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

Correlative Analysis - A Multi-technique Approach for Identification and Structure-Property Relationships
Moderator: K. Artyushkova, The University of New Mexico

2:00pm **AS-WeA1 Complementary Ultra Thin Film Analysis using Low Energy Ion Scattering (LEIS) and TOF-SIMS**, ***T. Grehl***, *P. Bruener,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *H. Brongersma, E. Niehuis*, ION-TOF GmbH, Germany

Ultra-thin film structures have become increasingly important and simultaneously gained complexity with regard to the number of layers and the elemental composition. Understanding the processes occurring during deposition is crucial for improving the film quality. Especially during the first stages of film growth, analytical techniques with high surface sensitivity and good detection limits are required to study the growth process.

Low Energy Ion Scattering (LEIS) lends itself well to these tasks with its ultimate surface sensitivity of a single monolayer and detection limits of down to 10 ppm. This is accomplished by bombarding the surface with noble gas ions of a few keV and measuring the energy loss of the backscattered ions at a fixed scattering angle. The energy spectrum is converted into a mass spectrum of the elements present at the sample surface. The absence of matrix effects allows a straightforward quantification.

Besides the composition analysis of the outermost atomic layer, depth profiling is available via two distinct methods. Static depth profiling exploits the fact that ions scattered in deeper layers lose additional energy proportional to the penetration depth. As this process involves neutralization and re-ionization, intensities are lower than for the ions scattered at the surface. Thus, these ion can be distinguished, giving information about the elemental distribution in the first few nm in a non-destructive way. Alternatively, dynamic depth profiling is available by using a second, low energy sputter ion beam to erode the surface while recording surface spectra at different depths. This yields a quantitative, high depth resolution depth profile. By observing the change in the static in-depth signal during sputtering, the sputter rate can be intrinsically and continuously determined.

The unique advantages of LEIS complement established techniques like TOF-SIMS. The latter is often hampered by sputter transients at interfaces and difficult quantification especially of matrix species, but excels as far as the detection of trace elements or the gaining of chemical composition information is concerned. We applied both LEIS depth profiling modes to a number of thin film sample systems. Hereby we show the possibilities arising from each of the two modes, as well as from the combination with TOF-SIMS. Specifically, we worked on model samples relevant to the semiconductor industry (high-k, SiGe). Some of these samples were designed for studying the response function of the in-depth signal in order to improve the understanding and to allow the application to real-world samples, e. g. to correct for varying erosion rates.

2:20pm **AS-WeA2 Multi-technique Characterization of Polymer Surfaces and Diamond-Like Carbon Films**, ***P. Mack***, *R.G. White, A.E. Wright*, Thermo Fisher Scientific, UK

Surface treatment of polymers produces materials that exhibit a wide range of surface compositions, properties and structures. The chemical and structural properties of these novel materials can be exploited for the fabrication of devices for bio-medical and electronics applications. Additionally, the wear-resistant properties of steel can be modified by coating the surface with a diamond-like carbon (DLC) film.

The combination of a variety of complementary surface-sensitive electron spectroscopies maximises the information available to the analyst for full quantitative surface characterisation of polymer surfaces and DLC films. The silicon content of a DLC film can affect its hardness, for example, and XPS is the ideal technique for chemical quantification of the silicon. The concentration of hydrogen in a DLC film also modifies its wear properties, but XPS cannot quantify this element. It is possible, however, to detect and quantify hydrogen using Reflected Electron Energy Loss Spectroscopy (REELS). When used together, XPS and REELS can provide a total quantification for polymer surfaces and DLC films.

This presentation will show how Thermo Scientific tools can be used to investigate the chemistry and structure of various polymer and DLC samples. Chemical changes produced by surface treatments were examined by high energy resolution XPS and argon profiling (both monomer and gas cluster). Complementary REELS measurements were used to examine the level of carbon unsaturation at the uppermost surface of each sample and to detect and quantify hydrogen.

2:40pm **AS-WeA3 Challenges Associated with Mathematically Correlating Data from Multiple Surface Characterization Techniques**, ***K.G. Lloyd***, *D.J. Walls, L. Zhang, J.P. Wyre*, DuPont Corporate Center for Analytical Sciences **INVITED**

There are now many examples of multivariate analysis of surface-specific technique data[1,2]. These include multivariate statistical methods such as Principal Components Analysis (PCA), Partial Least Squares (PLS), or Multivariate Curve Resolution (MCR) applied to so-called “hyperspectral” mapping data, in which hundreds of channels of spectral data are collected at each pixel of a two-dimensional pixel array spanning an area of interest. The idea of trying to mathematically correlate different sets of mapping data from the same area is not new[3], and falls under the broader category of ‘image fusion’ used in conjunction with remote sensing applications[4]. However, this approach is not prevalent in the surface science literature, with the notable exception of Fulghum and Artyushkova[5,6].

There are good reasons for this, from both the experimental and modeling perspectives. This talk will discuss the challenges associated with mathematically correlating spectroscopic and mapping data from multiple surface-specific techniques. Examples from the literature and the analytical lab will be discussed.

[1]V. S. Smentkowski, J. A.Ohlhausen, P. G. Kotula, M. R. Keenan, *Applied Surface Science* **2004**, *231*, 245.

[2] M. S. Wagner, D. J. Graham, B. D. Ratner, D. G. Castner, *Surface Science* **2004**, *570*, 78.

[3] H. Hutter, M. Grasserbauer, Chemometrics and Intelligent Laboratory Systems **1994**, 24, 99.

[4] C. Pohl, J. L. Van Genderen., *International Journal of Remote Sensing* **1998**, *19*, 823.

[5] K. Artyushkova, J. E. Fulghum, ‘‘XPS and Confocal Microscopy Data Fusion for Polymer Characterization,’’ talk presented at American Vacuum Society 50th International Symposium held in Baltimore, MD November 2–7, **2003**.

[6] K. Artyushkova, S. Pylypenko, J. Fenton, K. Archuleta, L.Williams, J. Fulghum, *Microscopy and Microanalysis* **2006**, *12*(Suppl. 02), 1402.

4:00pm **AS-WeA7 Multi-technique Characterization for Interfacial Analysis, Depth Profile and Chemical Imaging**, ***S.V.N.T. Kuchibhatla***, *V. Shutthanandan, B.W. Arey, C.M. Wang, M.I. Nandasiri, N. Ponnusamy, T. Varga, S. Thevuthasan,* Pacific Northwest National Laboratory, *F. Liu, L. Huang, L. Porter, R.F. Davis,* Carnegie Mellon University, *T. Prosa*, Cameca Instruments Inc.

Nanoscale interfaces are finding use in a multitude of applications including fuel cells, LEDs etc. In addition, our group at EMSL, Pacific Northwest National Laboratory is interested in understanding the influence of interfaces on energy and environmental applications, in particular, radiation tolerance, and oxygen ion conduction. While a number of techniques are available to synthesize interfaces, their analysis is often challenging. Hence, the fundamental understanding required to develop next generation devices with controlled interfaces is not widely available in the literature. In this context, it is imperative to intelligently combine more than one analytical technique and as appropriate use new techniques with improved spatial and chemical resolutions (better chemical sensitivity and improved mass resolution) to achieve such a goal. Atom Probe Tomography (APT), a relatively new technique that compliments various surface and interfacial analysis tools, is capable of providing 3D-chemical images of various materials including multi-layer thin films with sub-nanometer spatial and a ppm level chemical resolution. This talk will focus on combining the information obtained from high-resolution scanning transmission electron microscopy, high-resolution Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy, atom probe tomography, x-ray reflectivity and diffraction analysis of two sets of multi-layer thin films. The first set of multi-layer thin films is synthesized using oxygen plasma-assisted molecular beam epitaxy consisting of samaria doped cerium oxide and scandia stabilized zirconium oxide. These films are expected to provide significantly enhanced oxygen-ion conduction relative to the films that are made of either of the materials. The second set of films, consisting of GaN, InGaN multi-quantum well structures, is prepared using metal-organic

chemical vapor deposition. These structures as green LED active regions were shown to have significant improvements in internal quantum efficiency when employing an InGaN buffer layer to modulate MQW interface roughness. The information such as layer thickness, elemental composition of the layers and interfacial roughness/mixing would be compared from various techniques mentioned earlier. Dopant distribution and any possible intermixing of the layers will be of major interest in the case of ceria-zirconia system. The interfacial roughness and any preferential segregation or clustering of In along with 2D/3D uniformity of the layers will be of most interest in the GaN-InGaN system.

4:20pm **AS-WeA8 Characterization of Lubricant Coated Cartridges Using Multiple Surface Analytical Techniques***, **X. Dong**, Z. Xiao, C. Kemp*, Eli Lilly and Company

Glide force is a key performance attribute for pharmaceutical injection devices. It is directly impacted by lubricant amount, lubricant distribution, and surface chemistry. However, obtaining accurate information on these lubricant properties has been a challenge within the industry because all of the surfaces are curved. Although ellipsometry has been routinely applied to measure the thickness of individual layers within flat samples, the analysis of multi-layered, curved samples, especially non-destructively, remains difficult. We have modified the sample stage and sample holder of a conventional ellipsometer to make it possible to examine lubricant distribution within drug containers with different geometric configurations and components, including those made of plastic and glass. To overcome the challenge introduced by curved surface, the area of the surface analyzed in any individual experiment is reduced to allow effective focusing of the beam. The mapping of large, curved areas may then be accomplished by assembling multiple individual analyses. The relationship between sprayed volume and lubricant thickness can thus be established through non-destructive analysis by ellipsometry. The surface chemistry of a fluorine containing lubricant was evaluated by FTIR-ATR and XPS, both before and after post-spray treatment. Fluorine concentration remains stable with mild treatment, but lubricant was depleted from the surface after severe treatment. This work demonstrated that the combination of multiple surface analytical tools can enhance our understanding of the device lubrication process.

4:40pm **AS-WeA9 Challenges in Surface and Interface Analysis of Thin Films***, **H. Piao**,* General Electric Co.*, Y.F. Hu,* Canadian Light Source Inc., Canada*, J. Fronheiser,* General Electric Co.*, V. Tilak,* General Electric Co., India*, M. Karadge, M. Morra*, General Electric Co.

Surface analysis methods play an important role in the characterization of thin films. The analysis of "nano-structured" films requires further development of existing surface analysis methods and exploration of new techniques. The aim of this presentation is to identify some of the challenges that exist in understanding surface and interface states of thin films using conventional X-ray Photoelectron Spectroscopy (XPS). Unique advances in thin film analysis using synchrotron-based X-ray Photoemission (XPS) and X-ray Absorption Near Edge Structure (XANES in both TEY and FLY modes) techniques are discussed. The presentation gives an emphasis on how these methods complement each other. Examples describing the characterization of thin films are given in two areas of technology that are growing in importance: (1) Gate oxide development on SiC and (2) corrosion inhibitor coatings.

5:00pm **AS-WeA10 A Comparison of AES and XPS Depth Profiling for Characterization of Multicomponent Thin Films***, **B.R. Rogers**, R.R. Harl*, Vanderbilt University

Auger electron spectroscopy (AES) depth profiling has been used to characterize thin films for decades. Thin film depth profiling using x-ray photoelectron spectroscopy (XPS) has become increasingly common due to recent advances in XPS instrumentation. Often the choice of which depth - technique is best for a particular sample is not clear. In this presentation I will compare the logistics and results of AES and XPS depth profiling of insulating and metallic multicomponent thin films. Depth profiles of SiO_xC_y and $CrSi_xN_y$ thin films acquired using both techniques will be presented. Sample preparation, analysis set-up, and analysis time will be compared. Signal to noise and interface sharpness of the resulting profiles will be compared. The ability to determine chemical state information from the acquired data will also be discussed.

5:20pm **AS-WeA11 Characterization and Fabrication of Patterned, Infiltrated Carbon Nanotube Forests with Applications to Thin Layer Chromatography***, **M.R. Linford**, D. Jensen, R. Davis, S. Kanyal,* Brigham Young University*, A. Dadson, M. Vail*, US Synthetic Corporation

Patterned forests of carbon nanotubes (CNTs) were used as a template to fabricate novel silica-based thin-layer chromatography plates (TLC). The resulting CNTs are infiltrated with elemental silicon by low pressure chemical vapor deposition of silane. Silicon coated CNTs are annealed in air to remove the CNTs and convert the silicon to silica. The resulting material is white, which is indicative and characteristic of silica. This process produces TLC plates that are porous and robust. The microfabricated TLC plates are characterized extensively by scanning electron microscopy (SEM), which shows the precise placement of the adsorbent material. Plates are also characterized by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and BET isotherm measurements. Unlike almost all other commercially available plates, these microfabricated structures do not require a binder to hold the adsorbent material together. Baseline separation of a CAMAG (Muttenz, Switzerland) five-component dye test mixture using toluene as the mobile phase was obtained. The chromatographic efficiencies of these microfabricated TLC plates are typically 70% higher than commercially available high-performance TLC plates, and sometimes much higher, also showing a 150% reduction in development time; these microfabricated TLC plates allow for both improved efficiency and speed of analysis.

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