Tuesday Morning, October 22, 2019

Applied Surface Science Division
Room A211 - Session AS+BI+RA-TuM

Quantitative Surface Analysis III/Other Surface Analysis Methods

Moderators: Karen Gaskell, University of Maryland, College Park, Alexander Shard, National Physical Laboratory

8:00am **AS+BI+RA-TuM-1 Oxygen Energy Filtering and Relative Sensitivity Factor Considerations for Making U and Pu Measurements by LG-SIMS***,* ***Todd Williamson,*** Los Alamos National Laboratory **INVITED**

During nuclear facility inspections, inspectors collect materials intended to show a history of the operations that have taken place within a facility. These materials can be particles obtained using cotton swipes, solid discarded or operationally related nuclear materials, or other items contaminated with nuclear materials. Analysis of these samples is an extremely powerful tool with which to determine facility operations and history. Uranium analysis by SIMS is a mature technique used by the IAEA and its Network of Analytical Laboratories for treaty verification. The analysis of mixed uranium-plutonium particles and solids is not as mature as a capability and has been identified by the IAEA as topic for increased R&D.

This presentation will cover two technical topics related to the analysis of mixed uranium-plutonium materials, relative sensitivity factors (RSF) and energy filtering to improve hydride correction. For a material that contains both U and Pu, while both elements will be sputtered and become ionized during SIMS analysis, they will do so with different efficiencies. This ionization difference tends to be sample-type (matrix) dependent. This phenomenon is known as the relative sensitivity factor (RSF). This presentation will discuss our investigations into determining accurate RSF values for U:Pu and U:Np inter-element measurements. With accurate RSF values, which should be universal for a given sample type, the measured inter-isotope ratios can be corrected to their true values. In a mixed actinide sample, there is ^{239}Pu present which will be unresolvable from ^{238}U^{1}H. This will prevent a conventional hydride correction on measurements, and there are not other clean masses in a mixed actinide sample where a hydride signal can be easily measured. Without a hydride correction the measurement of smaller concentration isotopes will have poor accuracy due to interference from large hydride interferences from major isotopes, and ^{239}Pu measurements will be highly inaccurate. The presentation will discuss our use of energy filtering mediated by an intentionally introduced partial pressure of oxygen in the sample analysis chamber, which changes ionization behavior.

8:40am **AS+BI+RA-TuM-3 Utilizing Large Geometry Secondary Ion Mass Spectrometry for Age-Dating of Individual Uranium Particles***,* ***Christopher Szakal****, D Simons, J Fassett,* National Institute of Standards and Technology (NIST)*; A Fahey,* Corning Inc.

Secondary ion mass spectrometry (SIMS) is routinely utilized by the International Atomic Energy Agency (IAEA) and its global partner laboratories for the isotopic analysis of individual uranium particles as part of nuclear safeguards efforts. One additional isotopic analysis that has repeatedly been requested by the IAEA involves the development of a capability to perform single particle age-dating, which would provide information about the last time that the nuclear material was purified or enriched. Previously reported efforts in multiple countries have reported the ability to use SIMS and/or large geometry (LG)-SIMS for this purpose, but with the caveat that the measurement can only be viable if the particles are large enough, old enough, and/or enriched enough. We present a new methodology, complete with propagated uncertainties, that advances the individual uranium particle age-dating measurement to include smaller, younger, and lower enriched nuclear material than previously envisioned. Additionally, we will provide insights into utility of this measurement advance within the aims of global nuclear safeguards objectives.

9:00am **AS+BI+RA-TuM-4 Peak Shape Analysis in TOF SIMS: Best Practices and Limiting Precision in Accounting for Detector Saturation***,* ***Lev Gelb****, A Walker,* University of Texas at Dallas

We compare strategies for analyzing high-mass resolution TOF SIMS data sets affected by detector saturation. The detectors used in many instruments undercount ions due to saturation effects. If two or more ions arrive within a very short interval (the "dead time") only the first ion is recorded. This changes both the total number of ions collected and their statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed.

We demonstrate an approach to correct for dead time errors in which a probability model for the detector behavior is developed and used in peak fitting of the "uncorrected" data. This approach has many advantages over previous methods which required an estimate of the variance, and it behaves better under conditions of poor data quality (low counts or high saturation.)

Using both synthetic and experimental data, we examine how saturation affects apparent peak shape, position and intensity, the effects of background on estimated peak position and shape, the dependence of peak-location precision on the total number of counts, how interference between satellite peaks is best accounted for, and the biases exhibited by different data analyses. Finally, we extend these methods to imaging data taken at high mass resolution and compare the results obtained with analyses performed at unit-mass resolution.

9:20am **AS+BI+RA-TuM-5 Electronic Structure and Band Gaps of Industrially Relevant Materials Investigated by Photoelectron Spectroscopy and REELS (Reflection Electron Energy Loss Spectroscopy)***,* ***Paul Mack****, T Nunney,* Thermo Fisher Scientific, UK*; H Meyer III,* Oak Ridge National Laboratory

Many inorganic and organic materials have been created and evaluated for use in a diverse range of applications, such as microelectronics, solar cells and TV displays. The electronic properties of these materials can be tuned by modifying their elemental or chemical state composition. Ideally, the analyst would like to characterize both the composition and electronic properties of a given material in a single experimental run, enabling correlation between electronic properties and composition to be established.

In this work thin films of industrially relevant materials, such as polydioctylfluorene, which is a polymer light emitting diode (PLED), and HfO_2 were analysed using a multi-modal approach. (Thermo Scientific ESCALAB Xi^{+} and Nexsa tools, configured with multiple surface analysis techniques, were used for the analysis.)

X-ray photoelectron spectroscopy was used to measure elemental and chemical state composition (together with some electronic information) and ultraviolet photoelectron spectroscopy was used to measure ionization potentials and the energies of the highest occupied molecular orbitals (HOMOs). Information about the band gap and lowest unoccupied levels (LUMOs), which cannot be determined with XPS or UPS, was measured with REELS. Energy level diagrams for the materials could then be constructed using the information from the complementary spectroscopic techniques.

Due to the low kinetic energy of photoelectrons generated by the ultraviolet source, UPS is a particularly surface sensitive spectroscopy. When analyzing samples stored in the atmosphere, the resulting data is typically dominated by surface adventitious carbon. This carbon needs to be removed, but with care not to damage the underlying material being studied. The use of an argon cluster ion beam for this kind of careful sample preparation was demonstrated in this work.

9:40am **AS+BI+RA-TuM-6 Practical References for Low Energy Ion Scattering by Ca and F***, S Průsa, T Šikola,* Brno University of Technology, Czech Republic*;* ***Hidde Brongersma,*** IONTOF Technologies GmbH, Germany/Eindhoven University of Technology, Eindhoven, The Netherlands, Germany

Low-Energy Ion Scattering (LEIS) is known for its extreme surface sensitivity. It is just as well suited for the analysis of amorphous, isolating, extremely rough surfaces, as for flat single crystals. Thus LEIS is applicable to any type of sample that can be taken into vacuum. Since matrix effects are generally absent, or relatively small in LEIS, a quantitative analysis is straightforward. However, the theory to quantitatively predict the atomic sensitivities of the elements falls short. Therefore, an accurate quantification relies on well-defined reference materials. Practical references should be chemically inert, easy to clean and inexpensive. The powder of calcium fluoride, CaF_2, has been suggested as practical reference for Ca and F [1], while the powder of calcium carbonate, $CaCO_3$, has also been suggested for Ca [2].

A complication is that the composition of the outer atomic layer of a material is generally fundamentally and radically different from that of the atoms below this surface. Thus it is unlikely that the F/Ca ratio in the outer surface of CaF_2 will be 2. In fact, precisely this difference makes the LEIS information unique and complementary to that of analytic techniques such as XPS, Auger and (TOF-) SIMS which probe several to many atoms deep. The difference is also highly relevant, since the outer atoms of a surface largely control important processes as adhesion, catalysis, electron emission and growth

It will be shown how the F/Ca atomic ratio, the Ca and F atomic densities, as well as the roughness factors for CaF_2 and $CaCO_3$ have been determined.

[1] T. Gholian Avval, C.V. Cushman, P. Brüner, T. Grehl, H.H. Brongersma, M.R. Linford,

Surf. Sci. Spectra, to be published (2019)

[2] R.M. Almeida, R. Hickey, H. Jain, C.G. Pantano, J. Non-Cryst. Solids 385 (2014) 124

11:00am **AS+BI+RA-TuM-10 Extreme-Ultraviolet-Assisted Atom Probe Tomography***, **Norman Sanford**, L Miaja Avila,* National Institute of Standards and Technology (NIST)*; P Blanchard,* National Institute of Sandards and Technology (NIST)*; D Diercks, B Gorman,* Colorado School of Mines*; A Chiaramonti,* National Institute of Sandards and Technology (NIST)

Laser-assisted atom probe tomography (L-APT) often returns compositional biases that deviate from a specimen's true chemical makeup [1]. In our L-APT studies of GaN, which utilize a 355 nm laser, we find stoichiometric composition (50% Ga, 50% N) only when the pulse fluence is roughly 2E-7 J/cm^2. Higher fluences return nonphysical, Ga-rich compositions; lower fluences give nonphysical N-rich compositions. L-APT of other materials, including SiO2, exhibit similar biases. L-APT is a thermally-activated mechanism. The specimen is subjected to a strong electric field that is held just below the threshold for field evaporation of ions; evaporation is triggered by thermal transients imparted by the incident laser pulses. Motivated by the need to improve the quantitative accuracy of atom probe tomography, we explored an alternative, photoionization-triggered pathway for field evaporation by replacing the conventional laser on an L-APT tool with a pulsed, extreme-ultraviolet (EUV) source—thus realizing the XAPT [2,3]. The tabletop EUV source is an ultrafast, amplified Ti:sapphire laser driving an Ar-filled capillary waveguide. Pulsed, coherent EUV is produced via high-harmonic generation [4]. The respective characteristics of EUV pulse width, repetition rate, wavelength (energy), and fluence, incident on a specimen tip are: 10 fs, 10 kHz, 30 nm (42 eV), and 2.5E-8 J/cm^2. Comparative XAPT and L-APT analyses were performed on specimens of GaN and SiO2 (amorphous fused silica). For SiO2, L-APT returned an off-stoichiometry composition of 41% Si and 59% O; XAPT yielded 33% Si and 66% O (stoichiometry). For GaN, XAPT found 49% Ga and 51% N; L-APT yielded laser-pulse-fluence-dependent composition and returned 68% Ga and 32% N for a fluence of roughly 2E-6 J/cm^2; L-APT conditions giving stoichiometric GaN appear above. The uncertainty of these measurements is 1—3 at. %. All specimens were examined at 50 K. XAPT-derived mass spectra show reduced occurrences of molecular ions and reduced "thermal tails" (persistent field emission following the laser pulse). Ongoing work for presentation at the meeting includes comparative studies of InGaN, Mg:GaN, and AlGaN. In all cases examined thus far, the XAPT approach offers measurable improvements over L-APT.

1. D. J. Larson, et al, Local Electrode Atom Probe Tomography (Springer, New York, 2013)

2. A. N. Chiarmonti, et al, MRS Advances (in press, 2019)

3. L. Miaja Avila, et al, Frontiers in Optic (FiO), Optical Society of America, Wash. DC, p. FTu5C. 3 (2018)

4. L. Miaja Avila, et al, Phys. Rev. Lett. 97, 113604 (2006)

11:20am **AS+BI+RA-TuM-11 A Multi-Technique Approach for Complete Thin Film Characterisation***, **Sarah Coultas**, J Counsell, N Gerrard, C Blomfield,* Kratos Analytical Limited, UK*; C Moffitt,* Kratos Analytical Limited*; T Conard,* IMEC, Belgium

The application of thin film technology is of commercial importance across a range of industries and is commonly used to influence both the physical and chemical properties of bulk materials. Ranging in thickness from tens of Angstroms to microns, their applications are used across a broad range of disciplines including the semiconductor, biomaterial and energy harvesting industries. Herein, we provide a multi-technique investigation of layered thin film and ultra-thin film coatings using a model system for gate oxide structures. The combination of techniques allows one to build a complete picture of the chemistry of these materials and how subtle differences in chemistry and stoichiometry can influence the properties of a substrate to enhance its application specificity. X-ray Photoelectron Spectroscopy (XPS) was used to characterize the surface chemistry of these layered thin film materials. Using monochromated Al-Kα (1486.6 eV) X-rays, it was possible to gain quantitative chemical information from the uppermost 10 nm of the surface. In this study, we illustrate how angle-resolved XPS (ARXPS) can be used as a more surface sensitive approach to probe only the topmost 1-3 nm, and how one can utilize maximum entropy modelling (MEMS) to recreate a concentration depth profile from the resulting data.

In contrast to increased surface sensitivity, high energy excitation sources can be used to extend the analysis depth of a material to >15 nm. Here, we describe the use of a monochromated Ag-Lα (2984.2 eV) X-rays to delve deeper into the bulk structure. In combination with ARXPS, the greater excitation energy and increased analysis depth allows one to measure elemental core levels which are not accessible using the conventional Al-Kα source. In light of this, one can build a more detailed description of the structure of these thin film materials and their use in relevant applications.

11:40am **AS+BI+RA-TuM-12 Polymeric Barrier Coatings for Silicone Elastomer against Diffusion of Isocyanate in Vacuum Casting Processes***, **Martin Wortmann**, R Petkau,* Bielefeld University of Applied Sciences, Germany*; N Frese,* Bielefeld University, Germany*; E Moritzer,* Paderborn University, Germany*; A Gölzhäuser,* Bielefeld University, Germany*; B Hüsgen,* Bielefeld University of Applied Sciences, Germany

The vacuum casting process is used industrially to replicate prototypes of polyurethane (PUR). Due to the diffusion of 4,4′-methylene diphenyl diisocyanate (MDI), a PUR resin component, the silicone casting molds used in this process show a progressive degradation, which leads to the failure of the casting molds after a few casting cycles [1]. In this contribution, we present ways to protect the surface of the silicone elastomer by various thermoplastic polymer coatings. The polymers investigated were dissolved in different volatile solvents and coated on pretreated silicone surfaces. For this purpose, the compatibility of those polymer solutions with polydimethylsiloxane (PDMS) was investigated and their diffusion coefficients with respect to MDI were measured. Polymer coatings that have exhibited a high diffusion barrier have been used to drastically increase the output of the casting molds.

[1] M. Wortmann et al., *Polymer Plast Tech Eng* 57, 1524 (2018).

12:00pm **AS+BI+RA-TuM-13 pARXPS Study of GeSbTe Surface Oxidation***, **Ludovic Goffart**,* ST Microelectronics/LTM/CEA-LETI, France*; C Vallée,* Laboratoire des Technologies de la Microélectronique (LTM), France*; B Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; J Reynard, D Benoit,* ST Microelectronics, France*; G Navarro,* CEA-LETI, France

This work is focusing on the oxidation of the well-known GST material ($Ge_2Sb_2Te_5$, GST225) widely used in storage optics like CD, DVD and Blu-ray. This time, we use the GST for its electrical properties to create a non-volatile memory. The GST we use in this work is modified from the GST225 chemical composition to comply with the specifications needed in automotive applications, the most important being a good stability and cycling at high temperature environment.

This non stoichiometric GST composition leads to instability in its structure, therefore more aging and oxidation which conflict with the objectives of this new PCM cell. Added to this is some atomic segregation during crystallographic relaxation, which leads to low cycling durability of the cell and lower crystallization temperatures. To counter these effects, the GST material is doped but this makes more complex the chemical characterization of the material.

To understand and overcome these problems, different GST materials (from 225 to Ge rich) have been characterized using the pARXPS technique which is an angular resolved XPS. With this technique a very complete chemical characterization of the surface of these samples have been performed to gather useful information of atomic segregations and surface oxidation, by acquiring 8 simultaneous angles at the same time for different element windows. This is only possible by developing a complex fitting model for the large amount of spectra obtained. This model has to deal with the complex feature of the spectra obtained since some peaks were overlapping. Physical constraints are then necessary to obtain a realistic fit of the spectra. Once the model optimized, the aging of the samples have been studied by monitoring the evolution of specific XPS shapes with time. As a result, the oxidation kinetic and the thickness of the oxidized surfaces are quantified and finally a depth profile reconstruction of the different chemical bonds is performed. In addition to pARXPS, TEM-EDX analysis were performed to confirm the fitting model developed and profile depth reconstruction obtained with pARXPS technique.

Author Index

Bold page numbers indicate presenter