Applied Surface Science
Room 101B - Session AS+AC-TuM

Practical Surface Analysis II: Microanalysis, Nanoanalysis, Atom Probe, and All Things 'Small'

Moderators: Arun Devaraj, Pacific Northwest National Laboratory, Daniel Gaspar, Pacific Northwest National Laboratory

8:00am **AS+AC-TuM1 Progress Toward Atomic-Scale Tomography*,* *Thomas Kelly,*** CAMECA Instruments Inc. **INVITED**

There have been efforts of late to produce three-dimensional images at the atomic scale where every atom is accounted for and the position information is quite precise. All atoms in a two-dimensional thin film of boron nitride were imaged and identified by Krivanek et al. [1]. Scott et al. were able to produce three-dimensional images using electron tomography that show every atom in a gold nanoparticle containing over 7000 gold atoms [2]. Using atom probe tomography (APT), Moody et al. have shown three-dimensional images of several million atoms in an aluminum alloy where each atom is positioned correctly in a face-centered cubic lattice and 60% of the atoms are detected [3]. These are all impressive and important developments. They suggest what atomic-scale microscopy might ultimately achieve: recording with high precision the position and identity of every atom in a technologically relevant structure. This capability can fairly be termed atomic-scale tomography (AST).

If AST is to be achieved, it appears that APT and electron microscopy should be used synergistically to capture the strengths of one technique to overcome the limitations of the other. This question has been explored in detail [4] and the conclusion is that there are some ways that AST can be achieved. The instrumental developments needed to reach AST with APT and (S)TEM as a basis include: trajectory corrections for precise atom placement and detecting 100% of the atoms without ambiguity in identity. The former may be achieved by imaging the specimen apex to enable precise ion trajectory simulation toward the detector. An electron column integrated into an atom probe can, in principle, record the specimen apex shape throughout an entire atom probe experiment. Detectors for recording all atoms might be based on superconducting materials [5]. If these detectors also record an ion's kinetic energy, then most time of flight-based ambiguities in peak identification can be eliminated [6].

Once these instruments are combined, the full analytical capabilities of each can be used synergistically. This presentation will outline approaches that should be pursued to reach this end and review the current plans to build an atomic-scale tomograph.

[1] O. L. Krivanek, et al., *Nat. Lett*, vol. 464, p. 571, 2010.

[2] M. C. Scott et al., *Nature*, vol. 483, pp. 444–447, 2012.

[3] M. P. Moody et al., *Micros Microanal*, vol. 17, pp. 722–723, 2011.

[4] T. F. Kelly et al., *Microsc. Microanal.*, vol. 19, pp. 652–664, 2013.

[5] R. F. McDermott, J. R. Suttle, and T. F. Kelly, "Unpublished research," 2015.

[6] T. F. Kelly, *Micros Microanal*, vol. 17, pp. 1–14, 2011.

9:20am **AS+AC-TuM5 Atom Probe Tomography and Electron Microscopy Investigation of Composition and Structure of Functionalized Carbon*,* *Chilan Ngo*,** *D.R. Diercks, M.B. Strand, S. Pylypenko,* Colorado School of Mines

Carbon is one of the most studied materials due to its broad range of properties, versatility, and low cost. Functionalization or doping of carbon with heteroatoms is an effective way to tailor the properties of carbon and further modify the material for various applications. While significant efforts have been placed on understanding the composition, structure and properties of doped carbon supports, there is a lack of understanding regarding the 3-D distribution of dopant within high surface area materials. In this work, we expand the understanding of nitrogen-functionalized carbon materials by focusing on analysis of nitrogen distribution through atom probe tomography (APT), transmission electron microscopy (TEM), and complementary characterization techniques. Specifically, APT analysis has been applied to provide unique, high-resolution insight into the composition/structure of high-surface area carbon – demonstrating feasibility of the technique towards such materials. Nitrogen-doped carbon nanospheres were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different nitrogen concentration and varied relative distribution of nitrogen functionalities. Sample preparation was performed via focused-ion beam (FIB), in order to isolate C spheres into a workable APT tip. The work presented herein provides a foundation not only for further understanding of N-doped carbon materials and N-containing nonprecious catalysts (NPMCs) employed in a variety of important catalytic reactions, but also to prepare model high-surface area materials, compatible for study via *in situ* liquid and electrochemistry TEM techniques.

9:40am **AS+AC-TuM6 Advanced XPS Imaging and Spectromicroscopy: a Review of Current Capabilities*,* *Olivier Renault,*** CEA-University Grenoble Alps, France

At the practical level, XPS imaging is still poorly used today. This is due to on the one hand to instrumental issues with for instance the difficulty to produce nice secondary electron images to help quick navigation at the surface; on the other hand, lower counting statistics of core-level images necessitate high transmission imaging spectrometer and in some cases post-processing of image data sets using, e.g, PCA. XPS imaging and spectromicroscopy is nevertheless complementary to ToF-SIMS and Auger as it provides quantification and chemical speciation, besides accessing the mesoscopic scale. It should therefore deserve a much broader use to better understand laterally heterogeneous systems. On some instruments, electronic band structure imaging, equivalent to ARUPS microscopy, is becoming possible in routine use, widening significantly the capabilities of photoelectron microscopy with laboratory sources for important applications, e.g., novel 2D materials. In this contribution, we will review through various examples from graphene doping [1] to oxide-based resistive memories and single layer MoS2, the current capabilities of XPS imaging and spectromicroscopy as implemented with a PEEM-based commercial instrument enabling core-level images with sub-µm scale lateral resolution. The benefits of band structure imaging for 2D semiconducting materials will be addressed [2]. Finally, perspectives regarding photoelectron microscopy with hard x-rays will be drawn [3].

This work was performed on the Nanocharacterization platform of CEA-MINATEC.

[1] H. Kim, O. Renault et al., Appl. Phys. Lett. 105, 011605 (2014).

[2] M. Frégnaux, O. Renault et al., Surf. Interface Anal. 2016 (in press).

[3] M. Patt et al., Rev. Sci. Instrum. 85 (11) (2014) ; C. Zborowski, O. Renault et al., Appl. Phys. Lett. 2016 (accepted).

11:00am **AS+AC-TuM10 Challenges and Solutions for Confined Volume Characterization in Semiconductor Systems*,* *Wilfried Vandervorst,*** IMEC & KULeuven, Belgium **INVITED**

Pushing the limits in IC-technology towards the nanometer scale, novel materials and in particular interfacial interactions in 3D-devcies play a crucial role leading to a demand for concepts suited to probe very small volumes and enable atomic scale observations.

Atom probe tomography (APT) can provide 3D-composition analysis within very small volumes (a few nm^3) with high sensitivity and accuracy. Nevertheless the presence of many materials with different evaporation fields and inhomogeneous laser-tip interactions creates tip distortions and trajectory aberrations inducing severe artefacts in reconstructed profile. Limits in mass resolving power, the presence of multiple charge states, cluster emission and variable detection efficiencies and strong laser power effects do hamper accurate and precise quantification and/or deviation from the correct composition.

Complementary to the resolving power of APT, is the application of scanning probes which enable to grasp the electrical activity of dopants or identify conduction paths within such volumes. As SPM is inherently a 2D-method, concepts for expanding into the depth dimension are explored (cfr Scalpel SPM, ion beam sputtering icw SPM) with applications in logic device engineering, failure analysis and memory cell development.

As APT and SPM suffer from a poor productivity and a lack of statistical averaging over large areas as required in more production oriented metrology. A solution can be found through ensemble measurements whereby spatial resolution is provided by the device under investigation and not by the probing beam. We will illustrate this concept through applications of "self focusing SIMS" which allows to determine the composition from trenches as small as 20 nm without having an ion beam with nm-resolution. Moreover within the area of selective area deposition SF-Sims may provide a unique analysis capability sampling defectivity of self-assembled monolayers and limited selectivity.

Similarly crystallinity in narrow trenches (< 50 nm) can be obtained through channeling RBS whereby again we use a large beam but nevertheless probe the information from an array of very fine features. In all these cases, the averaging over a large array provides excellent statistics and in some cases dramatically improved productivity through the enhanced signal versus the case of a very focused probe beam. The latter is ultimately exemplified in Raman experiments on narrow SiGe-trenches where we demonstrate that very narrow features (20 nm) provide a significantly enhanced (50-100x) compared to its blanket counterpart enabling to probe composition and structural properties from a small volume.

11:40am **AS+AC-TuM12 Characterization of Protein G B1 Immobilized Gold Nanoparticles using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**

Y.-C. Wang, ***David Castner****,* University of Washington

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto nanoparticle surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have significant impact on the clinical outcomes of these carriers by impacting its biostability and efficacy.

In this work, Protein G B1, a protein that will selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs using either carbonyldiimidazole (CDI) chemistry or through a maleimide-cysteine bond. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the protein G B1 immobilization. Unlike conventional NP characterization techniques such as dynamic light scattering (DLS) and UV/Vis, XPS and ToF-SIMS can provide additional information on the surface elemental composition, protein coverage and orientation.

XPS analysis confirmed the AuNP functionalization with both the maleimide and OEG-SAMs. After incubation with protein, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of both SAMs. Loosely bound protein on the AuNPs was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization, CDI activation, and protein immobilization by identifying signature secondary ions from each step of the protein immobilization process. Further, by utilizing high surface sensitivity and small sampling depth (2nm) of ToF-SIMS, the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite end of the protein. As expected, the non-site specific CDI chemistry did not lead to a well-defined orientation on the AuNPs. In contrast, we were able to control the orientation of the immobilized protein using maleimide functionalized AuNPs and cysteine mutants of Protein G B1. The systematic characterization of this study provided detailed information about protein-nanoparticle interactions that advances our understanding of the complex protein-NP interface.

12:00pm **AS+AC-TuM13 What's New in Wetting? Inorganic Nanotubes at a Water Interface - A Molecular View**

Sidney Cohen*, O. Goldbart, I. Kaplan-Ashiri,* Weizmann Institute of Science, Israel*; P. Glazyrina,* Ural Federal University, Russia*; H.D. Wagner,* Weizmann Institute of Science, Israel*; A. Enyashin,* Ub Ras, Russia*; R. Tenne,* Weizmann Institute of Science, Israel

Wetting of solid surfaces is a complex and subtle phenomenon which has been studied carefully over the past 200 years. A good understanding of wetting can explain many key physical interactions at interfaces, notable examples being in lubrication, composite materials, and capillarity. Wetting phenomena continue to intrigue the scientific community due to the complexity of this seemingly simple process. In recent years, specific nano-scale aspects of wetting have been revealed, highlighting the importance of a molecular-level understanding of wetting. The study of nanotube wetting encompasses the old/new, as well as nanoscale aspect of these endeavors. Proven importance of nanotubes as fillers in ultra-strength nanocomposites, where the interfacial interactions in the nanocomposite are controlled by wetting, lends a technological push to the field. Inorganic nanotubes (INT) formed from tungsten and molybdenum disulfides disperse very well in a variety of polymers, enabling preparation of nanocomposites with enhanced mechanical properties, thermal stability and improved rheological behavior. Nonetheless, the nature of the interaction between a nanotube and polymer liquid has received little attention and is poorly understood.Here we present a combined experimental and theoretical study on the microscopic interaction of WS_2 nanotubes (INT-WS_2) with water. The unique experimental approach is based on manipulation and pull-out of individual nanotubes from water films while monitoring the forces generated with a cantilever in an atomic force microscope (AFM). This method draws on concepts of the classic Wilhemy Balance Technique, while exploiting the exquisite force control of the AFM. The AFM experiments were contrasted with parallel experiments in an environmental scanning electron microscope (ESEM). Detailed theoretical calculations based on density functional theory (DFT) predicted well the interaction energy for large, closed cap nanotubes, but vastly underestimated the interaction energy with small, open-ended nanotubes. For those small diameter tubes, force-field molecular dynamics (MD) simulations together with a thermodynamic analysis qualitatively explain the observed behavior, strongly implicating a dominant capillary effect. Visualization of the pullout in the ESEM together with AFM force traces allow precise modelling of the meniscus formation during pullout, reflecting the energetics of the interface at, and inside the nanotube wall.**Acknowledgment:** Supported by the Israel National Nano-Initiative, the Israel Science Foundation, H. Perlman Foundation. and Act 211 Government of the Russian Federation, contract № 02.A03.21.0006.

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