Tuesday Afternoon, November 1, 2011

Applied Surface Science Division
Room: 102 - Session AS-TuA

Imaging and 3D Chemical Analysis - Part II

Moderator: W. Stickle, HP ADL Corvallis

2:00pm **AS-TuA1 Integration of an External Cavity Quantum Cascade Laser Into a Scattering-Type Infrared Scanning Near-Field Optical Microscope**, ***A.S. Lea***, *M.S. Taubman, M.C. Phillips,* Pacific Northwest National Laboratory, *M. Raschke*, University of Colorado, Boulder

Molecular nanostructures, polymer and supramolecular assemblies, proteins, biomembranes, correlated systems, and many other natural and synthetic materials gain their unique functionalities from intra- and intermolecular interaction and electron correlations on mesoscopic length scales of 10's of nm. Gaining a molecular level understanding of the materials structure and function has remained a major experimental challenge. This is due to the lack of experimental techniques that can routinely provide a chemically specific spectroscopic identification with simultaneous nanometer spatial resolution on the relevant length scale associated with the size and interactions of the molecular building blocks: within the 10 – 100 nm range. We have developed an instrument for spectroscopic infrared vibrational near-field nanoimaging capable of ultrahigh spatial resolution down below 10 nm, vibrational spectral information in the 14 to 2 um range, sensitivity down to the molecular level, and applicability under ambient and environmental conditions. There are few instruments that can provide near field IR nanoimaging at high resolution, but except for the aforementioned instrument, none are broadly tunable over a large spectroscopic range nor has resolution that approaches 10nm.

We are integrating a Quantum Cascade Laser to the new instrument as a complementary IR light source to the femtosecond OPO chain. QCLs are a monopolar semiconductor laser devices that can be fabricated to cover significant regions of the mid IR spectrum, specifically 3.5 to 20 microns. Moreover, these devices work extremely well in the molecular fingerprint region (8 to 12 microns), which will be of particular use in this instrument as this is where many fundamental vibrational bands are found, where MCT IR detectors work best, and the region is relatively free from water interference. The rapid scanning capabilities of External Cavity QCLs (ECQCLs) in the 100s of Hz, will allow IR spectra to be taken point by point across the sample, allowing rapid spectral data coverage. This is to be compared with the Hz-rate scanning of the OPO chain. The second significant advantage of QCL incorporation will be its ease of use (permitting wide-spread usage), low cost and ruggedness. This presentation will cover the integration of an ECQCL into the existing scattering-type IR scanning near-field optical microscope and demonstrate its ability to provide spatially resolved IR spectroscopic signatures on a sub-100nm scale. Ultimately, we anticipate this instrument will be able to provide chemical binding information of molecular adsorbates on nanostructured materials.

2:20pm **AS-TuA2 An Investigation Into the Aging of Paintings using Surface Analysis Techniques**, ***T.S. Nunney***, Thermo Fisher Scientific, UK, *J.J. Boon,* AMOLF, Netherlands, *E.S.B. Ferreira*, Swiss Institute for Art Research (SIK-ISEA), Switzerland

The understanding of the processes involved in the aging of artworks is of considerable importance in maintaining these pieces for future generations. Delamination of paint layers, chemical reactions of constituents in and between paint layers, interactions with the material that the paint was applied to, and the influence of the environment on the works can all have an effect on their appearance. By understanding these processes, conservators can attempt to retain the appearance as the artist intended.

Surface analysis has been used to investigate a cross-section sample taken from "Autumn in Oschwand" (1906) by Cuno Amiet (1868-1961). The painting has become lighter in certain areas, and the cause of this was investigated. EDS analysis indicated that a higher proportion of lead had accumulated near the surface of the outer paint layer. XPS imaging of the sample in conjunction with multivariate statistical analysis of the data allows the chemical state of the individual components to be distinguished, from lead carbonate (or "lead white" pigment) to the lead soaps that are causing the change in the appearance of the painting, and the copper, chromium and arsenic pigments that form the paint layers. These analyses were compared with spectra from reference pigments to identify the original paints used. Further investigation using Raman and FTIR microscopy was used to complete the analysis.

2:40pm **AS-TuA3 Probing Insect Tissue by NEXAFS Imaging: A Chemical Characterization of Cuticle from an African Flower Scarab *(Eudicella gralli)***, ***J.E. Baio***, University of Washington, *C. Jaye,* National Institute of Standards and Technology, *E. Sullivan,* Woodland Park Zoo, *D.A. Fischer,* National Institute of Standards and Technology, *D.G. Castner, T. Weidner*, University of Washington

Insect cuticle is a matrix of structural proteins and long chain polymers of chitin. The chemical composition of the cuticle is dictated by the biomechanics of the insect. Regions of the exoskeleton where extra stiffness is required - this matrix become mineralized and form scalarites. Elastic portions of the cuticle are rich with pliable structural proteins. While engineers have set out to copy these biomineralization processes and design materials that mimic the extraordinary structural capabilities of these exoskeletons – a complete understanding of the structure of this chitin/protein/mineral matrix does not currently exist. In this study, we set out to spatially resolve the chemistry, at the cuticle surface, of an African Flower Scarab *(Eudicella gralli)* by near edge x-ray adsorption fine structure (NEXAFS) imaging. The NEXAFS images are produced by a new parallel process magnetic field electron yield optics detector, and a full field incident soft X-ray beam on the sample. The rapid parallel process magnetic field electron yield optics detector (LARIAT:Large Area Imaging Analytical Tool) produces a series of two-dimensional NEXAFS spatial images as the incident soft X-ray energy is scanned above a K or L absorption edge. A spatially resolved view of cuticle surface chemistry was created by mapping spectral features within the carbon (270-370 eV), nitrogen (380-430 eV), and oxygen (520-580 eV) K-edge spectra. Distributions of protein and chitin rich regions around the beetle were defined by changes in intensity of π^*(284.5 eV) and C-H* (290 eV) within the C K-edge spectra. Regions of high mineralization were observed around the edges of the beetle's head and were assigned by tracking the intensities of the calcium (330-360 eV) and iron (700-740 eV) L-edges. These images also showcase the strengths of NEXAFS imaging, which unlike other photoelectron spectroscopy modalities, allowed us to collect high quality spectra over a large field of view (12 mm x 18 mm) at a range of x-ray incidence angles, with little beam damage to the tissue.

3:00pm **AS-TuA4 Surface Cleaning of Organic and Inorganic Materials with Argon Cluster Ion Beams**, ***A.E. Wright***, *P. Mack, O. Greenwood*, Thermo Fisher Scientific, UK

Surface analysis of many materials can be impeded by the presence of contaminant substances at the surface. Signals from these contaminants can dominate a photoelectron spectrum, leaving little contribution from the underlying material of interest. Spectroscopic analysis of contaminated samples can be a considerable challenge in surface science, so methods of cleaning samples are of some importance. One common method of removing contamination *in vacuo* is argon ion sputtering, which can be effective at removing surface materials. Damage to the underlying material can be substantial with argon ions, however, particularly at high impact energies. Ion impacts can disrupt polymer structures and reduce inorganic oxides, so that the surface after cleaning does not closely resemble the intact material.

The recent development of argon cluster ion beam sources promises significant improvements in depth profiling of soft materials. Cluster beams can offer exceptionally gentle sputtering, and so may be ideally suited to removal of contaminants and surface modifications from a variety of samples.

In this presentation, we evaluate the utility of argon cluster ions for the surface cleaning of various materials, in combination with the Thermo Scientific ESCALAB250Xi surface analysis instrument for characterisation of the samples. The results of gas cluster profiling on polymeric and inorganic materials will be presented, with spectroscopic and imaging analyses showing the benefits of this method.

4:00pm **AS-TuA7 Structure Determination of Heterogeneous Materials through 3D Imaging using XPS and Multivariate Analysis**, ***K. Artyushkova***, The University of New Mexico, *S.J. Coultas, S.J. Hutton, A.J. Roberts*, Kratos Analytical Inc.

The sputtering of solids with ion beams followed by analysis with photoelectron spectroscopy has been widely used as it offers a powerful strategy for the in-depth characterization of complex inorganic materials. The combination of imaging techniques with depth profiling to create three-dimensional information is an obvious and exciting extension of these experiments. Recent introduction of cluster ion beams, such as coronene,

into XPS instrumentation offers capabilities in quantifying the chemical and molecular gradients in the near surface region of soft materials, such as polymers and biomaterials. XPS data can be acquired as a function of sputter depth into organic materials while maintaining molecular integrity.

There are only a handful number of studies combining XPS imaging and depth sputtering. One of the biggest problems when dealing with 3D imaging data sets is visualizing the lateral distribution of chemical moieties as a function of depth. When multispectral images are acquired at each sputtered depth, four-dimensional datasets can result with a full spectrum acquired at each voxel of the space. These datasets represent a huge amount of data which can only be interpreted with assistance of Multivariate Analysis.

In this research we report on application of various types of MSA methods such as two-step PCA and two-step MCR-ALS, PARAFAC, MFA, Tucker and 3D MCR-ALS to multispectral XPS imaging data acquired as a function of sputtering depth for different heterogeneous biomaterials and polymers. The component images extracted from MSA, which show the spatial distribution of the various chemical components, will be visualized in 3D individually or together representing an overall chemistry of individual layers.

4:20pm **AS-TuA8 Interface Orientation Dependent Field Evaporation Behavior in Multilayer Thin Films**, ***J.G. Brons***, University of Alabama, *A.A. Herzing, K.L. Henry, I.M. Anderson,* National Institute of Standards and Technology, *G.B. Thompson*, University of Alabama

Intermixing between thin film layers can alter mechanical and thermal transport properties, phase stability and growth textures. Quantification of the degree of intermixing is crucial to identify the mechanisms of intermixing and their scaling effect on properties as listed previously. Atom probe tomography has received considerable attention for this type of characterization because of its ability to identify and provide reconstructions of atoms with near atomic spatial 3D resolution. In general, these atom probe reconstruction algorithms assume a constant evaporation field across the surface of the specimen. In reality, chemical inhomogeneity (i.e. discrete interfaces) modulates the evaporation field at the specimen surface. This introduces reconstruction artifacts and degrades the spatial resolution of the atom probe tomography technique. Multilayer thin films provide ideal specimen geometries to measure and quantify these artifacts since thin films can be deposited with near atomic layer precision and can exhibit large planar surfaces with various degrees of intermixing across the interfaces. A series of Fe/Ni and Ti/Nb multilayers with bilayer repeat distances of 4 nm have been sputter-deposited onto n-doped Si [001] substrates. The multilayers were annular focus ion beam milled into the required needle-shaped geometry for the atom probe analysis with the film interfaces oriented with the bilayer chemical modulations parallel and perpendicular to the specimen apex. This was done to compare field evaporation behavior at these limiting geometries. The atom probe compositional profiles were then compared to Electron Energy Loss Spectroscopy (EELS) compositional profiles to determine the fidelity of the reconstructions through cross-comparison microscopy. The best agreement between the profiles was seen for Fe/Ni (similar field strengths) in a perpendicular-to-the-apex orientation.

4:40pm **AS-TuA9 Atom Probe Tomography and Spectroscopic Analysis of Wide Bandgap Nanostructures**, *N. Dawahre, G. Shen, W. Baughman, S. Balci, S. Wilbert, N. Harris, L. Butler, S. Kim,* ***P. Kung***, University of Alabama

Wide bandgap ZnO based semiconductors are materials of great importance in an increasingly large number of optoelectronic devices for energy applications, including high efficiency low cost photovoltaics, solid-state lighting, ultraviolet light emitting and laser diodes, transparent electronics, transparent conducting windows that can be a potentially cheaper and more abundant substitute to ITO for photonic devices, and higher performance scaffold than TiO2 in sensitized solar cells. The material's wide bandgap, large exciton binding energy, and piezoelectricity can now be exploited at the nanoscale through the realization of nanobelts, nanoribbons and nanowires, leading to a dramatically expanded range of applications (e.g. chemical sensors and mechanical energy harvesting devices, etc). Enhancing our understanding of the chemical purity of ZnO nanostructures and understanding of the interfaces in ZnO based nano-heterostructures with atomic resolution is essential in order to enable the development of novel devices while further improving the performance of existing ones.

In this talk, we report the use and development of atom probe tomography (APT) in order to image the chemical composition of well aligned ZnO nanowires synthesized by thermal chemical vapor deposition and its relation to other material spectroscopic characteristics. The ZnO nanowires used were on various substrates, including sapphire, GaN and Si. The nanowires were single crystalline, 0.5-20 um long with a diameter controllable from 50 to 150 nm and a density on the order of 10^8 per cm^2.

We subsequently discuss the sample preparation techniques employed and the influence of various APT measurement parameters on the quality of the data collected. Atoms probe tomography (APT), which combines a field ion microscope and a time-of-flight mass spectrometer, is an analytical technique which is unmatched in identifying composition at the atomic scale and in 3D. However, proper interpretation of the APT data required thorough analysis of the mass spectra. Data analysis was also carried out in correlation with the nanowire synthesis conditions (e.g. carrier gas and dopant) and with other characterization techniques aimed at assessing the nanowire optical and electrical properties. These included high resolution transmission electron microscopy along with energy dispersive spectroscopy mapping, confocal Raman spectroscopy and imaging, confocal photoluminescence and imaging, as well as terahertz time domain spectroscopy.

5:00pm **AS-TuA10 Probing 3D-Semiconductor Structures**, ***Vandervorst***, IMEC, Belgium **INVITED**

The trends in advanced semiconductor devices and technologies call for the ability to probe compositional and impurity distributions with a depth resolution approaching near-atomic resolution. At same time, quantitative interpretation is of utmost importance in particular in multilayer structures and at interfaces such as local silicide composition and phase, interfacial interactions high k metal gate, etc.. At the same time one must admit that the advent of nanoscale devices and three-dimensional structures like Finfets, nanowires necessitates techniques which provide 3D-resolution. In this paper we will discuss recent approaches in extracting local 2D, 3D information on dopant distributions, carrier distribution, defects in thin dielectrics, phase and composition analysis, detection of small voids in ultra narrow interconnect lines (> 15 nm) as well as in (large, > 50 micron!) Cu-interconnects (TSV's).

For nanosale 1D and 2D characterization we presently rely on concepts such as EXLE-SIMS for ultra high depth resolution dopant profiling, SSRM for 2D- carrier analysis, C-AFM for dielectrics, (S)TEM (+ELNES, EDX, HAADF) for quantitative composition analysis. 3D-characterization represents a serious challenge and one must rely on concepts like the tomographic Atom Probe to extract 3D-composition analysis on the nm-scale or Tomographic TEM. We will show examples for both cases and address the issues of Atom Probe in particular as the latter, although very appealing, does contain many artifacts as well. The latter are linked to sample preparation, laser-tip interaction, and reconstruction artifacts as well as issues inherently linked to instrument performance (mass resolution, sensitivity,..) and underlying physics (linked to sample heterogeneity). For analysing 3D-dopant distributions in Finfets, this can be complemented with tomographic SSRM and SIMS through Fins.

For back-end applications, the detection voids in narrow Cu-lines (15-30 nm) can be done using EDX whereas their analysis in the very large Cu TSV's requires sophisticated ion milling approaches (plasma based FIB, slcie and view) as excessive milling times and surface topography evolution (curtaining) can hide the required information.

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