

Thursday Afternoon, November 12, 2009

Applied Surface Science
Room: C2 - Session AS-ThA

Chemical State Depth Profiling

Moderator: G.L. Fisher, Physical Electronics

2:00pm **AS-ThA1 Factors Affecting XPS Sputter Depth Profiling of Organic Materials**, S.J. Hutton, I.W. Drummond, S.C. Page, C.J. Blomfield, Kratos Analytical Ltd, UK

The sputter profiling of *inorganic* materials during X-ray Photoelectron Spectroscopy (XPS) is a well established technique to investigate quantitative chemical composition variations with depth. Until recently XPS sputter depth profiling of *organic* materials has suffered from several seemingly intractable problems, not least the significant ion induced surface damage. Secondary Ion Mass Spectroscopy (SIMS) of organic materials using noble gas or liquid metal ion sources suffered related problems. These problems have largely been overcome for the SIMS analysis of a wide range of organic materials by the introduction of cluster ion sources such as SF₅ and C₆₀. Advantages of cluster sources include an increase in secondary ion yield over conventional mono-atomic sources and a reduction in beam induced damage of the surface.

Following on from these innovations in SIMS, cluster ion sources have been utilised for XPS sputter profiling of organics. These sources have been shown to significantly reduce ion induced surface damage of organic materials as measured by XPS thus making the XPS sputter profiling of organic materials feasible.

In this study we investigate the sputter profiling of several model polymer films using a new polyaromatic hydrocarbon (PAH) (coronene) cluster ion source. Initial results demonstrate that yield volumes per incident ion are dependent on the nature of the polymer, with approximate values of: 90 nm³ for poly(lactic-co-glycolic acid) (PLGA); 117 nm³ for polyacrylic acid (PAA); and 142 nm³ for polylactic acid (PLA). Other polymers, such as polystyrene (PS), do not appear to be sputtered by cluster sources under the currently reported conditions. Early results also indicate that various experimental parameters, such as incident beam energy, affect the sputter yield and amount of ion beam induced surface damage.

Clearly there is a need to investigate the various parameters which may influence ion yields and damage with the aim of optimising sputtering conditions for a range of organic materials. The work presented here attempts to elucidate the effects of variables such as ion incident energy; ion beam angle of incidence; sample temperature and ion mass on the sputtering performance of the aforementioned PAH ion source on several thin polymer films.

2:20pm **AS-ThA2 On the Understanding and Optimization of Etching Parameters for Optimal ToF-SIMS 2D and 3D Analysis of Biological Cells**, J. Brison, D.S.W. Benoit, M. Dubey, M. Robinson, P.S. Stayton, D.G. Castner, University of Washington

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) combined with cluster ion beams is now widely used to image biological samples in two and three dimensions. Cluster ion beams (e.g., Bi₃⁺, C₆₀⁺) have indeed been shown to provide higher molecular ion yields with lower chemical damage in depth, allowing successful 2D imaging as well as molecular depth profiling of complex biological samples. In parallel, much research has been conducted to improve the sample preparation protocols to insure that the biological samples are preserved as close as possible to the living state for ToF-SIMS analysis under ultra high vacuum (UHV) conditions.

However, ToF-SIMS is not yet routinely used to solve biological problems because the data interpretation is complicated and the fundamental cluster ion/sample interaction is not fully understood. In this work, we combined ToF-SIMS with other complementary surface characterization techniques (i.e., XPS, AFM, SEM, etc.) to supplement the complex ToF-SIMS 2D and 3D datasets obtained from biological samples. For this purpose, human HeLa cells were seeded on silicon substrates and prepared according to different protocols (fixation with paraformaldehyde, cryofixation, etc.) for UHV analysis. The HeLa cells were also treated with bromine labeled small interfering RNA (siRNA) and with bromodeoxyuridine (BrdU) to provide a target for ToF-SIMS and XPS analysis. A series of ToF-SIMS experiments dealing with the different ion species (Bi₁⁺, Bi₃⁺, and C₆₀⁺), and various beam parameters (single beam, dual beam, different energies and fluences) was designed to obtain a reproducible and reliable depth profile of single HeLa cells when analyzed by the above listed techniques. XPS along with principal component analysis, for the first time has been used to image and provide quantitative elemental information about individual cells. Our

results also show that AFM and SEM provide a better understanding of the effect of topography on the ToF-SIMS data.

2:40pm **AS-ThA3 On the Way to Optimal 3D Molecular Imaging with ToF-SIMS: A Comparison between C₆₀ Single Beam and Bi_n/C₆₀ Dual Beam Depth Profiling**, J. Brison, S. Muramoto, D.G. Castner, University of Washington

Many ToF-SIMS 3D molecular images are acquired in the dual beam mode, where a high-energy beam (e.g., Ga⁺ or Biⁿ⁺ at 25keV) used at low fluence for analysis is combined with a low-energy beam for sputtering/etching (e.g., C₆₀ⁿ⁺ at 10 keV, Cs⁺ at 250 eV). Because its fluence is kept below the static limit, the effect of the high-energy analysis beam is sometimes neglected in the data interpretation, with the chemical damage entirely attributed to the etching beam. The influence of the analysis beam on the quality of ToF-SIMS depth profiles has been studied for inorganic samples [1], but no systematic study has been reported for organic samples. Because organic samples, and specifically biological samples and cells, are complex and fragile, a systematic study is necessary to understand, quantify, and model the influence of the ToF-SIMS parameters on the quality of ToF-SIMS 3D molecular images. These parameters include the species, fluence, energy, bombardment angle, and electrical charge of each primary ion beam.

In this paper, we have performed multiple depth profiles of a polymeric sample (100 nm thick tetraglyme on Si) in the single beam mode (C₆₀ for analysis and etching) and compared them to those obtained in the dual beam mode (Biⁿ⁺ for analysis and C₆₀ⁿ⁺ for etching). For all depth profiles we kept the same parameters for the etching beam (i.e., C₆₀ at 10 keV, 500 x 500 μm², 1nA) and we varied the analysis conditions (i.e., species, area, energy, and fluence). We found that the analysis beam could significantly improve or degrade the quality of ToF-SIMS depth profiles, depending on the analysis beam parameters. At very low fluence (3 to 8% of the total primary ion fluence, depending on the sample and on the ion species), Biⁿ⁺ improves the quality of the ToF-SIMS 3D images because of its higher lateral resolution. At higher Biⁿ⁺ fluences, the high clean up efficiency of the C₆₀ beam [2] can no longer remove the chemical damage induced by the analysis beam and the quality of ToF-SIMS data (molecular signals and interface width) degrades with the increasing Biⁿ⁺ fluence (or decreasing C₆₀ fluence).

[1] T. Grehl, R. Mollers, E. Niehuis, *Appl. Surf. Sci.* 203-204 (2003) 277.

[2] A. Wucher, J. Cheng, N. Winograd, *J. Phys. Chem. C* 112 (2008) 16550.

3:40pm **AS-ThA6 Teaching Laser Desorption Mass Spectrometry Old and New Tricks in Postionization and Depth Profiling**, L. Hanley, University of Illinois at Chicago **INVITED**

Secondary ion mass spectrometry (SIMS) has seen improvements in spatial and depth resolution that now approach the tens of nanometer limit for even polymeric and biological samples. Laser desorption-based strategies such as matrix-assisted laser desorption ionization (MALDI) and laser desorption postionization mass spectrometry (LDPI-MS) [1,2] display spatial resolution that barely approaches one micron. Depth resolution in laser desorption methods is even worse at tens of microns and typically requires new sample sections to be prepared for each depth. Nevertheless, MALDI-MS and LDPI-MS remain attractive because of the more detailed chemical information they often provide, especially when applied to chemically complex samples and those with higher molecular weight species. Ultrashort pulse laser irradiation is known to cause minimal laser induced damage when interacting with soft biological materials. Data will be presented evaluating the prospects for employing ultrashort laser pulses for depth profiling in mass spectrometric imaging. Ongoing experiments utilizing single photon ionization of laser desorbed neutrals via vacuum ultraviolet radiation will also be presented for detection and selectivity that are complementary to MALDI-MS. These strategies will be applied to the analysis of molecular analytes within intact bacterial biofilms grown on biomaterials surfaces.

[1] L. Hanley and R. Zimmermann, *Anal. Chem.*, to be published June 2009.

[2] G.L. Gasper, R. Carlson, A. Akhmetov, J.F. Moore, and L. Hanley, *Proteom.* 8 (2008) 3816.

4:20pm **AS-ThA8 Surface Damage Evaluation of Organic Materials Irradiated with Ar Cluster Ions**, *J. Matsuo, S. Ninomiya, K. Ichiki, H. Yamada, M. Hada, T. Aoki, T. Seki*, Kyoto University, Japan

Soft materials, such as organic or biological materials are of interest since last decade, because of their structural, functional and environmental flexibility. However, very few techniques are available for soft material analysis, because energetic probes destroy structure and change chemical states of soft materials during the analysis. SIMS analysis and molecular depth profiling of soft materials with polyatomic and cluster ions have been demonstrated recently. The multiple collisions and high-density energy deposition of these ions on solid surfaces induce enhancement of sputtering and secondary ion yields, as well reduced residual surface damage compared with other techniques.

We have demonstrated that molecular depth profiling with large Ar cluster ions is possible for poly-carbonate (PC) and poly-styrene (PS), which is difficult to analyze with C_{60} ion beam. These results indicate that extreme low energy beam is necessary for molecular depth profiling. In case of large Ar cluster beam, the kinetic energy of a few eV/atom, which is comparable to the bonding energy of molecules, is realized. In addition to this, no Ar remains on the surface, because of its low binding energy. Therefore, Large Ar cluster ion beam irradiation rarely leads to damage accumulation on the surface of the polymers, and these characteristics as etching beam are also suitable for other depth profiling techniques. The surface chemical states of the polymers were measured with X-ray photoelectron spectrometry (XPS) before and after etching. The chemical states of the poly methyl methacrylate (PMMA) sample etched with Ar atomic ion beams differed significantly from those of the unirradiated sample, whereas the chemical states were maintained even after etching with large Ar cluster ion beams. According to the detail analysis of C1s and O1s spectra, atomic composition and chemical state are very close to the ideal values.

Atomistic mechanism of energetic cluster impacts and prospect for this technique will be discussed in conjunction with possible applications.

4:40pm **AS-ThA9 Optimization of C_{60} Sputtering Conditions for Polymer Depth Profiling by TOF-SIMS**, *S.R. Bryan*, Physical Electronics, *S. Iida*, ULVAC-PHI, Japan, *G.L. Fisher, J.S. Hammond*, Physical Electronics, *N. Sanada, M. Suzuki*, ULVAC-PHI, Japan

Depth profiling of polymer materials by Secondary Ion Mass Spectrometry (SIMS) has been practiced for many years using atomic primary ion beams such as Cs^+ or Ar^+ . The analytical information provided was limited to elemental profiles due to extensive damage to the polymer structure during sputtering. The recent introduction of C_{60}^+ ion beams on TOF-SIMS instrumentation has generated significant scientific interest because of its ability to sputter a variety of organic materials to significant depths while maintaining structurally significant molecular ions in the mass spectrum. From the published studies to date, it has become clear that a high sputter yield is critical to the ability to depth profile polymers while maintaining a steady state signal of structurally significant molecular ions. In this study, we evaluate the C_{60}^+ experimental parameters of beam energy and angle of impact on the ability to depth profile several polyunsaturated polymers, such as polycarbonate (PC) and polystyrene (PS), which have proven to be difficult in earlier studies. The results verify that conditions which increase the sputter yield, such as higher beam energy or more glancing angle of impact, minimize the accumulated damage rate as a function of dose. By optimizing the C_{60}^+ sputtering conditions, the number of organic materials that can be depth profiled with acceptable damage accumulation will be significantly increased.

5:00pm **AS-ThA10 Metrics for Polymer Depth Profiling with C_{60} Ion Sources**, *J.S. Hammond, S.S. Alnabulsi, S.N. Raman, J.F. Moulder*, Physical Electronics

C_{60} ion sources on XPS systems have recently been shown to provide a powerful capability for organic contamination removal and for depth profiling many organic and polymer materials. However the depth of uniform sputter yield has been found to depend on the impact energy of the C_{60} ion and the composition of the sample. To quantify the relative importance of other parameters that can extend the depth profiling range and uniformity of sputter yield during polymer depth profiling, Zalar azimuthal rotation during C_{60} sputtering, the angle of incidence of the C_{60} ion beam, sample temperature and integrated X-ray exposure has been explored. AFM imaging of the crater bottom at various depths of a sputter profiled sample has been used to characterize the sputtering process. Results will be presented for various materials using these different analysis conditions to improve the uniformity of sputter rates and interface definition of multi-layer polymer films.

5:20pm **AS-ThA11 Organic Depth Profiling of a Model Binary System: The Demonstration of Charge Transfer between Secondary Species**, *A.G. Shard*, National Physical Laboratory, UK, *A. Rafati*, University of Nottingham, UK, *J.L.S. Lee*, National Physical Laboratory, UK, *M.R. Alexander, M.C. Davies*, University of Nottingham, UK

In recent years, it has been demonstrated that cluster ion beams may be used to ablate some materials, particularly organic materials, without the significant accumulation of damage. For such materials it is therefore possible to use cluster ion beam sputtering in conjunction with a surface analytical technique, such as SIMS or XPS, to obtain depth profiles and three-dimensional images of the distribution of species in the near-surface region. For SIMS organic depth profiling to find wide acceptance as an analytical tool it is important that it is able to measure physically meaningful quantities, such as the local concentration of a species within a blend. Building upon our recent advances in the understanding of organic depth profile using model multilayers[1], we have investigated a model miscible binary mixture of codeine and poly(lactide) using both SIMS and XPS as analytical techniques.

We show that these samples possess an overlayer of almost pure poly(lactide), which fortuitously allows the direct comparison of different samples in terms of secondary ion yield behaviour. By comparing between data obtained from samples with different concentrations, it is found that secondary ion intensities do not scale linearly with composition. However, it is possible to relate secondary ion intensities to local concentrations for a binary system. The dependence of secondary ion yield on composition is described in terms of a model based on the kinetically limited transfer of charge between secondary ions and secondary neutrals. In this case, secondary ions from codeine, which contain a basic amine group, have an enhanced yield when dilute in poly(lactide). The enhancement diminishes with increasing concentration. The suppression in secondary ion yield for ions arising from poly(lactide) has the same functional form as the enhancement for secondary ions from codeine. The model is found to describe the data very well and has some wider implications for the interpretation of SIMS data from organic systems.

[1] A.G. Shard, F.M. Green, P.J. Brewer, M.P. Seah, I.S. Gilmore, Journal of Physical Chemistry B 112 (2008) 2596-2605.

Authors Index

Bold page numbers indicate the presenter

— **A** —

Alexander, M.R.: AS-ThA11, 2
Alnabulsi, S.S.: AS-ThA10, 2
Aoki, T.: AS-ThA8, 2

— **B** —

Benoit, D.S.W.: AS-ThA2, 1
Blomfield, C.J.: AS-ThA1, 1
Brison, J.: AS-ThA2, **1**; AS-ThA3, 1
Bryan, S.R.: AS-ThA9, **2**

— **C** —

Castner, D.G.: AS-ThA2, 1; AS-ThA3, 1

— **D** —

Davies, M.C.: AS-ThA11, 2
Drummond, I.W.: AS-ThA1, 1
Dubey, M.: AS-ThA2, 1

— **F** —

Fisher, G.L.: AS-ThA9, 2

— **H** —

Hada, M.: AS-ThA8, 2
Hammond, J.S.: AS-ThA10, **2**; AS-ThA9, 2
Hanley, L.: AS-ThA6, **1**
Hutton, S.J.: AS-ThA1, **1**

— **I** —

Ichiki, K.: AS-ThA8, 2
Iida, S.: AS-ThA9, 2

— **L** —

Lee, J.L.S.: AS-ThA11, 2

— **M** —

Matsuo, J.: AS-ThA8, **2**
Moulder, J.F.: AS-ThA10, 2
Muramoto, S.: AS-ThA3, **1**

— **N** —

Ninomiya, S.: AS-ThA8, 2

— **P** —

Page, S.C.: AS-ThA1, 1

— **R** —

Rafati, A.: AS-ThA11, 2
Raman, S.N.: AS-ThA10, 2
Robinson, M.: AS-ThA2, 1

— **S** —

Sanada, N.: AS-ThA9, 2
Seki, T.: AS-ThA8, 2
Shard, A.G.: AS-ThA11, **2**
Stayton, P.S.: AS-ThA2, 1
Suzuki, M.: AS-ThA9, 2

— **Y** —

Yamada, H.: AS-ThA8, 2