Tuesday Afternoon, October 19, 2010

Applied Surface Science
Room: Cochiti - Session AS-TuA

Advances in Surface and Interface Imaging
Moderator: A.V. Walker, University of Texas at Dallas

2:20pm AS-TuA2 Advanced Chemical State Analysis Method with Standard Spectra Measured with a Higher Energy Resolution of 0.1 % in Auger Electron Spectroscopy, *K. Tsutsumi,* **M. Shima**, *A. Tanaka, T. Tazawa*, JEOL Ltd., Japan

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are very famous for elemental and chemical state analysis at a solid surface. In generally, XPS has been utilized for these analysis in an area of more than a few 100 mm^2 on a solid surface. In contrast, AES has been used rarely for chemical state analysis, but for elemental analysis at a minute area of less than 100 mm^2. The reason for it is approximately caused by the following three problems.

It is difficult to detect any peak shifts between chemical state differences because almost peaks in an AES spectrum are broader than XPS.

It is difficult to measure stably a standard AES spectrum for an insulator sample because a focused electron beam irradiation causes stronger surface charging.

A focused electron beam often makes some elements change to another chemical state.

Among these problems, No.2 and No.3 can be solved in many cases by some special pre-sampling and measurement techniques. However No.1 has been recognized as the biggest problem for the chemical state analysis in AES because some commercial Auger instruments could not obtain sharper peaks in a spectrum with a poor energy resolution of 0.5-0.6 % or the others could not have a sufficient sensitivity with an energy resolution of higher 0.1 %. So, the chemical state analysis in AES has been carried out only for some specific elements showing a bigger chemical shift of more than a few eV.

Now we had measured more than 400 standard spectra by the latest analyzer for pure materials or compounds with the energy resolution of higher than 0.1 %, which included shaper peaks and fine structures with little electron beam damage. Those spectra show that Auger spectra for compounds have different peak shapes and different peak positions.So, it is possible to distinguish them by the peak shape difference, even if some standard spectra of different chemical states have quite similar peak positions each other.

In this report, we can propose an advanced chemical state analysis by higher energy resolution AES, which is a spectrum separation method from a practical spectrum including several chemical states by comparison of peak shape difference. As an example application, this method was applied for the depth profile result of a natural oxide layer on a pure tin oxide plate with an energy resolution of 0.1 %. The result showed that it was clearly consisted of three layers (SnO_2/SnO/Sn subst.) by the waveform separation of Sn MNN to each chemical condition of Sn^{4+}, Sn^{2+}, and Sn^0. Moreover, it was found that the quantitative analysis of chemical state of Sn was also possible by comparison of the absolute intensity of standard spectrum.

2:40pm AS-TuA3 3D Atom Probe Analysis of Embedded Nanoclusters in Oxide Matrix, *S. Kuchibhatla, V. Shutthanandan, B. Arey,* Pacific Northwest National Laboratory, *R. Ulfig, T. Prosa,* Cameca Instruments Inc., **C.M. Wang, S. Thevuthasan**, Pacific Northwest National Laboratory, *P. Clifton*, Cameca Instruments Inc.

The influence of embedded nanoclusters on the optical, magnetic and electrical properties of bulk and surface oxides has been an active area of investigation. The establishment of new atom probe tomography (APT) and related high-resolution chemical imaging facilities at EMSL, the Environmental Molecular Sciences Laboratory, provides a world-class user facility for performing nanoscale microscopy. In this study we report on Au-rich nanoclusters that have been embedded into MgO and TiO_2 substrates. The effect of high temperature annealing on the properties of the matrix and the secondary phase (Au) are studied in detail. Electron microscopy analysis has shown that the embedded metal particles are often associated with various defects, which further contribute to property modification.

We report the first Local Electrode Atom Probe (LEAP®) analysis of bulk MgO and TiO_2 implanted with 2 MeV Au ions using the accelerator facility at EMSL. Both as-implanted and annealed samples were critically analyzed using a combination of APT and the results are compared with high-angular

annular dark-field scanning transmission electron microscopy (HAADF STEM) imaging. High-resolution transmission electron microscopy (HRTEM) clearly resolves the Au-rich nanoclusters and allows observation of the pronounced vacancy clustering associated with these features [1]. These Au-rich nanoclusters were also observed in the atom probe data with the average cluster size (~ 5 nm diameter) in good agreement with those seen using HRTEM. The APT technique, however, due to the high three-dimensional (3D) spatial resolution, is also able to detect the presence of finer-scale Au clusters. It can also directly measure residual Au composition within the MgO matrix and any MgO-Au mixing within the clusters. Besides variations in compositional microstructure, evolution of mass spectrum quality as a function of Au content is also observed. Efforts are ongoing in EMSL to confirm this observation and eliminate the possibility of any contribution from experimental artifacts.

During the course of this presentation we will highlight the advantages of using 3D APT in combination with electron microscopy. Specifically, correlative microscopy provides a means to evaluate the capability of APT to detect the presence of the vacancy clusters.

[1] Wang et al., Applied Physics Letters **87**, 153104, 2005

3:00pm AS-TuA4 Novel Nanoscopic Light Source for Tip‑Enhanced Raman Spectroscopy, **Y.-T. Li**, University of Cambridge, UK, *D. Roy*, National Physical Laboratory, UK, *M.E. Welland*, University of Cambridge, UK

The invention of the Atomic Force Microscope (AFM) in 1986 has pushed the frontier of nanoscience, particularly in the semiconductor industry and biosciences. These instruments allowed atomic scale imaging of surfaces at ambient conditions. Researchers around the world are working to add new functionalities to the AFM probe to acquire both chemical and topographical information at the nanoscale.

In this work the authors present a novel nano-probe designed for Tip-Enhanced Raman Spectroscopy (TERS), which provides chemical and structural information with nanometer scale spatial resolution. This probe can act as a sensor for chemical analysis either by Raman or fluorescence Spectroscopy.

In TERS, a sharp metal (gold or silver) tip (<50 nm) is produced by electrochemically etching and a laser beam is focused onto the tip-end. There is an enhancement in the electric field at the end of the tip which gives a near-field enhacment of the Raman signal. Results obtained shows chemical and topological information with ~30nm spatial resolution of single Carbon Nanotubes. However, the two major challenges in TERS are (a) coupling the light at the tip-end to achieve a high enhancement factor, (b) reducing the background (far-field) signal. There are significant inconsistencies in the reported values of the enhancement factor in literature. In this work we present a new approach for calculating the Raman enhancement factor. This was performed by near-field and far-field measurements on a bi-layer film made of two different materials having distinct Raman signatures. This method eliminates the errors in calculating the enhancement factor arising from measurements on single layer/nanostructures.

To address the issue of background signal, a novel approach is demonstrated by coupling light through a grating etched onto the tip-shaft fabricated by Focused Ion Beam (FIB). The grating is purposely used to couple the laser beam with the surface plasmon to generate a new localised light source at the tip end. This new nanoscopic light source is equivalent to the size of the tip apex thereby overcoming the diffraction limit. With this new light source, background free TERS and fluorescence measurements can be performed at ambient conditions. This tip can also be used in various other applications including fluorescence correlation spectroscopy with concentrated samples.

4:00pm AS-TuA7 Imaging of Coal Speciation Using TOF-SIMS and Scanning Transmission X-Ray Microscopy (STXM), **B.P. Yatzor**, University at Buffalo, *H.D. Liang*, China University of Mining and Technology, China, *J.A. Gardella Jr.*, University at Buffalo

4:20pm AS-TuA8 From Depth Profiling to FIB Sectioning for 3D TOF-SIMS Imaging of Organics, **G.L. Fisher**, *S.R. Bryan*, Physical Electronics, *P. Lu*, General Motors Company, *N. Smith*, Oregon Physics, *C. Szakal*, NIST

TOF-SIMS characterization of materials in the range of several microns from the sample surface has become somewhat routine. Nevertheless, there are practical limitations to the use of ion beam sputtering for probing both organic and inorganic specimens beyond the surface region. Certain matrix components do not sputter well and are susceptible to ion beam-induced

molecular damage. This accumulated beam damage gives rise to incorrect molecular distributions. Some matrix components may sputter at a different rate than others which results in a misrepresentation of the elemental and molecular distributions. Finally, the time requirements to achieve uniform (i.e. representative) depth profile analysis under ideal instrumental conditions can become prohibitive. Even under optimized experimental conditions, the efficacy of sputter depth profiling for 3D TOF-SIMS imaging is limited to < 5 μm in the case of a favorable matrix and to < 300 nm in the case of an unfavorable matrix. An alternative approach for 3D TOF-SIMS imaging the interior of a specimen is to utilize FIB milling and sectioning. With FIB milling, the interior of a specimen is revealed to depths of ~ 50 μm within a reasonable analytical timeframe. Additionally, 3D chemical imaging of ~ 10 μm deep volumes may be achieved in the same time it would take to perform a low voltage sputter depth profile. The advantage of the FIB-TOF approach is that the artifacts caused by sputter depth profiling, i.e. differential sputtering and accumulated ion beam damage to matrix molecules, are avoided. The union of successive FIB sectioning and TOF-SIMS analysis cycles to achieve 3D chemical imaging will be discussed and illustrated using inorganic and organic examples.

4:40pm AS-TuA9 Mapping of a Polymer Surface Reaction: Determination of the Spatially Resolved, Hydrolytic Degradation Kinetics of a Micropatterned Bioresorbable Membrane, *M.D. Marchany, I.T. Ozbolat, B. Koc, J.A. Gardella, Jr.*, SUNY at Buffalo

Poly(L-lactic acid) (PLLA) is a synthetic, bioresorbable polyester that is extensively used and studied for many [FDA-approved] commercial applications – such as therapeutic drug delivery and tissue engineering scaffolds.[1] It is generally accepted that the degradation process of bioresorbable polyesters: a) is diffusion-based,[2] b) occurs in a region of finite thickness, forming an erosion front that moves towards the center of a polymer structure,[2] and c) its rate increases with higher polymer surface area.[3] Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has been previously used to determine initial (before the onset of weight loss) degradation kinetics at bioresorbable polymer surfaces.[4] This analytical method, combined with the high lateral resolution capabilities of imaging with a bismuth ion source, and image processing algorithms, allowed us to determine the spatially-resolved initial degradation kinetics of micropatterned PLLA membranes at several pH levels. The results show that the degradation reaction occurs at different rates, and that these rates depend on the area of the feature. The findings of this study imply that polymer degradation can be controlled not only in a temporal manner, but also in a microspatial manner, by altering micropattern geometry and size distribution across the polymer membrane.

1. Lee, J, Gardella, Jr., J. *Analytical and Bioanalytical Chemistry*. **2002**. 373. 526.

2. Mathiowitz, E, Jacob, J, Pekarek, K, Chickering III, D. *Macromolecules*. **1993**. 26. 6756.

3. Buchanan, FJ, 2008. Degradation Rate of Bioresorbable Materials: Prediction and Evaluation. Cambridge, UK. Woodhead Publishing Limited.

4. Lee , J, Gardella Jr., J. *Analytical Chemistry*. **2003**. 75. 2950.

5:00pm AS-TuA10 Approaches towards Analyzing XPS Multispectral Image Series (Multi-Sample Analysis) and Combining Multiple Spectroscopic, Microscopic and Macroscopic Analytical, *K. Artyushkova*, University of New Mexico

Applications of multivariate analysis (MVA) methods to surface analysis imaging datasets have increased quite significantly in recent years. Multivariate analysis of 3D imaging TOF-SIMS and XPS data is now quite widely applied (even routinely used by some research groups). Data preprocessing, scaling and selection of appropriate multivariate analysis method have been discussed in the literature quite extensively in a couple of recent years.

What has been addressed in a lesser extent is an important problem of combining quantitative analysis of imaging datasets from the same analytical method from various samples (multi-sample 3D imaging) or combining various analytical data (spectroscopic, imaging, or scalar) obtained for the same sample (multi-modal analysis).

Approaches to quantitatively combine imaging datasets from multiple samples will be discussed on example of multispectral XPS imaging data sets acquired from various paper samples.

Multi-modal analysis will be discussed on example of combining spectroscopic (XPS, XANES), microscopic (SEM) and macroscopic (BET surface area and pore size distribution) data from set of non-Pt group metal electrocatalysts for oxygen reduction reaction treated at different temperatures.

5:20pm AS-TuA11 Atomic Scale Structural and Chemical Analysis of Internal Interfaces in Inorganic Materials, *B.P. Gorman, H.L. Guthrey,* Colorado School of Mines*, A.G. Norman, Y. Yan, M. Al-Jassim,* National Renewable Energy Laboratory*, R.P. O'Hayre,* Colorado School of Mines
INVITED

Fundamentally, photovoltaic and fuel cell devices rely upon interfaces for electrical power generation. However, the undesirable formation of poor quality interfaces can also serve to decrease power efficiency. In the case of photovoltaics, interfaces control the generation and extraction of photogenerated charge carriers; however, the formation of dislocations and dopant clustering can result in recombination centers, thus reducing the ability to extract charge carriers. In fuel cells, the three phase boundary between the electrode, gas, and electrolyte controls the cell power output; however, surface contamination at this interface can reduce the electrochemical reaction rate, and thus the power output of the cell. Understanding both of these interfaces at the atomic structural and chemical level allows for a greater understanding of the formation of interface degradation. In order to fully understand the atomic scale chemistry and structure of interfaces in photovoltaics and fuel cells, we have applied a combination of in-situ FIB / SEM electrical probing using EBIC and ex-situ impedance spectroscopy with high resolution analytical STEM imaging and laser pulsed atom probe tomography. These techniques have been applied to III-V based photovoltaics to gain an understanding of dopant profiling across quantum structures and tunnel junctions, and to probe the initial stages of phase separation in multicomponent epilayers. Similarly, EBIC has been used to identify dislocations and grain boundaries in polycrystalline Si photovoltaics, and to determine the atomic level chemistry and structure at these interfaces that leads to an interface acting as a recombination center. Finally, a combination of STEM and atom probe tomography have illustrated 10-17 / cm^3 changes in local Pt, C, and O chemistry and structure around Pt catalysts for use in polymer electrolyte fuel cells. In order to enable atom probe analysis on materials with widely varying field evaporation characteristics, new FIB specimen preparation techniques were required. Details on the complex experimental methods and instrumentation developed in order to enable all of these investigations are illustrated.

Authors Index

Bold page numbers indicate the presenter

— A —
Al-Jassim, M.: AS-TuA11, 2
Arey, B.: AS-TuA3, 1
Artyushkova, K.: AS-TuA10, **2**
— B —
Bryan, S.R.: AS-TuA8, 1
— C —
Clifton, P.: AS-TuA3, 1
— F —
Fisher, G.L.: AS-TuA8, **1**
— G —
Gardella Jr., J.A.: AS-TuA7, 1
Gardella, Jr., J.A.: AS-TuA9, 2
Gorman, B.P.: AS-TuA11, **2**
Guthrey, H.L.: AS-TuA11, 2
— K —
Koc, B.: AS-TuA9, 2
Kuchihbatla, S.: AS-TuA3, 1

— L —
Li, Y.-T.: AS-TuA4, **1**
Liang, H.D.: AS-TuA7, 1
Lu, P.: AS-TuA8, 1
— M —
Marchany, M.D.: AS-TuA9, **2**
— N —
Norman, A.G.: AS-TuA11, 2
— O —
O'Hayre, R.P.: AS-TuA11, 2
Ozbolat, I.T.: AS-TuA9, 2
— P —
Prosa, T.: AS-TuA3, 1
— R —
Roy, D.: AS-TuA4, 1
— S —
Shima, M.: AS-TuA2, **1**

Shutthanandan, V.: AS-TuA3, 1
Smith, N.: AS-TuA8, 1
Szakal, C.: AS-TuA8, 1
— T —
Tanaka, A.: AS-TuA2, 1
Tazawa, T.: AS-TuA2, 1
Thevuthasan, S.: AS-TuA3, **1**
Tsutsumi, K.: AS-TuA2, 1
— U —
Ulfig, R.: AS-TuA3, 1
— W —
Wang, C.M.: AS-TuA3, 1
Welland, M.E.: AS-TuA4, 1
— Y —
Yan, Y.: AS-TuA11, 2
Yatzor, B.P.: AS-TuA7, **1**