Applied Surface Science Division
Room 320 - Session AS+EM+SE-TuA

Surface Analysis Using Complementary Techniques

Moderators: Samantha Rosenberg, Sandia National Laboratory, **Carl A. Ventrice, Jr.**, SUNY Polytechnic Institute

2:20pm **AS+EM+SE-TuA-1 Origins of the Emergent Phenomena at Oxide Interfaces Studied with Complementary X-Ray Spectroscopic and Scattering Techniques***, **Alexander Gray**,* Temple University **INVITED**

Atomic-level design of complex-oxide heterostructures that exhibit functional electronic and magnetic phenomena has become a diverse and vibrant subfield of condensed matter physics and material science. Of particular interest are the material systems wherein rich physics and intricate interplay between various degrees of freedom at the interface give rise to functional properties not observed in the constituent materials. Detection and characterization of these interfacial properties present a unique practical challenge due to the lack of direct yet non-destructive techniques that are capable of probing minute changes in the electronic and magnetic states at a buried interface with element specificity and Ångstrom-level spatial resolution. In this talk, I will discuss several recent studies in which we utilized a combination of complementary x-ray spectroscopic and scattering techniques to understand the origins of the emergent low-dimensional ferromagnetic states in $LaNiO_3$/$CaMnO_3$ and $CaRuO_3$/$CaMnO_3$ superlattices. Depth-resolved standing-wave photoemission spectroscopy was used to probe the depth-dependent changes in the electronic states, while soft x-ray resonant magnetic scattering was used to extract the element-specific magnetic profile of the interface. The results of the experiments were compared to and interpreted using state-of-the-art first-principles theoretical calculations.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Award DE-SC0019297.

3:00pm **AS+EM+SE-TuA-3 Multi-Technique Forensic Analysis by Co-Incident XPS & Raman Imaging***, **Robin Simpson**, P. Mack,* Thermo Fisher Scientific, UK

For more than 100 years fingerprint analysis has been ubiquitous in the forensic sciences and is still a core method for identifying individuals in forensics. The techniques used to analyze fingerprints are either structural, for identifying the features of the fingerprints, or chemical, characterizing the composition of the deposited material. Many of these chemical characterization techniques are destructive to the sample preventing any further analysis from being performed or the sample from being preserved as evidence for a later date. Here we show the benefits of using XPS to analyze fingerprints, where the elemental and chemical state composition of a sample can be acquired non-destructively from the top 10 nm of the surface.

In this investigation, we build on our previous work investigating fingerprint analysis. In that study, XPS and XPS mapping techniques were utilized to identify and characterize the contamination of fingerprints. Fingerprints contaminated with TiO-$_2$, and PbO deposited on the silicon wafer can be chemically mapped and visualized using XPS using principal component analysis, PCA.

In this study, we also discuss other examples of forensic analysis including the identification of pharmaceutical substances using complementary XPS and Raman analysis. To achieve this an “over the counter” multi-component analgesic tabletwas crushed to a powder form and deposited onto the substrate. The powder is mapped rapidly using XPS imaging and the data is processed by PCA. This information was used to identify areas for further analysis by high-resolution XPS and Raman. Further Raman analysis was used to characterize the composition of the 3 areas of the sample and identify the compounds contained in them. These are shown to be aspirin, paracetamol, and caffeine through comparison with known sample spectra in the OMINC Raman spectral database.

In the final two examples of forensic analysis workflows in this presentation, we discuss the identification and differentiation between overlapping ink and paint samples deposited on paper or fabric substrates. Raman mapping is used to differentiate between two paint samples that have virtually identical chemistry when analyzed via XPS, and rapid XPS imaging is used to identify the order of events between the deposition of computer-printed ink and handwritten ink from a ballpoint pen.

3:20pm **AS+EM+SE-TuA-4 Comparison of Methods to Quantify Silicone on Hair***, **Michaeleen Pacholski**, B. Johnson, T. Case, T. Powell, D. Carsten, J. Stratton,* The Dow Chemical Company*; C. Ji,* The Dow Chemical Company, China*; M. McIvor, N. Goodman, S. Yusuf, M. Upshur,* The Dow Chemical Company

Silicone has been used as a conditioning agent on hair for a long time.Silicone deposition can produce numerous benefits in reducing the coefficient of friction, improving combability and decreasing frizz.It can be delivered in multiple ways such as conditioning shampoo, rinse off conditioners, leave in conditioners and detangling products.Regardless of how it is delivered to the hair surface, the quantification of silicone on hair is an important metric for R&D product development and marketing.In a large analytical group there are many techniques that can be used including XPS, XRF, ICP, GC and IR.Each has different limits of detection, amount of sample required, time involved to both acquire and analyze the data, etc.A set of samples was generated using both shampoo and rinse off conditioner on both brown and bleached hair for a comparison study.The amount of silicone varied from low to high levels.Comparison of the techniques showed general agreement between all techniques within expectations.These experiments can now guide internal work based on the needs of the specific project and what instrumentation is available within that region.

4:20pm **AS+EM+SE-TuA-7 Progress Towards Atomic Scale Analytical Tomography***, **Brian Gorman**,* Colorado School of Mines*; T. Kelly,* Steam Instruments, Inc*; M. Holtz,* Colorado School of Mines **INVITED**

Atomic-Scale Analytical Tomography (ASAT) has been recently defined as the ability to identify every atom in its place. Specifically, ASAT is the ability to determine the isotopic identity and sub-Angstrom position of 100% of the atoms in a specific volume. Taking this a step further, ASAT should also be able to determine the local electronic structure of these atoms, thus giving rise to true 3-D atomic structure / electronic property relationships. ASAT datasets of semiconductor nanostructures will reveal the 3-D position of individual dopant atoms with pm spatial resolution, the 3-D position of nuclear spin isotopes, nanometer scale changes in strain due to structural defects and lattice mismatch, the 3-D position of point defects such as vacancies, and any electronic band structure changes at all these atomic-scale features.

Undoubtedly, ASAT is a lofty metrology goal but is nearly within reach. Contemporary metrology techniques such as (Scanning) Transmission Electron Microscopy ((S)TEM) are not currently capable of ASAT. (S)TEM can image atomic positions with better than 0.01 nm resolution in some specimens and tilt-series tomographic imaging can give 3-D information, sometimes at atomic resolution. Analytical STEM can be performed at atomic resolution in some cases, although identifying a single atom in 3-D is only possible in limited specimens and with poor depth resolution. Atom Probe Tomography (APT) can provide mass spectral information on individual atoms, however, 3-D image reconstruction methods are constrained by multiple empirical assumptions and lack of information about the specimen that limit the spatial resolution.

Recently, it was demonstrated that correlative TEM and APT on the same specimen can approach ASAT. We used (S)TEM imaging of the specimen before and after APT to define the analyzed 3-D volume. 4-D STEM diffraction was used to define atom positions within that volume (a dataset known as the specimen function) using information about the crystal space group, orientation, and lattice parameters. Individual isotopic nuclear spins are accurately placed within a semiconductor quantum do to within 0.05 Anstroms.

More work needs to be done using correlative TEM and APT to achieve ASAT, including demonstrating the ability to capture structural features such as interfaces and defects as well as 100% efficiency ion detectors. In the near future, ASAT will be achieved through integration of 100% efficiency ion detectors, improved data handling algorithms, and integration of TEM and APT into a single instrument.

5:00pm **AS+EM+SE-TuA-9 Investigating 2d-Materials Using Correlative Spectroscopy & Microscopy***, **Tim Nunney**, R. Simpson, P. Mack, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this presentation, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

5:20pm **AS+EM+SE-TuA-10 Surface Analysis in Fujifilm Electronic Materials Research & Development Laboratory: Applications on Chemical Mechanical Planarization***, **Hong Piao,*** FUJIFILM Electronic materials USA., Inc.*; Y. Liang, K. Huang, B. Duong, J. McDonough, Y. Zhang, H. Lee, B. Hu,* FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization (CMP) is a chemical reaction assisted polishing process in the semiconductor manufacturing industry. It has played a key role on integrated circuit (IC) manufacturing to anisotropically remove overburden material or specific layers in the film stacking and to planarize the topography at the wafer surface. Specific slurry formulations have been designed towards to the device structure and materials to be polished. The surface chemical processes at the interface of the wafer/slurry/pad have significant influence on the CMP performance. As device geometries are continuously shrinking as well as the introduction of new interconnect materials, the technological requirements on CMP performance have become more stringent. Thus, in-depth understanding of surface chemical processes which occur during polishing remains essential to the improvement of slurry design, the development of next-generation CMP processes and post-CMP cleaning applications.

Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of "nano-structured" materials in other fields.Surface analysis tools (XPS, Tof-SIMS and AFM) at FUJIFILM Electronic Materials U.S.A., Inc. combined with other complementary testing methods have already shown great promise as a means of achieving fundamental knowledge to the mechanisms involved in CMP processes [1].

This review continues to highlight the promising role that surface chemical analysis methods can and should play in understanding the complex interplay that drives design of CMP slurry formulation for contributions to the CMP technology. Examples describing the CMP characterization have been given in several aspects that are growing in importance: (1) Cu, Co and Ru CMP, (2) Defects (organic residues,metal contaminants and particles) removal in a post-CMP cleaning process and (3) CMP consumables: root cause analysis of pad stains.

[1]Hong Piao, Yannan Liang, James McDonough, Tawei Lin, Hyosang Lee, Carl Ballesteros, Eric Turner, Abhudaya Mishra and Richard Wen, "*Industrial Applications of Surface Science in Chemical mechanical Planarization*", The AVS 65th International Symposium, Oct. 21-26, 2018, Long Beach, California.

5:40pm **AS+EM+SE-TuA-11 Investigating GeTe as an Ovonic Threshold Switch with Spectroscopic and Electronic Techniques***, **Melissa Meyerson,** M. Kalaswad, M. King, D. Adams, J. Custer, P. Kotula, M. Rodriguez, S. Rosenberg,* Sandia National Laboratories

Ovonic threshold switches (OTS) are a class of two or three terminal devices that exhibit a sharp transition between resistive and conductive operating regions. This transition is temporary, with the device reverting to a resistive state once bias is de-asserted from the device. The volatile resistive behavior makes OTS devices very attractive as select devices for phase change memory, voltage controlled tunable filters, and other applications. Metal telluride thin films show unique temperature dependent characteristics that may make them good materials for OTS devices. In this study, we examine the effect of annealing temperature on the chemical, physical, and electronic properties of GeTe thin films including exploring changes in crystallinity, chemical composition, and switching behavior. More specifically, X-ray photoelectron spectroscopy shows a chemical transition that occurs between 125 °C and 150 °C that results in an increase in metallic Ge and decrease in metallic Te relative to the concentration of GeTe present. Similarly, X-ray diffraction shows a transition from amorphous to crystalline GeTe around 160 °C. The films are further characterized with transmission electron microscopy, energy dispersive X-ray spectroscopy, and surface electronic measurements including ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy to determine the band gap.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

6:00pm **AS+EM+SE-TuA-12 Multi-Technique Analysis of Organic and Inorganic Semiconductors for Composition and Electronic Information***, **Paul Mack,*** Thermo Fisher Scientific, UK*; M. Modreanu,* Tyndall National Institute-University College Cork, Ireland

Photoelectron spectroscopy has been used for many years to analyse the elemental and chemical composition of a broad range of industrially relevant materials, from polymers to semiconductors.In recent years, with the development of novel organic and inorganic semiconductors, there has also been an increasing demand to measure electronic parameters alongside the elemental and chemical state information.

In this work, complementary electron spectroscopic techniques were used to comprehensively characterise organic and inorganic semiconductors for composition and electronic properties.X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental and chemical composition of the organic semiconductor, P3HT, and a range of ferroelectric films with the general formula, $Hf_xZr_yO_z$.Ultraviolet photoelectron spectroscopy (UPS) and reflection electron energy loss spectroscopy (REELS) were then used together to measure the ionisation potential, band gap and electron affinities of those samples.

Author Index

Bold page numbers indicate presenter