Applied Surface Science

Room: 610 - Session AS-MoA

Quantitative Surface Analysis II. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

Moderator: S. Asher, National Renewable Energy Laboratory

2:00pm **AS-MoA1 Cluster Primary Ion Beams Advance the Capability of Bio-Molecule Analysis by SIMS**, ***J.C. Vickerman***, The University of Manchester, UK **INVITED**

The analysis of bio-molecular systems using SIMS with atomic primary ion beams has been bedevilled by three principal limitations - the static limit, the inability to sputter large molecules intact and the very low ionisation probability. The static limit, imposed because of the extensive bombardment induced chemical damage generated by high energy atomic primary ions, limits the amount of material accessible for analysis to 1% of the surface layer, greatly limiting detection sensitivity, the pixel size that can be usefully imaged and eliminating the possibility of molecular depth profiling. Atomic primary ions do not appear to be capable of sputtering intact organic molecules molecular weight much above 500 daltons in significant quantities. This places a major limitation on the value of SIMS in bioanalysis. Finally in common with all desorption mass spectrometries, the ionisation probability of the sputtered species is usually well below 10^{-3}, placing a further limitation on detection sensitivity and the useful minimum pixel size in SIMS imaging. It is clear that making progress into lifting some or all of these limitations would have a dramatic effect on the value of SIMS in bio-analysis. Over the last 10 years the possibility that cluster primary ion beams would lift some of these limitations has been increasingly investigated. The capability of liquid metal ion sources to generate cluster ions such as Au_n^+ and Bi_n^+ has been exploited.[1,2] Gas sources have been used to deliver SF_5^+ and C_{60}^+ ions.[3,4] It has been shown that these ions can greatly increase the yield of higher mass ions by orders of magnitude and enable ions up to ~3000 daltons to be detected. Nevertheless the metal cluster ions still generate significant bombardment induced chemical damage such that the static limit is still necessary.[5] However the larger cluster ions such as C_{60}^+ generate far less bombardment induced chemical damage and for many systems the static limit can be lifted.[5] This greatly increases the potential for high sensitivity analysis, imaging with sub-micron resolution and most significant - molecular depth profiling.[6] This latter development offers the possibility of 3D molecular imaging of bio and organic systems.[7] This paper will review the progress that has been made and will suggest that to fully exploit the benefits of cluster primary ions new approaches to analysis may be required.

[1]N. Davis, D.E. Weibel, P. Blenkinsopp, N. Lockyer, R. Hill, J.C. Vickerman, App. Surf. Sci 203-204 (2003) 223-227

[2]F. Kollmer, App. Surf. Sci 231-232 (2004) 153-158

[3]C.M. Mahoney, S.V. Robertson, G. Gillen, Anal. Chem. 76 (2004) 3199-3207

[4]D.E. Weibel, S. Wong, N.P. Lockyer, P. Blenkinsopp, R. Hill, J.C. Vickerman, Anal. Chem. 75 (2003) 1754-1764

[5]E.Jones, N.P. Lockyer and J.C. Vickerman, Int J, Mass Spectrom., 260 (2007) 146-157

[6]J. Cheng, A. Wucher and N. Winograd, J. Phys. Chem. B 110, 8329-8336 (2006).

[7]J. S. Fletcher, N. P. Lockyer, S. Vaidyanathan, and J. C. Vickerman, Anal. Chem., 79 (2007) 2199-2206

2:40pm **AS-MoA3 Detector Dead-time Effects in the Multivariate Analysis of ToF-SIMS Spectral Images**, ***M.R. Keenan***, Sandia National Laboratories, *V.S. Smentkowski,* General Electric Global Research, *J.A. Ohlhausen*, Sandia National Laboratories

The time-to-digital converters typically employed for ToF-SIMS have a dead-time that is significant with respect to the distribution of times-of-flight characteristic of a given nominal mass. When data are acquired with high mass resolution, it is generally the case that only a single secondary ion can be detected at any given mass per primary ion pulse, regardless of how many ions actually reach the detector. Consequently, the data become non-linear in the sense that the signal intensity is no longer proportional to the local composition. This phenomenon often manifests itself as "saturation," for instance, finding isotope ratios that deviate significantly from generally accepted values. The data non-linearity also poses significant problems for multivariate statistical analysis techniques (MVSA), which fundamentally assume an underlying linear additive model. In these cases, extraneous components are often discovered that simply describe the non-linearity and can ultimately confound chemical interpretation. Dead-time correction procedures have been described, previously, for time-of-flight mass spectrometry. These typically rely upon observing a statistically significant number of ion pulses at each volume element, a situation that is not practical for ToF-SIMS spectral images composed of large numbers of pixels, 3D depth profiles and stage rastering measurements. In this paper, various dead-time effects on ToF-SIMS spectral images will be described. We will also propose a novel data pretreatment protocol that is suitable for use with MVSA. The new method involves a transformation to linearize the data, which is similar to previously published corrections, together with a scaling step to properly account for the non-uniform noise characteristic of dead-time-limited data. The ability of the new protocol to enable the extraction of accurate, meaningful components while excluding noise during MVSA will be illustrated with simple, intuitive examples.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:00pm **AS-MoA4 Quantitative Nanoscale Analysis of Surfaces with Topography using ToF-SIMS**, *J.L.S. Lee,* ***I.S. Gilmore****, M.P. Seah*, National Physical Laboratory, UK

Surface topography is a crucial issue for the analysis of innovative devices such as microfluidic systems, MEMS devices, fibres, composite materials, sensors, organic electronics and biomedical devices. The strength and durability of these components is critically dependent on their nanoscale surface chemistry and molecular interactions. However, quantitative characterisation of surfaces with topography remains a significant challenge due to the lack of systematic and validated measurement methods.[1] In particular, surface topography can causes many unwanted artefacts in ToF-SIMS spectra and images, including ion shadowing effects caused by distortions in the extraction field, reduced mass resolution caused by the spread in the time of flight of secondary ions, distortions in the images due to the angular differences between the primary ion beam and the analyser with respect to the sample, loss in signal due to the limited angular acceptance of the analyser, and potential problems in charge compensation of insulating samples. This presents enormous technical challenges to process engineers and R&D scientists developing new products and processes. Here, we present a systematic study of the effects of surface topography on SIMS. Experimental data are acquired for model cylinders, fibres and spheres, for both conducting and insulating samples. The results are in good agreement with those obtained using an ion optics simulation program, SIMION,[2] allowing us to understand the effects of surface topography and provide guidance to practical analysts for identifying and reducing topographical effects. In addition, the use of multivariate methods for images with surface topography is investigated using principal component analysis (PCA) and multivariate curve resolution (MCR), extending from our previous work on mixed organic systems on flat surfaces.[3] With careful application and suitable data preprocessing methods, multivariate analysis is shown to improve data interpretation and allows for the rapid processing of high-resolution raw spectral data in SIMS images.

[1] S Rangarajan and B J Tyler, J. Vac. Sci. Technol. A 24(5) (2006) 1730-1736

[2] SIMION version 8.0, Scientific Instrument Services, Inc., 1027 Old York Rd., Ringoes, NJ 08551, USA

[3] J L S Lee, I S Gilmore and M P Seah, submitted.

3:40pm **AS-MoA6 Cluster Primary Ions: Spikes, Sputtering Yields, Secondary Ion Yields and Inter-Relationships for Secondary Molecular Ions for Static SIMS**, ***M.P. Seah***, National Physical Laboratory, UK **INVITED**

A framework is provided to describe the enhanced sputtering yields and secondary ion yields of molecular fragments, from molecules on substrates, achieved when using cluster primary ions. Analysis of published sputtering yield data shows that one particular model of sputtering, that includes spikes, is an excellent quantitative description of the yields for a wide range of monatomic and polyatomic primary ions. Evidence will be shown of the model validity for clusters of up to more than 10 atoms over 3 orders of magnitude in sputtering yield. Using data from one primary ion, within this model, extremely good descriptions of measurements reported with other primary ions is achieved. This theory is then used to evaluate the important molecular ion yield behaviour for static SIMS. This leads to universal dependencies for the de-protonated molecular ion yields, valid for all primary ions, both single atom and cluster, over 5 decades of emission intensity. This formulation permits the prediction of the $(M-H)^-$ secondary ion yield for different, or new, primary ion sources, e.g. Bi_n^+ and C_{60}^+, for the analysis of organic materials. Optimal primary ion sources are predicted and discussed. For analysing materials, raising the molecular secondary ion yield is extremely helpful but it is the ratio of this yield to the disappearance cross section that is critical. Data are evaluated and a description is given to

show how this varies with the cluster type to provide a further universal dependence. Optimal analytical conditions are discussed.

4:20pm **AS-MoA8 The 3D Atom Probe Instrument - Introduction to the Technique and Some Applications in Material Science**, ***L. Renaud***, CAMECA, France **INVITED**

The 3D atom probe is a quantitative technique that provides atomic scale 3D element mapping of chemical heterogeneities in sample.[1] The sample has to be prepared in the form of a very sharp tip. Under the effect of high electrical field, the atoms at the surface are evaporated by field effect and projected on a position sensitive detector.[2] This detector allows the localization of the impacts in synchronism with the measurement of the time of flight of the evaporated atoms. At the end of the analysis, it is possible to rebuild in 3D near an atomic scale, the analyzed volume (typically 70nm x 70nm x 200nm), atom by atom. The goal of this presentation is to demonstrate the contribution of the 3D-AP in materials science. For this purpose, we will make first a brief introduction to the technique. Some results obtained with this technique will be shown in order to evaluate the contribution of the instrument in materials science (especially for quantification measurement). In the last part of the presentation, new developments and future applications of the instrument will be discussed and also we will make an insight to the sample preparation issue

[1]D. Blavette et al., Nature 363 (1993) 432 - 434

[2]L. Renaud et al., Nuclear Instruments and Methods in Physics Research Section A: Vo 477, Issues 1-3, 21 January 2002, 150-154

5:00pm **AS-MoA10 Composition of Surfaces: A Comparison of LEIS and ToF-SIMS**, *D. Breitenstein, R. Kersting,* ***B. Hagenhoff,*** Tascon GmbH, Germany, *R. ter Veen, H. Brongersma*, Calipso B.V., The Netherlands

Low Energy Ion Scattering (LEIS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) enable the analysis of the atomic and chemical surface composition of vacuum sustainable samples. Applying LEIS, the surface of a sample is hit by noble gas ions (He^+, Ne^+, ...) of low energy (1-5 keV). Elastic collisions with individual surface atoms can cause backscattering of the projectiles. Analyzing the energy of these scattered noble gas ions, and moreover knowing their mass and initial energy, the identity of the atomic collision partner can be calculated. Therefore, LEIS enables the quantitative determination of the elemental composition of the samples‘ outermost monolayer. Ions scattered in deeper layers, loose extra energy along the in- and outgoing trajectories. This is used to obtain non-destructive high-resolution depth profiles (0-10 nm). In ToF-SIMS the surface of the samples is also bombarded with atomic - or even polyatomic - projectiles. In contrast to LEIS the energy (10-25 keV) and the mass (e.g. Bi_3^+: 627 u) of these projectiles is relatively high. The impact of these projectiles leads to a formation of collision cascades in surface near regions resulting in a desorption of particles (electrons, neutral and ionized atoms as well as molecules). The ions can be mass separated and detected in a ToF analyzer providing elemental and molecular information on the first 1-3 surface monolayers. Both techniques provide useful information on the surface composition of solids. However, this information differs for LEIS and ToF-SIMS in several aspects: Firstly, LEIS offers the lower information depth. Whereas ToF-SIMS probes the uppermost three monolayers, LEIS generates information on the outermost monolayer. Secondly, ToF-SIMS offers information on the elemental as well as molecular composition of the surface, whereas with LEIS solely elemental information can be obtained. Furthermore, in terms of quantification, LEIS is superior to ToF-SIMS. Finally, ToF-SIMS allows a laterally resolved probing of the sample down to a resolution of 100 nm whereas in LEIS the lateral resolution is restricted to 0.1-1 mm. This paper compares results of applying LEIS as well as ToF-SIMS to well-defined samples such as Langmuir-Blodgett monolayers but also to analytically relevant samples like nanoparticles. It will highlight the strengths of both techniques and the synergism obtained in applying both methods.

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