

Applied Surface Science Division Room A211 - Session AS-ThM

Advances in Depth Profiling, Imaging and Time-resolved Analysis

Moderator: Carl A. Ventrice, Jr., SUNY Polytechnic Institute

8:00am **AS-ThM1 What Really Lies Beneath the AVS Surface? Depth Profiling Can Help Provide the Answer, Fred Stevie, C. Zhou, R. Garcia, North Carolina State University** **INVITED**

Scratch the surface of the AVS and you will find a lot more than semiconductors. AVS Divisions range from electronic materials to thin films to vacuum technology to biomaterials.

Depth profiles obtained using AES, XPS, or SIMS have typically been used to provide in-depth elemental analysis. SIMS excels in depth resolution and detection limit. Rotation of the sample during analysis (Zalar rotation) can maintain good depth resolution for materials that do not sputter evenly. Application of electron beams aids the study of insulators. Standards can be created to quantify the elemental components. [1]

Analysis in depth of biomaterials has shown tremendous strides as the sources used to remove material have evolved. Initial studies of depth profiles with argon, then molecular beams such as SF₅⁺, larger still with C₆₀⁺, and now cluster beams with argon produced ever higher secondary ion yields and made possible in-depth analysis without loss of chemical state. Continued development has resulted in three-dimensional organic analysis. [2] Some success has been achieved for quantification of organic additives, especially when the additive contains an element not present in the matrix. [3-4]

A significant limitation is the achievable depth. Profiles are typically less than 100 μm. However, some technologies need depth information on a millimeter scale. Sample preparation methods, such as etching, beveling, cross sections, and back side analysis, can be employed. Cryogenic microtome can be used to obtain a cross section of organic layers subsequently analyzed with ToF-SIMS. [5] EDS can provide in depth information on samples where material has been removed at a series of depths using FIB. [6] The emergence of plasma FIB (PFIB) instruments with microamp currents makes possible deeper profiles and exposure of larger areas for analysis by other techniques. The xenon plasma FIB can remove material as much as 50 times faster than a conventional gallium FIB. [7,8]

[1] Secondary Ion Mass Spectrometry, F. A. Stevie, Momentum Press (2016)

[2] J. Bailey, R. Havelund, A. G. Shard, I. S. Gilmore, M. R. Alexander, J. S. Sharp, D. J. Scurr, ACS Appl. Mater. Interfaces 7, 2654 (2015)

[3] Chaunzhen Zhou, Fred A. Stevie, Stephen C. Smith, J. Vac. Sci. Technol. B36, 03F115 (2018)

[4] S. C. Smith, C. Zhou, F. A. Stevie, R. Garcia PLOS ONE 13, e0209119 (2018)

[5] C. Zhou, D. Sun, R. Garcia, F. Stevie, Anal. Methods 10, 2444 (2018)

[6] R. Garcia, F. A. Stevie, L. Giannuzzi, Microscopy and Microanalysis Proceedings (2019)

[7] Noel S. Smith, John A. Notte, and Adam V. Steele, MRS Bulletin 39, 330 (2014)

[8] www.tescan.com/en-us/technology/fib-sem/

8:40am **AS-ThM3 TOF-SIMS Tandem MS Imaging of (Sub-)Monolayer Coatings for Device Processing, David M. Carr, G.L. Fisher, Physical Electronics**

One common objective in research, failure analysis and reverse engineering is to ascertain the 2D/3D composition and structure of molecules in devices as a result of various processing steps. Often there is insufficient background information and a lack of reference spectra to properly interpret the analytical observations. Two device processing case studies will be presented highlighting the benefits of adding MS/MS imaging to conventional TOF-SIMS experiments. The data was acquired on a PHI nanoTOF II designed for simultaneous TOF-SIMS (MS¹) imaging and tandem MS (MS²) imaging [1-4].

In the first case study, a carbon residue was observed by Auger electron spectroscopy (AES) imaging on e⁻ beam lithography-patterned and etched device structures. TOF-SIMS tandem MS imaging was applied to characterize the composition and structure of the sub-monolayer residues. In the second case study, functionalized molecules containing bipyridine

and triphenylphosphine ligands were patterned by a photolithography method and loaded with metals including Au, Pd and Pt [5]. TOF-SIMS tandem MS imaging was employed to confirm the presence and elucidate the structure of metal-organic ligands.

References

[1] G.L. Fisher, *et al*, *Anal. Chem.* **88** (2016) 6433-6440.

[2] G.L. Fisher, *et al*, *Microscop. Microanal.* **23** (2017) 843-848.

[3] C.E. Chini, *et al*, *Biointerphases* **13** (2018) 03B409.

[4] T. Fu, *et al*, *Nature Sci. Rep.* (2018) accepted 06 December 2018.

[5] R. Müller and A. Welle at Karlsruhe Institute of Technology (KIT) and C. Barner-Kowollik at Queensland University of Technology (QUB) are acknowledged for providing the samples for analysis.

9:00am **AS-ThM4 TOF-SIMS at the Edge, Alan Spool, D. Bilich, Western Digital Corporation**

TOF-SIMS instruments are designed to extract secondary ions in the direction normal to the surface by creating a potential difference between the sample and the extraction device. The optimum geometry for getting the highest transmission is for the sample to consist of a functionally infinite flat plane. When sample topography deviates from this ideal significantly, secondary ion transmission is reduced. The effect on the yield of each secondary ion is a function of the ion mass, but also the initial ion emission angular and momentum magnitude distributions. The yields of the lightest atomic ions are least affected by topography, and the yields of heavier molecular fragments and ions most significantly affected.

To quantitatively explore these effects, two samples presenting topographic challenges were used in this study.

1. The edge of a magnetic recording disk is tightly controlled and therefore reproducible. The disk is extremely flat. The surface produces homogeneous signals for atomic species and molecular fragments of the disk lubricant and adsorbed hydrocarbons and other organic species where ion yield is not affected by topography. There is a slight bevel at the edge, much smaller in size than the edge effect on secondary ion collection. The sample height drop off past the edge in this experiment was effectively infinite.

2. A Si coupon was etched to produce a deep enough crater that ion yields from the crater bottom were affected by the topography. A lighter etch was performed over a wider area sufficient to reach dynamic equilibrium (and thus produce a surface damaged identically to that at the crater bottom). The sample was then exposed to air and allowed to oxidize and be contaminated by adventitious organics before analysis. This sample represents the condition where at a distance from the sample, the surface is essentially flat, but near to the surface the ion extraction will see non-normal fields that affect secondary ion trajectories.

With these samples, it was possible to look at the effect of the topography on the yields of a variety of secondary ions, and at a variety of instrumental conditions, both in the IonTof TOF-SIMS 5 and in the Physical Electronics NanoTof II. The analysis results of the two types of topographic challenges are shown to be differently affected by instrumental conditions. No one condition gives the ideal remediation for all topographic challenges.

The work with the edged sample promises to provide a simple test for differences in the initial angular and momentum magnitude distributions. Such distributions may provide added clues to secondary ion formation mechanisms.

9:20am **AS-ThM5 Variation of SIMS Secondary Ion Yield of Si and Mg Dopants in GaN Grown by MOCVD, M. K. Indika Senevirathna, Clark Atlanta University; A.Y. Kozhanov, M. Vernon, G.B. Cross, Georgia State University; G. Cooke, Hiden Analytical Ltd, UK; M.D. Williams, Clark Atlanta University**

We present a study of the secondary ion yield of silicon and magnesium dopant species as a function of the primary ion beam energy in n-doped and p-doped gallium nitride, respectively. The epilayers were grown by metal organic chemical vapor deposition and depth profiled using a Hiden quadrupole secondary ion mass spectrometer. To our knowledge, this is the first such study for this matrix material system. The yields for oxygen and cesium primary beams were determined by varying the beam acceleration voltage of the primary ion beam from 0.5 kV to 5 kV at a fixed beam current. The results determine the primary beam energies for optimal species sensitivity.

Thursday Morning, October 24, 2019

11:00am **AS-ThM10 Probing the Surface Structure of Au-Pt Core-Shell Nanoparticles**, C. Engelbrekt, Ich Tran, M. Law, University of California, Irvine

Au-Pt core-shell structures (Au@Pt) of atomically-thin platinum shells on gold nanoparticle (NP) cores have been developed through a mild aqueous one-pot synthesis protocol. The loading and homogeneous deposition of Pt on the starch-capped Au NPs can be finely tuned by simply adjusting concentration and the reduction rate of the Pt precursor from 0 to 30 wt% Pt. These Au@Pt NPs have shown impressive catalytic performance for a range of energy relevant reactions due to inherently improved activity of the Pt shells through synergetic interaction with the Au cores.^{1,2} Details of the core-shell interface, in particular the atomic-scale and electronic structure of the metal catalyst surface, are crucially important to understand and optimize catalytic properties of the Au@Pt NPs. Characterizing the surface of small nanoparticles with this sensitivity is challenging and most convincingly done by elemental mapping with TEM. However, for Au and Pt, which are very close in atomic mass, lattice parameters and X-ray emission lines, this approach is not sufficient. Here, we have used an array of surface sensitive spectroscopic techniques to characterize the structure of the bimetallic NP surface – specifically, detailed analysis of XPS core-level and valence band photoemission spectra, in combination with elemental analysis using ion scattering spectroscopy (ISS). ISS provides the elemental composition of the surface-exposed atoms, which is very difficult to probe with other techniques. We show that the interface structure involves surface alloying, and sub-surface Pt localization, rather than a simple formation of the Pt overlayer in Au@Pt NPs. Furthermore, time-dependent ISS can potentially be used as a gentle (mild) depth-profiling characterization technique for this kind of core-shell structure and a comparison with a depth-profiling characterization using argon cluster modes will be discussed.

(1) Engelbrekt, C.; Šešelj, N.; Poreddy, R.; Riisager, A.; Ulstrup, J.; Zhang, J. "Atomically thin Pt shells on Au nanoparticle cores: facile synthesis and efficient synergetic catalysis", *J. Mater. Chem. A* **2016**, 4 (9), 3278–3286.

(2) Seselj, N.; Engelbrekt, C.; Ding, Y.; Hjuler, H. A. H. A.; Ulstrup, J.; Zhang, J. "Tailored Electron Transfer Pathways in Au_{core}/Pt_{shell}-Graphene Nanocatalysts for Fuel Cells", *Adv. Energy Mater.* **2018**, 1702609, 1702609.

11:20am **AS-ThM11 Correlating Multiple Data Streams for Valence State Identification in Transition Metal Oxide during XPS Depth Profiling**, Zhenzhong Yang, C. Wang, M.H. Engelhard, Z.H. Zhu, Y. Du, Pacific Northwest National Laboratory

Transition metal oxides (TMO) of perovskite (ABO₃) structures exhibit a broad range of structural, compositional, and functional properties, which can be further tuned or even drastically transformed by means of judicious defect engineering. TMOs have a unique capability to incorporate large amount of oxygen defects owing to the multivalence nature of the transition metal cations, which can be directly probed by XPS. XPS is a surface sensitive technique. In order to study the deeper layers, depth profiling by Ar sputtering is often adopted. However, the sputtering process may change the valence state of the transition metal cations, and thus the data analysis affected by the data acquisition condition can be inaccurate or erroneous.

In this talk, using perovskite SrCrO₃ and its reduced structure, SrCrO_{2.8}, as model (SCO) materials, I will show how the XPS depth profiling data can reveal the valence state change and redox chemistry occurring in the deeper layers of the SCO thin films. In our experiments, the XPS Cr2p spectra suggested that a tensile strain applied by the substrate could stabilize the reduced SrCrO_{2.8} structure near the interface (~10 nm) region. To examine whether the conclusion is correct, we compared SCO samples with different strain states and processing history. By correlating x-ray diffraction (XRD), transmission electron microscopy (TEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS) data and density functional theory calculations, we achieved quantitative agreement and concluded that the Cr 2p spectra were not affected by the Ar beam during the XPS depth profiling process.

11:40am **AS-ThM12 Using Atom Probe Tomography for Three-dimensional Visualization of Sb Segregation in InAs/InAsSb Superlattices**, Nicole Kotulak, J.A. Nalde, M.E. Twigg, K.E. Knipling, U.S. Naval Research Laboratory; D. Lubyshev, J.M. Fastenau, A.W.K. Liu, IQE Inc.; E. Aifer, U.S. Naval Research Laboratory

Developing materials for mid-wavelength infrared (MWIR) photodetectors has been ongoing, with recent focus on structures that can operate at higher temperatures and across a larger portion of the MWIR range. In recent years, InAs/InAsSb strained layer superlattices (SLS) have been

extensively studied and shown to achieve these performance parameters, out-performing the incumbent technologies [1]. Over the course of InAs/InAsSb SL development, as well as in similar Sb-containing device structures, it has been observed that Sb does not remain strictly within the intended layer [2-4].

The segregation of non-common-atoms at a growth interface and into the following layer leads to non-abrupt and asymmetric interfaces, which can cause changes to the optoelectronic properties of the SLS, including fundamental parameters such as band gap and effective mass [2,5,6]. For devices that rely on the precise engineering of the optoelectronic properties of the SLS in order to accomplish performance metrics, non-abrupt interfaces can, ultimately, detrimentally affect device performance, impacting suitability for specific tasks and environments [7]. Understanding the layer compositions at a near atomic-scale can enable these non-idealities to be included in bandstructure simulations to enable device design and optimization [8,9].

In this work, we use atom probe tomography (APT) to harvest 3D compositional data in an MWIR nBn T2SL photodetector consisting of 734 periods of alternating InAs and InAsSb, of which 31 total periods were analyzed. The resulting analysis shows a non-negligible concentration of Sb in the InAs layers, as well as a below-target Sb concentration in the InAsSb layers. While the background concentration of Sb stays consistent as growth of the T2SL progresses, there is an observable increase in the peak Sb concentration from the earliest-grown periods analyzed to the last-grown. These profiles demonstrate corroboration of a non-binary Sb profile observed using complementary techniques, and serve to assist in improving models of Sb-containing SLS for the development of high performance photodetectors.

[1] D. Z. Ting, et al., *IEEE Photonics Journal* 10, 6804106 (2018).

[2] J. Steinshnider, et al., *Phys Rev Lett* 85, 2953–2956 (2000).

[3] H. Haugan, et al., *J Cryst Growth* 436, 134–137 (2016).

[4] K. Kanedy, et al., *Appl. Phys. Lett.* 112, 042105 (2018).

[5] M. W. Wang, et al., *Appl. Phys. Lett.* 66, 2981 (1995).

[6] S. B. Rejeb, et al., *J Phys D: Appl. Phys* 43, 325102 (2010).

[7] K. Shiralagi, et al., *J of Elec Materi* 26, 1417–1421 (1997).

[8] X. Lü, et al., *Appl. Phys. Lett.* 104, 232106 (2014).

[9] F. Szmulowicz, et al. *Phys. Rev. B*, 69, 155321 (2004).

12:00pm **AS-ThM13 Multi-technique Surface Analysis of Graphenes**, Kateryna Artyushkova, Physical Electronics and University of New Mexico; B.W. Schmidt, J.E. Mann, A.A. Ellsworth, J.G. Newman, Physical Electronics
Several techniques currently being used to determine the thickness of graphene films include optical contrast, Raman and scanning probe microscopy. These methods provide accurate information on thickness but limited information on other important parameters as chemical purity, homogeneity of coverage and defect density. Surface analytical techniques, such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), have the potential to fill this gap.

Surface analysis of graphene poses multiple challenges. The thickness of single-layered graphene is on the order of 0.4 nm, while even the most surface-sensitive spectroscopic techniques have on the order of 1-5 nm sampling depth. The surface carbon contamination due to adventitious carbon adds another level of complexity in trying to understand graphene chemistry and homogeneity accurately.

In this report, we will present an analysis of commercially available graphene samples prepared on several types of substrates, such as SiO₂ and PET. The chemical structure and thickness of graphene samples were studied by a combination of XPS and TOF-SIMS depth profiling and angle-resolved XPS. The challenges and successes of this multi-technique analysis of graphene will be discussed.

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