

Thursday Morning, November 1, 2012

Applied Surface Science
Room: 20 - Session AS-ThM

Applications of Large Cluster Ion Beams

Moderator: A.V. Walker, University of Texas at Dallas,
C.M. Mahoney, Pacific Northwest National Laboratory,
M.L. Pacholski, The Dow Chemical Company

8:00am **AS-ThM1 Comparison of Primary Ion Beams for XPS Sputter Depth Profiling of Organic Samples.** *S.J. Hutton, C.J. Blomfield, S.J. Page, W. Boxford*, Kratos Analytical Ltd., UK

Several types of cluster ion sources are available aimed at facilitating X-ray Photoelectron Spectroscopy (XPS) sputter depth profiling of organic materials. These ion sources may be categorised as either carbon based sources (e.g. Coronene) or Ar cluster ion sources. Both types of source may be fitted to modern XPS instruments. Experimental parameters such as primary ion voltage, primary ion incidence angle and cluster size may be optimised to improve profiling results. The sample environment may also be controlled to extend the range of polymers which are amenable to sputter profiling. Sample parameters which have been shown to be important include rotation with respect to the ion beam and sample temperature.

In this study we compare the performance of Carbon and Ar based cluster ion sources on a range of organic thin films, from fields as diverse as organic PV materials, OLED's, cross-linked plasma polymers and multilayers. Samples were analysed under a range of sample conditions with both sources. Direct comparison allows the efficacy of ion beams to be rated for a range of sample types.

8:20am **AS-ThM2 Molecular SIMS - Revolutionized by Cluster Primary Ion Beams?**, *J.C. Vickerman*, The University of Manchester, UK
INVITED

The introduction of metal cluster and polyatomic primary ion beams had dramatically enhanced the capability of SIMS for the molecular analysis of complex, particularly organic materials. The metal cluster beams, based on gold and bismuth resulted in a very significant increase in ion yield of larger 'molecular' ions in the m/z range above 300. This has enabled significant advances in 2D imaging of bio-systems, although the analysis is still restricted to the static regime. Polyatomic ion beams such as SF₅⁺, C₆₀⁺ and Ar_n⁺ (n>50) have introduced a completely new analysis paradigm by enabling analysis and imaging far beyond the static limit such that molecular depth profiling and 3D imaging of organic and biological systems has become possible.

The paper will discuss some of the most recent advances and seek to assess the future opportunities for SIMS analysis using cluster ion beams.

9:00am **AS-ThM4 New Organic Reference Materials for Cluster Ion Sputter Depth Profiling.** *A.G. Shard, S. Spencer, S. Smith, I.S. Gilmore, R. Havelund*, National Physical Laboratory, UK

Over the past three years, the availability of multilayered organic reference materials has enabled rapid progress in cluster ion beam sputtering for organic depth profiling. These materials have provided manufacturers and practitioners with a common benchmark against which the performance of different experimental methods can be judged. Furthermore, such reference materials are invaluable in providing experimental evidence against which theory can be tested. Reference materials based on Irganox 1010 and Irganox 3114 [1] have been extensively used in this regard [2,3,4]. Results from a VAMAS interlaboratory study, completed in 2011, using argon cluster ion beams as the sputtering source are briefly presented to demonstrate the relevance and utility of these reference materials. These sources demonstrate a remarkable repeatability of better than 1% relative standard deviation in sputtering yield. Depth resolutions close to 5 nm at low impact energies can be achieved. The materials also demonstrate that electrons used for charge compensation can cause very significant molecular damage which affects profiles to a significant depth, often over many tens of nanometers. Whilst this reference material has been extremely valuable, it is not suitable for the full range of analytical methods used in conjunction with cluster ion beam sputtering and may not be representative of all molecular species of analytical interest. As examples, the Irganox 1010 and Irganox 3114 are difficult to distinguish using either XPS or positive SIMS analysis. Alternatives are being studied, such as those materials which are of great commercial importance to the organic electronic industry, e.g. aluminium tris(hydroxyquinolate). In this work, we describe the development of new reference materials including amino acids,

fluorinated compounds, specifically for XPS analysis, and compounds used in organic displays. The precision and accuracy of the layer thicknesses and the stability of the materials will be described along with their performance in cluster ion sputter depth profiling experiments. Additionally, research into a new class of reference material based upon binary mixtures of organic compounds with known compositions will be described.[1] A. G. Shard, F. M. Green, P. J. Brewer, M. P. Seah and I. S. Gilmore, *J. Phys. Chem. B* 2008; 112: 2596.[2] A. G. Shard, R. Foster, I. S. Gilmore, J. L. S. Lee, S. Ray and L. Yang, *Surf. Interface Anal.* 2011; 43: 510.[3] P. Sjovald, D. Rading, S. Ray, L. Yang, and A. G. Shard, *J. Phys. Chem. B* 2010; 114: 769.[4] D. Mao, A. Wucher, and N. Winograd, *Anal. Chem.* 2010; 82: 57.

9:20am **AS-ThM5 Characterization of Nano-objects with Nanoprojectile-Secondary Ion Mass Spectrometry.** *C.-K. Liang, J.D. DeBord, M. Eller, S. Verkhovurov, E. Schweikert*, Texas A&M University

The uniqueness of nano-objects due to functionalities not present in bulk size is well documented. Yet methods for molecular characterizations of isolated entities below micrometer dimensions are lacking. One reason is the minute amount of sample for analysis; another is that the characteristics of analytical signals from objects of nanoscale dimensions can be affected by their size, shape and environment. Our approach for the characterization of nano-objects is based on the method of event-by-event bombardment-detection. Bombardment is with a sequence of individual nanoprojectiles, specifically Au₄₀₀⁴⁺ accelerated to velocities of up to 30 km/s. The impacts cause abundant secondary ion emission. We will report on the modulation of the ejecta as a function of the nano-objects' size, shape and environment and describe the critical parameters for the accurate assay of their surface and core compositions.

9:40am **AS-ThM6 Organic Solar Cell Composition Profiling by Large Clusters Ions: How can we Optimize the Information Retrieved?**, *T. Conard, A. Franquet, E. Voroshazi, D. Cheyns, P. Favia, W. Vandervorst, IMEC, Belgium*

Organic material composition profiling has always been very challenging. Recently, it has been shown that using a Gas Clusters Ion Beam source (GCIB) with large Ar-clusters, organic information can be preserved while profiling. However, very little studies have been performed yet about the influence of beam parameters on the spectra/profiles obtained. We investigated systematically the influence of the sputter parameters in a dual beam TOFSIMS experiment (Bi_n⁺/Ar_m⁺) on organic solar cells composed of PCBM and P3HT. Environmental stability of organic solar cells prepared with oxide transport layers is considerably enhanced; hence the critical importance to be able to also investigate organic/inorganic interfaces with large ion clusters.

Qualitatively, it is known that the average energy per atom is an important parameter to keep organic information: For low eV/atom, no sputtering occurs and for high energy per atom, the molecular information is lost. We show for a layer of mixed P3HT:PCBM that the transition to the loss of molecular information occurs sharply at about 6eV/atom, independently of the primary cluster energy. However, we also observe a significant variation of the intensity of the molecular peaks within the energy-region where molecular information is kept. It occurs both towards the higher and the lower eV/atom limits. These are the consequence of the dual beam experiment. At the lower eV/atom limit, the molecular information is lost due to the damage induced by the analysis beam. Towards the higher eV/atom limit, we observed a decrease of the intensity of the molecular PCBM peak by a factor 2 between 2.8 and 4.0 eV/atom. This is interpreted as a partial degradation of the PCBM due to the sputtering.

Composition variations within the formed layers and/or polymer degradation are important for solar-cells devices performances. For a system like PCBM:P3HT mixed layer, one may follow the sulfur intensities throughout the layer as an indirect indication of segregation. This allows, for instance to use of energy-filtered TEM to analyze de-mixing of layers. By comparing TEM and molecular profiling, we show in this study that segregation within layers and degradation of solar cells can be analyzed by dual beam TOF-SIMS.

Finally, the interfaces between the organic and inorganic layers in a solar cell are also critical to the quality of the devices. However, the optimal analysis parameters of inorganic material using cluster ion source may significantly differ from the optimal parameters for organic layers (for instance sputtering rates). We will thus focus on the determination of the best trade-off parameters for heterogeneous systems.

10:40am **AS-ThM9 Molecular Imaging of Cells and Tissues with Ar Cluster Ion Beams**, J. Matsuo, S. Nakagawa, M. Py, T. Aoki, T. Seki, Kyoto University, Japan

Because molecular, structural and chemical state information is considered invaluable in life science, various mass spectroscopic techniques, such as secondary ion mass spectrometry (SIMS), matrix-assisted laser desorption ionization (MALDI) and desorption electrospray ionization (DESI), have been examined intensively during the last decade. The SIMS technique is considered to have the highest spatial resolution, but it is necessary to increase secondary ion yields of bio-molecules. It has been reported that cluster ion beams can enhance the secondary ion yields, because of the high-density energy deposition and multiple collisions near surfaces. Clusters such as SF₅, C₆₀, Au₃, and Bi₃ were found to be quite useful for SIMS of organic materials. Because these primary ion beams cause significant damage on organic surfaces, the primary ion dose is limited to a certain threshold value (known as "the static-limit", ~10¹² ions/cm²). Therefore, the intensity of bio-molecular ions (>500 Da) is too low to obtain high-resolution mass images.

Because Ar cluster ions provide much less damage on the surface than conventional ion beams, much attention is devoted to molecular depth profiling of organic multilayer and molecular imaging with Ar cluster-SIMS. We have developed a new SIMS imaging system with focused Ar cluster ion beam. An orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer, which allows the use of a continuous beam, was employed in a new bio-imaging system. There was no need to use the ion-bunching technique in this system, and therefore there was no need for tradeoff between beam diameter and mass resolution, which is a problem in mass-imaging of biological samples with conventional SIMS. SIMS spectra of cells with Ar cluster ions are quite different from that with Bi₃ ions. Lipid molecular ions found in the mass range over 600 Da, are clearly observed with Ar cluster ions. Furthermore, background level of the spectra with Ar cluster ions is much lower than that with Bi₃ ions. This is attributed to the lower velocity of the primary ions.

The latest results of this system and its performance in molecular imaging of cells and tissues will be presented and discussed.

Acknowledgements

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J. Matsuo, S. Ninomiya, H. Yamada, K. Ichiki, Y. Wakamatsu, M. Hada, T. Seki and T. Aoki, *Surf. Inter face Anal.* (2011) 42, 1612

11:00am **AS-ThM10 Observation of High Ionization Probability for Desorption/Ionization Induced by Neutral Cluster Impact and its Application in Bioanalytics**, B.-J. Lee, M. Baur, University of Applied Sciences Esslingen, Germany, C.R. Gebhardt, Bruker Daltonik GmbH, Germany, M. Dürr, University of Applied Sciences Esslingen, Germany

Desorption and ionization induced by neutral cluster impact is a very soft method for transferring surface-adsorbed biomolecules into the gas phase [1]. The neutral clusters with a mean size of 10³ to 10⁴ molecules are seeded in a He beam which results in a narrow velocity distribution and an energy density of 0.5 to 0.8 eV/molecule. Using SO₂ clusters, the method furthermore makes use of the dipole moment of the cluster's constituents which allows both for solvation and charge transfer processes in the cluster. 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 comparably low energies of the impacting clusters and without any fragmentation of the biomolecules.

In order to quantify the ionization probability during cluster-induced desorption and ionization, samples with well defined amount of substance, especially oligopeptides such as angiotensin II and bradykinin, were prepared by means of drop casting the respective solution on a SiO₂ surface. A biased grid in front of the target was used to transfer ions of one polarity into the time-of-flight mass spectrometer; simultaneously, the correlated ion current from the target was measured. In case of oligopeptides, the positive ion signal is dominant and both positive ion mass spectra and extracted charge per pulse were measured as a function of the number of cluster pulses applied. Comparison of the total charge desorbed from the respective sample with the amount of substance applied then yields the ionization efficiency which was found to be 3 to 4 % in the case of the investigated oligopeptides. The result is discussed with respect to the desorption and ionization mechanism during cluster-surface impact, taking into account the influence of functional groups and preparation conditions.

We furthermore show that desorption and ionization induced by neutral cluster impact can be successfully combined with ion trap mass spectrometry for applications in bioanalytics. Especially when the cluster beam is produced by a pulsed nozzle with pulse duration in the sub-millisecond regime, all ions generated during one pulse can be collected in

the ion trap. In combination with the high ionization efficiency of the process, femtomol sensitivity was achieved in the case of various oligopeptides; multiple sample arrays and low sampling time then allows for batch-type analysis of biosamples.

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

11:20am **AS-ThM11 Analysis of Molecular Surfaces Using a Pulsed Beam of Large Argon Clusters**, N. Havercroft, ION-TOF USA, Inc., D. Rading, S. Kayser, R. Moellers, F. Kollmer, E. Niehuis, ION-TOF GmbH, Germany

In the last few years it has been demonstrated that massive argon cluster ions can successfully be applied as primary ion projectiles in SIMS [1-7]. They can not only be applied to sputter organic surfaces without damaging the molecular information, it also has been shown that they desorb larger molecular ions effectively [4] with little fragmentation [2][7]. Although the secondary ion yield decreases with increasing cluster size [4][6], the ability of these projectiles to produce cleaner spectra emphasizing molecular ion signals makes them interesting for analysis purposes as well [5-7]. However, the generation of short primary ion pulses has been difficult due to the large cluster size distribution which typically ranges from hundred to several thousand atoms/cluster. The resulting flight time dispersion of the different cluster sizes determines the primary ion pulse lengths and thus limits the mass resolution.

We equipped a standard TOF.SIMS 5 instrument with a newly developed Ar cluster ion source. The 90° pulsing system of this primary ion gun enables the generation of long as well as short primary ion pulses. The long pulses are suited for sputtering purposes in a dual beam experiment whereas the short pulses are used for high mass resolution TOF-SIMS spectrometry. The pulsing system also allows the selection of a specific cluster size range out of the large distribution with a mass resolution of about 2 for long and 80 for short pulses.

In this study we will apply large Ar clusters ranging from several hundred to several thousand atoms/cluster at different beam energies to a variety of molecular surfaces. We will present and compare data about the influence of the cluster size and beam energy on the sputtering as well as analysis capabilities emphasizing on the spectra appearance and the fragmentation behavior.

[1] N. Toyoda, J. Matsuo, T. Aoki, I. Yamada, D.B. Fenner, *Nucl. Instr. and Meth. in Phys. Res.*, **B 190**, (2002) 860-864

[2] S. Ninomiya, Y. Nakata, K. Ichiki, T. Aoki, J. Matsuo, *Nucl. Instrum. Methods*, **B 256** (2007), 493

[3] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo,

Rapid Communications in Mass Spectrometry, **23**, (2009), 1601-1606

[4] K. Mochiji, M. Hahinokuchi, K. Moritani, and N. Toyoda, *Rapid Commun. Mass Spectrom.* **23** (2009) 648

[5] S. Ninomiya, Y. Nakata, Y. Honda, K. Ichiki, T. Seki, T. Aoki, J. Matsuo, *App. Surf. Sci.*, **255** (2008), 1588-1590

[6] S. Rabbani, A.M. Barber, J.S. Fletcher, N.P. Lockyer, J.C. Vickerman, *Anal. Chem.*, **83**, (2011), 3793-3800

[7] S. Kayser, R. Moellers, D. Rading, F. Kollmer, E. Niehuis,

to be published in *Surf. Interface Anal.* SIMS XVIII Proceedings

11:40am **AS-ThM12 Electropray Droplet Impact/SIMS: Some Insights into the Collisional Events**, K. Hiraoka, Y. Sakai, S. Ninomiya, R. Takaishi, University of Yamanashi, Japan

Electropray droplet impact (EDI) uses the water droplets with charge number of 60-300 and masses of 6.2X10⁵-1.6X10⁷ u. The charged droplets impact the sample surface with the velocity of about 12 km/s. Because this value is higher than sound velocities of solids, the supersonic collision takes place at the moment of collision. The supersonic collision is followed by the enormous pressure build-up at the interface and electronic excitation for the species near the colliding interface will follow. The observation of the ionic products by mass spectrometry and the surface analysis by XPS are regarded as the study of the ionization/desorption processes induced by the supersonic collision. For the sample of self-assembled monolayers, only the molecular ions of organic layer but no adducts with gold atoms were observed. In addition, no gold cluster ions but only Au⁺ was observed after Au surface was exposed. This indicates no ablation but atomic- or molecular-level etching takes place in EDI. For all the organic and inorganic samples investigated, no modification of components on the surface was observed after EDI irradiation as far as XPS measurements are concerned. Non-selective etching means that all the elements of the samples are desorbed with the same probabilities. These results suggest that the collisional events taking place in EDI is highly non-thermal. The water

clusters do not penetrate into the sample but they are reflected backward in very short time, maybe in ps. The high ionization efficiency for EDI (useful yield: ~10%) may be explained by the curve crossing mechanism. The sample of AgF was only one example found so far that suffered from surface modification. Due to the very reactive nature of F atoms, the surface was enriched by Ag during EDI irradiation. The CF_3^- and CF_3COO^- ions observed at the start of irradiation decreased and were taken over by $[\text{AgF}_3\text{OH}]^-$ and $[\text{CH}_3\text{COOAg} + \text{CH}_3\text{COO}]^-$. The enrichment of silver on the AgF sample (i.e., reactive loss of fluorine) is evident. The ions CF_3^- and CF_3COO^- originated from CH_3COOH used for the electrospray of 1 M aqueous CH_3COOH solution. Supersonic collision and followed chemical reactions are complicated and the mechanism of desorption/ionization in EDI remains to be elucidated.

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