

Monday Afternoon, October 29, 2012

Applied Surface Science
Room: 20 - Session AS-MoA

Quantitative Surface Chemical Analysis, Technique Development, and Data Interpretation - Part 2

Moderator: J.A. Ohlhausen, Sandia National Laboratories, S. Suzer, Bilkent University, Turkey

2:00pm **AS-MoA1 Polyatomic and Gas Cluster Ion Beam Depth-Profiling: A Model Indicating the Most Appropriate Source for an Arbitrary, Known Polymer Matrix and Estimates of Polymer Sputter Rates**, P.J. Cumpson, N. Sano, NEXUS XPS Facility, Newcastle University, UK

There has been excellent progress in the SIMS community in recent years[1,2] to identify the optimum conditions and primary ions for SIMS depth-profiling of polymers. A key step forward was the identification of Type I and Type II behaviour[3], in which polymer damage is dominated by cross-linking and polymer backbone bond-scission respectively. In many cases it is difficult, especially for a non-expert, to judge which of these two types a given polymer matrix is likely to be. For example, PAA, PMAA, PMA and PMMA are of types I, II, I and II respectively, even though their structures are very similar.

We examine this system in detail, largely in the context of XPS where polyatomic and cluster ion sources are set to become much more popular. We develop equations based on a 3D Ising "resistor removal" model. Some of the difficult parameters in this model can be estimated from literature values for rates of cross-linking and bond scission of polymers seen in radiation treatment at much higher energies. This model leads to some reasonably simple equations allowing analysts to make objective estimates of (a) which primary ion source is most appropriate for a particular polymer matrix, and (b) an estimate of the sputter-rate, for any arbitrary polymer matrix whose repeat unit is known.

The reliability of the model is tested using measured sputter rates for samples of 20 polymers using polyatomic (coronene) and GCIB (argon cluster) sources. White-light interferometry combined with a novel kinematic mount for semi-automatic measurement of sputter crater volume have accelerated and improved the accuracy of these measurements.

Finally, based on the new model, we tabulate and plot estimated values for 103 polymers of technological significance.

[1] N. Winograd, *Anal Chem* 77 (2005) 143A

[2] J. S. Fletcher, X. A. Conlan, E. A. Jones, G. Biddulph, N. P. Lockyer, J. C. Vickerman, *Anal Chem* 78 (2006) 1827

[3] C. M. Mahoney, *Mass Spectrometry Reviews*, 29 (2010) 247

2:20pm **AS-MoA2 XPS Profiling of Biosensor Materials with Argon Cluster Ions**, P. Mack, R.G. White, T.S. Nunney, Thermo Fisher Scientific, UK, J.J. Pireaux, P. Louette, N. Wehbe, L. Houssiau, FUNDP, Namur, Belgium

Sensors for biological compounds are becoming increasingly important in a wide variety of applications. These devices are typically composed of complex stacks of thin/ultrathin layers of biochemical compounds. The overall behaviour of the sensor is strongly influenced by the elemental and chemical properties of the individual layers, but the interactions at layer interfaces may also have an effect.

There is an increasing requirement for compositional profiling of these devices, combining the chemical selectivity and surface specificity of XPS with some kind of ion beam sputtering. Traditional methods such as argon monomer ion profiling can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials. Over the last few years, there have been numerous studies and investigations into the use of argon cluster beams for depth profiling with the goal of preserving chemical information during analysis of organic materials.

This talk will present data from cluster profiling studies of amino acid based biosensors. The chemical variation between amino acid layers is very subtle, but it will be demonstrated that the combination of rapid acquisition XPS and argon cluster profiling is able to characterise the changes in chemistry throughout the layer stack.

2:40pm **AS-MoA3 ToF-SIMS and NanoSIMS Imaging of Uranium Distributions in the Sediment of Hanford Site**, Z. Zhu, Z. Wang, Pacific Northwest National Laboratory

Nuclear materials processing over the past seventy years has left approximately 55 million gallons of nuclear wastes stored in underground tanks at Hanford site. Some of these wastes are leaking into the ground and the DOE has been working on developing remediation technologies. As a part of these activities, sediment samples have been extensively studied to understand chemical speciation and aqueous mineral chemistry. Although concentrations and distributions of radioactive elements, such as uranium (U), plutonium (Pu), and technetium (Tc) are of great interest, U is the most important one because its concentration in the wastes is significantly higher compared to other radioactive elements. Previous studies show that the sediment samples contain low concentration of U (<10 ppm). However, non-uniform distribution of U is found, and the U appears to be mainly in micron- or sub-micron-size particles. Although an understanding of the chemistry and speciation of these particles is important, it is extremely difficult to obtain the composition of these particles using conventional analytical capabilities such as AES, XPS, and SEM/EDX because of the low concentration of U in the samples. Secondary ion mass spectrometry (SIMS) can be effectively used to discover the chemical components of these U-containing particles with excellent sensitivity and decent spatial resolution. We used ToF-SIMS and Nano-SIMS to image some of these U-containing particles in the sediment samples. Preliminary results indicated that U was present across the sample at lower concentrations, while spots of sub-micron particles with much higher U concentrations were irregularly distributed. The major elements in these "hot" spots appeared to be uranium, sodium, phosphorus, and oxygen.

3:00pm **AS-MoA4 ToF-SIMS MCS_x^+ Dual Beam Depth Profiling with Improved Dynamic Range**, S. Kayser, ION-TOF GmbH, Germany, N. Havercroft, ION-TOF USA, Inc., F. Kollmer, R. Moellers, E. Niehuis, ION-TOF GmbH, Germany

In recent years MCS_x^+ depth profiling has become increasingly popular for the analysis of thin films using Time-of-Flight SIMS (ToF-SIMS). The MCS_x^+ mode offers quantitative or semi-quantitative SIMS data and allows for the measurement of electropositive and electronegative elements simultaneously by detecting MCS_x^+ and MCS_{x-1}^+ , respectively. In addition, the use of heavy cluster ions like Bi_3^+ or C_{60}^+ allows for a significant increase of the MCS_x^+ yields by a factor of up to 1000 with respect to Ga as primary ion projectile and leads to a remarkable improvement of the achievable detection limits [1].

However, one disadvantage of current TOF-SIMS instruments for the quantification in MCS_x^+ mode is the limited dynamic range, which restricts the possibility of achieving high sensitivity on the MCS_x^+ clusters and of using the Cs_x^+ intensity for normalization. The normalization is especially important for the analysis of layer systems where sputter rates or the cesium surface concentration might change from layer to layer. This requires a registration system which is able to detect more than 100 secondary ions of a specific element per primary ion gun pulse with high linearity.

We have developed a new registration system for TOF-SIMS, which increases the useable dynamic range by a factor of 100 i. e. 1E7 counts/sec with an excellent linearity. In addition, the maximum pulsed primary ion current of the bismuth liquid metal ion gun was increased in order to further improve the detection limits for low concentration elements. In this paper we will discuss the characteristics of this new experimental setup and the benefits for the quantitative depth profiling in the MCS_x^+ mode.

[1] E. Niehuis, T. Grehl, F. Kollmer, R. Moellers, D. Rading, SIMS Europe, Muenster, 2006

3:40pm **AS-MoA6 Surface Diffusion of Carbon on Metals and Complications for Auger Spectroscopy of Carburized Steels**, W.D. Jennings, Case Western Reserve University **INVITED**

The development of low temperature colossal super saturation of stainless steels produces carburized case hardened materials with superior corrosion resistance and mechanical properties. Auger characterization of these materials requires line scan analysis of steel cases that contain substantial carbon concentration. Long acquisition times and surface migration of contaminating carbon complicate the measurement process, and lead to the need for continuous ion sputtering during acquisition of Auger spectra. This process in turn leads to the further complication of differential sputtering effects which alter the apparent composition of the material. This study details the corrections to the Auger relative sensitivity factors needed to achieve accurate characterization of these materials. Fundamental measurements of carbon surface diffusion are also presented.

4:20pm **AS-MoA8 Charge Referencing Complex Organic Materials in XPS using Hexatriacontane**, *L. Lohstreter*, Medtronic, Inc.

Excess charge build up on insulators can obscure interesting chemical shifts during XPS analysis. The common practice to correct for this is to charge reference the C1s peak of organic materials to 285 eV, the C-C, C-H bond that is ubiquitous due to atmospheric hydrocarbon contamination. However, for samples with complex organic chemistry, it is often the very information within the C1s envelope that is in question. Moreover, the peak can be convoluted with no distinct shoulders. This makes shifting the maximum of the peak to 285 eV a dubious process with little assurance that it will correlate to the true chemistry of an unknown sample. This work will show that even unknown, complex C1s envelopes can be accurately charge referenced with a combination of an application of hexatriacontane to the surface and spectral subtraction. Applications in model material characterization and plasma treated surfaces will be discussed.

4:40pm **AS-MoA9 PADI: Ambient Surface Analysis of Polymers and Molecules – Metrology Development for Reliable Analysis**, *T.L. Salter, I.S. Gilmore*, National Physical Laboratory, UK

Reliable and repeatable measurements are essential for the strong uptake of any analytical technique. Ambient surface mass spectrometry has demonstrated exciting and revolutionary measurement capability but for wider acceptance in industry they need a secure metrology foundation. Plasma sources are increasingly being used since the development of DART (direct analysis in real time) in 2005 and subsequent imaging methods such as PADI (plasma assisted desorption ionisation)² and LTP (low temperature plasma)³. Here, we commence establishing the essential metrology for PADI, which has already been shown to be successful at analysing pharmaceuticals² and personal care products⁴. A detailed study of the instrumental contributions to the spectral repeatability is conducted. Firstly, we identify and separate out the contributions to the repeatability (relative standard deviation) of the peak intensities. We show that the Thermo LTQ-Orbitrap mass spectrometer used in the study has a noise distribution approximately as expected for random noise. However, the standard deviation of the peak intensity is proportional to the peak intensity which is clearly not random but related to systematic effects in the source operation. Optimisation of the plasma source is essential for ensuring robustness and reliability. We show how the signal varies with geometry, helium flow rate and plasma power. Thermal imaging of the sample surface shows that the temperature rises approximately linearly with plasma power and at 19 W is 70°C. To reduce the effects of damage for surface sampling, we recommend keeping the surface temperature below 40 °C by operating at less than 15 W. General guidance is given for practical analysis. Importantly, PADI can analyse a wide variety of polymers. Analysis of polymers gives mass spectra with repeating series containing different fragments and adducts. Preliminary studies of sample surfaces after PADI analysis show that the chemical damage, quantified by XPS, is less than 10%. With the recommended operating parameters, the plasma erodes the polymer sample at a rate of 0.87 nm s⁻¹ (for PMMA). This shows the potential for polymer depth profiling.

References

1. RB Cody, JA Laramee, HD Durst, *Analytical Chemistry* **2005**, *77*, 2297.
2. LV Ratcliffe, FJM Rutten, DA Barrett, T Whitmore, D Seymour, C Greenwood, Y Aranda-Gonzalvo, S Robinson, M McCoustra, M. *Analytical Chemistry* **2007**, *79*, 6094.
3. JD Harper, NA Charipar, CC Mulligan, XR Zhang, RG Cooks, Z Ouyang, *Analytical Chemistry* **2008**, *80*, 9097.
4. TL Salter, FM Green, N Faruqi, IS Gilmore, *Analyst*, 2011, *136*, 3274.

5:00pm **AS-MoA10 Ion Beam Analysis of Surfaces and Thin Films**, *L.S. Wielunski, R.A. Bartynski*, Rutgers University

Rutherford Backscattering (RBS) of ~2MeV He ions is well known technique used in surface and thin film analysis. This technique is very sensitive to heavy elements (Au, Pt, Hf, In, Ru) present on surface or in thin film on lower mass substrate (Si, Ti, Cr, Fe, Ge), but have very limited sensitivity for low mass elements on heavy mass substrates. Numbers of examples will be shown for both cases.

Nuclear reaction analysis (NRA) is very good alternative for detection of low mass elements in a heavy elements substrates. This technique uses similar experimental set-up as RBS but is using a different ion beam and it detects different particle. Examples will be shown for Li detection on steel and in LiFePO₄ crystal.

Detection of Hydrogen is not possible using RBS in a typical RBS geometry, and NRA can detect Hydrogen, but it require special high energy ¹⁵N beam (7MeV), but He Forward Scattering (FS) or Elastic Recoil Detection (ERD) can be used for Hydrogen detection and profiling. Examples of ERD will be shown and discussed.

Each of these techniques has its own limitations and advantages. Depth resolution and sensitivity will be discussed in details.

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