samples (Mg, Al, Si, Cu, Mo, Ag, Ta, Au) and metal alloys will be presented along with microscopy of ablation craters and a discussion of fluence dependence, useful yield, and instrumental sensitivity. Although the current system provides analysis on the micron scale, plans to extend its capability to the nanometer scale and to apply ablation to nanoparticles are being made and will be addressed.

3:40pm **AS-MoA6 Interlaboratory Study on Consistency and Reproducibility of Sputter Rate Measurements**, ***M.H. Engelhard***, *D.R. Baer*, Pacific Northwest National Laboratory

The method and procedures used by many researchers doing sputter depth profiling has evolved from the experience of many researchers using several generations of sputter ion guns. Often considerable instrument time is used to establish the sputtering rate for specific instrument configuration and operating conditions at the time of analysis. We have conducted an inter-laboratory "round robin" study help identify the types of variations actually observed in sputtering systems in use today to help determine the time frame for which calibration may be needed, depending on the type of information required by the analysis. The depth of thin layers was identified as a major information need in surface analysis by surveys done for E42 and ISO TC201. This "round robin" was undertaken as an ASTM International Interlaboratory Study (ILS 229) The results obtained from this study will be used to determine a required frequency of ion gun sputter rate calibration and for the development of a guide or standard.

In this poster we present results obtained from seven ILS-229 participants. Each participant was sent a package containing 7 SiO_2 coupons with known thickness measured using a J. A. Woollam Co. α-SE Spectroscopic Ellipsometer. The participants were asked to perform 5 depth profiles using identical ion gun settings at different time intervals: Immediately after turning the ion gun filament (minimal warm up), after a 60 minutes filament warm up period (typical warm up), at the end of the day (filament on all day), the following day (typical filament warm up of 60 min.), and after one week (typical filament warm up of 60 min.) The sputter rates were determined from a plot of the Si and O intensity as a function of sputter time. The time needed to sputter through the entire SiO_2 layer (when the O signal drops to 50% of the plateau value) is identified as the sputter time. The sputter time t_{sp} is determined using ASTM Standard Practice E 1636-04 "Analytically Describing Sputter-Profile and Linescan Profile data by an Extended Logistic Function". The results demonstrate both the excellent consistency of sputter conditions for many ion gun systems, but also the need to have a process to actually determine the stability of a specific ion gun system and configuration.

4:00pm **AS-MoA7 Post-Acquisition Mass Resolution Improvement in Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**, ***S.J. Pachuta***, *P.R. Vlasak*, 3M Company

Time-of-flight secondary ion mass spectrometers employing pulsed primary ion beams provide excellent mass resolution, on the order of 10,000 (full-width-at-half-maximum) over most of the spectral range. Unfortunately, even with all instrumental parameters optimized, ultimate mass resolution can only be achieved by sampling a relatively small area on a smooth surface oriented perpendicular to the extraction optics, under a uniform electric field. It is often difficult to meet these four criteria simultaneously.

These criteria fall into two categories, geometric and electrical. Mass resolution degradation due to geometric factors is the result of a distribution of flight times for ions of the same mass, caused by secondary ions originating from different vertical and horizontal positions within the analysis area, and, for rastered primary ion beams, by differences in the flight times of primary ions across the rastered area. Partial correction of these problems can be achieved in real time through hardware and software compensation, but the instrument must be well-tuned. For insulators,

electrical effects may be convoluted with geometric factors and influence mass resolution in a number of unpredictable ways.

For data acquired in "raw" mode (full spectrum at every pixel), it is sometimes possible to correct for these real-world difficulties after data acquisition. Two approaches are employed. The first involves subdividing the analysis area into a regular grid of smaller regions and extracting mass spectra from each region. The extracted spectra are individually calibrated by an automated process, and all or an optimized portion of the spectra are summed to produce a new spectrum with higher mass resolution than the original total spectrum. Interestingly, the spectral calibration information can be used as a diagnostic tool for instrument alignment and tuning.

The second approach is effective for improving mass resolution in spectra of rough surfaces, such as fabrics. Unlike the first approach, the analysis area is not subdivided into a regular pattern. Rather, spectra are obtained from regions of similar height, identified by any of four methods ranging from manual selection of regions-of-interest to automated pixel selection using principal component analysis and multivariate curve resolution. The automated methods have the advantage of simultaneously optimizing the mass resolution and the spectral counts without having to take a trial-and-error approach.

With these methods, mass resolution improvements of 20% - 50% are typical for smooth surfaces, and much larger improvements can be achieved for rough surfaces.

4:20pm **AS-MoA8 ToF-SIMS Analysis of Iron Oxide Particle Oxidation by Isotopic and Multivariate Analysis**, ***J. Ohlhausen***, *E. Coker, A. Ambrosini, J. Miller*, Sandia National Laboratories

A procedure for quantitative ToF-SIMS analysis of the re-oxidation of iron oxide particles in a ceramic matrix is discussed. Iron oxide is reacted with yttria stabilized zirconia (YSZ) to create a composite that facilitates the high temperature decomposition of CO_2 and H_2O. In the two step process, Fe_3O_4 is partially reduced to FeO by heating to high temperatures (>1300 °C) under inert atmosphere. It is then re-oxidized at < 1200 °C under CO_2 or H_2O yielding CO or H_2 respectively. The reactivity of this two step solar-thermochemical process is being investigated by varying the concentration of iron in YSZ up to and past its solid solubility point, thus affecting the size of iron oxide particles in the matrix, and hence their rate and extent of re-oxidation. For the SIMS experiment, the YSZ sample containing natural abundance iron oxide was mixed with an organic binder, isostatically pressed into a disc and calcined in air at 1450 °C. This disc (~ 10mm diameter, 2mm thickness) was thermally reduced at 1400 °C and then re-oxidized at 1100 °C in the presence of $C^{18}O_2$. The ratio of ^{18}O to ^{16}O shows the extent of oxygen exchange for each iron oxide particle.

For ToF-SIMS analysis, samples are prepared by cross-sectioning and polishing by conventional metallographic preparation techniques followed by ion milling with Cs^+ in the ToF-SIMS. ToF-SIMS data are acquired from the cross section only after surface contaminants are removed and a "bulk" condition exists on the exposed surface. Data are acquired in a fashion that maximizes the ability to correct for detector saturation, thus providing quantitative oxygen isotopic results with little error. Data analysis method uses a combination of multivariate analysis for particle identification and conventional analysis for quantitative isotopic ratioing. Details of analysis procedures will be discussed along with results for a range of iron oxide particle sizes.

Sandia National Laboratories is a multi program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:40pm **AS-MoA9 Informatics for SIMS: Identifying Molecules in Complex Mass Spectra**, ***I.S. Gilmore***, *F.M. Green, M.P. Seah, J.L.S. Lee*, National Physical Laboratory, UK

High-throughput screening using mass spectrometry for proteomics has driven the need to move from manual methods for protein identification to automated methods. Metabolomics has similar needs owing to the complex chemical mixtures studied. A combination of three important developments has allowed major progress in the automated interpretation of spectra to identify chemical and biological constituent substances. These are (i) the explosion in the amount of publicly available chemical information (PubChem[1], for example indexes over 71 million substances) (ii) advances in mass spectrometry search engines and fragmentation tools and (iii) rapid growth in high performance mass spectrometers (mass accuracy < 1 ppm and mass resolution > 100,000). These recent developments in informatics are the endeavours of a very much larger community than the surface analysis community. We can utilise this rich resource.

We show this in three parts. Firstly, we analyze the popular PubChem database in terms of the population of substances with mass when resolved with typical mass spectrometer mass accuracies[2]. In general, in ToF-SIMS the mass accuracy is ~ 30 ppm for an unknown substance. For a typical molecule (the modal mass in PubChem[1] is 385 u) there are ~ 30,000 substances within this mass tolerance[2]. In high performance mass spectrometers (~ 1 ppm mass accuracy) this range reduces to ~ 1000 substances which may be further reduced to around 50 substances using isotope pattern matching. Clearly, the mass accuracy in organic SIMS needs to improve significantly to benefit from chemical databases in the same manner as the metabolomics community. Secondly, we have previously shown how G-SIMS simplifies spectra so that the most structurally significant peaks are dominant and we now show a new development called the g-ogram[3]. This gives a visually simple chromatographic method to interpret spectra and allows separation of, for example, substrate, polymer and molecule peaks based on the fragmentation energy. Thirdly, we show how the G-SIMS spectra are a bridge to the informatics methods used by the metabolomics community providing identification automatically linked to public chemical databases. Present challenges and future opportunities will be discussed.

References

[1] *PubChem*; National Institute of Health, http://pubchem.ncbi.nlm.nih.gov/ 2011.

[2] F M Green, I S Gilmore & M P Seah, Analytical Chemistry 2011, dx.doi.org/10.1021/ac200067s

[3] R. Ogaki, I. S. Gilmore, M. R. Alexander, F. M. Green, M. C. Davies and J. L. S. Lee, Analytical Chemistry 2011, dx.doi.org/10.1021/ac200347a

5:00pm **AS-MoA10 keV Ion Impact Effect on the IonCCD™ Surface and Mass Spectra Peak Shape in Non-Scanning Sector-Field Instrument**, ***O. Hadjar***, *G. Kibelka, S. Kassan, C. Cameron, K. Kuhn*, OI Analytical

Particle-surface interactions are very important processes making physics practically impossible to apply without putting those interactions into the equation. For particle detection applications, the detection event is triggered by total or partial particle energy deposition upon impact on the detector. Mass spectrometry common ion detectors are Channeltr ons and MCPs, which inherently destroy the particle upon measurement. The IonCCD, a product from the rapidly emerging technology will be characterized against keV ion impact when used in a dispersive mass analyzer.

The IonCCD is used as focal plane array in a sector field instrument of Mattauch-Herzog geometry (MH-MS). When miniaturized, MH-MS is best suited for low mass range applications (< 100 u). Differently from the two first detector families that most often operate in particle counting mode (time resolved detection) the IonCCD operates in an integration mode (charge integrator). In this case, dispersed ions neutralize on the electrode pixels for a well-defined time known as the integration time. While the potential energy of the detected ions is used for detection, the ion kinetic energy leads to ion-surface interaction, an artifact amplified at extreme low mass detection. This latter can be eliminated by floating the IonCCD or operating it in higher magnetic fields.

The artifact manifesting in the mass spectra as distortion (negative peak) due to keV ion impact induced secondary electron emission was modeled and investigated experimentally using electronic stopping power fingerprints. We demonstrate that the artifact increases linearly with ion impact velocity and is dependent in an oscillatory fashion on ion nuclear charge. Both findings are in agreement with the electronic stopping of keV ions with the TiN surface of the IonCCD. 3D simion modeling suggests efficient peak artifact suppression by operating the IonCCD in higher B-field (> 4000 G) and less elegantly by IonCCD-magnet face retarding field. Same model was used to enhance the performance of the instrument, confirming the dynamic mass range (Mmax/Mmin) increase from 16 to 70.

The potential IonCCD damage upon keV ion impact through the nuclear stopping effect was investigated by means of atomic Force Microscopy and X-ray Photoelectron Spectroscopy. While AFM confirmed the expected increase in surface roughness, XPS showed no stoichiometry change due to implantation or preferential ion sputtering. The discoloration observed after extensive use was related to carbon layer formation in the roughened irradiated pixel area. Nuclear stopping effects do not seem to affect the detector performance at practical doses.

5:20pm **AS-MoA11 First use of ToF-SIMS for Screening Assays: Enzymes Active on Wood**, ***R.E. Goacher***, *E.A. Edwards, C.A. Mims, E.R. Master*, University of Toronto, Canada

Proteomic and metagenomic studies are rapidly increasing the number of proteins available for enzymatic screening. However, current high-throughput enzyme assays have limited applicability for an important class of biochemical substrates – complex solid materials. The present work aims

to utilize the strengths of Time-of-Flight Secondary Ion Mass Spectrometry for the direct measurement of enzyme activity on solid substrates. Particularly, ToF-SIMS is applied to the detection of wood-modifying enzymes.

Proof-of-principle ToF-SIMS enzyme assays were performed by immersing extracted wood fibers in solutions of commercial cellulase and laccase enzymes (utilizing water/buffer and denatured enzymes for controls). The laccase enzyme was also tested with and without several small molecule mediators. Principle Component Analysis (PCA) clearly distinguished cellulase tests from controls through the loss of polysaccharide peaks and relative enrichment of lignin peaks. Additionally, PCA distinguished laccase test samples (with mediator) from controls through a shift in lignin-characteristic peaks. The active laccase was indicated by a relative decrease in guaiacyl-lignin and syringyl-lignin peak intensities and increase in generic aromatic peaks, resulting from the cleavage of hydroxyl and methoxy groups from lignin benzoid units.

These proof-of-principle assays demonstrate that ToF-SIMS is capable of providing yes/no screening information for enzyme activity on complex solid substrates, such as wood.

[1] R. E. Goacher, D. Jeremic, E. R. Master. Analytical Chemistry 83(3), 2011, 804-812.

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