Monday Morning, October 31, 2011

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

Quantitative Surface Chemical Analysis and Technique Development - Part I
Moderator: I.S. Gilmore, National Physical Laboratory, UK

8:20am AS-MoM1 Characterization of Nano-structures from Analysis of the XPS Background: Automation and 3D-imaging, *S. Tougaard*, University of Southern Denmark **INVITED**

The XPS peak intensity and its background of inelastically scattered electrons varies strongly with the depth distribution of atoms. This phenomenon is the basis for a widely used method for nano-structure analysis.[1] With the rapid increase in the application of XPS, there is a growing need for automated XPS analysis. To meet this demand, a modified simpler and less accurate algorithm, which however is suitable for automation was developed.[2] For each XPS peak, this algorithm determines just two numbers: the total amount of atoms within the outermost ~ 10 nm and the approximate depth of the atoms. The validity of the algorithm was demonstrated experimentally by comparison to more elaborate quantification methods.[2] The algorithm is thus of interest for automated XPS analysis. Another application of the algorithm is in XPS imaging, where thousands of spectra must be analyzed. Here automatic data-handling procedures are crucial. Software that can automatically analyze thousands of spectra corresponding to the situation in XPS imaging is now being developed. The method produces nondestructively a 3-D image of the surface with nanometer depth resolution. The practical applicability of this to XPS imaging was recently demonstrated.[3-4]

In ref [3] the algorithms ability to produce images of Ag taken from a series of samples with increasing thicknesses of plasma patterned Octadiene (2, 4, 6 and 8nm) on Ag substrates was demonstrated. The obtained images of the amount of Ag atoms in the outermost few nano-meters were in good agreement with the nominal thicknesses. Produced images of atoms at different depths clearly proved the potentials of the method for quantitative and nondestructive 3-D characterization of nano-structures. Spectral noise is a major limitation in imaging because the time allowed to acquire the spectrum at each pixel is typically ~1 sec. Different procedures for noise reduction were studied in ref[4] and principal component analysis (PCA) was found to significantly improve the 3D images of a thermally patterned oxidized silicon where detailed 3-D images of the Si, O, and C atoms were determined on the nano-meter depth scale.

In the talk we will summarize the technique and discuss its limitations and potentials for both automation of conventional XPS data analysis and for 3D XPS imaging.

[1] S. Tougaard, Surf. Interf. Anal. 26 (1998) 249

[2] S. Tougaard, J. Vac. Sci. Technol., A21 (2003) 1081; A23(2005) 741

[3] S. Hajati, S. Coultas, C. Blomfield and S. Tougaard, Surf. Interf. Anal. 40 (2008) 688

[4] S. Hajati, J. Walton, N. Fairley, and S. Tougaard, Surf. Sci. 602 (2008) 3064

9:00am AS-MoM3 Characterization of Model Gradient Inorganic Thin Films with XPS Spectral Modeling, *L. Lohstreter*, Medtronic, Inc, *R. Sanderson, J. Dahn*, Dalhousie University, Canada

Information about the layer structure of surfaces at the angstrom level can be probed through X-ray Photoelectron Spectroscopy (XPS) by analyzing the structure of the entire spectrum, including the inelastic background. Model samples were prepared through a unique magnetron sputtering system to create thin film gradients ranging from two angstroms to hundreds of angstroms thick across a distance of seven centimeters. The system studied consisted of a titania wedge on a gold substrate. The samples were characterized using Variable Angle Spectroscopic Ellipsometry (VASE) to measure the thickness of the wedge along the sample at many points along the gradient. The thickness values from the XPS and VASE modeling were shown to have excellent linearity from two angstroms until the XPS photoelectron peak was extinguished. The effective attenuation lengths of the titania at the kinetic energies of the various gold photoelectron peaks were also measured and compared to theoretical values for inelastic mean free path. The values were within 29% of each other.

9:20am AS-MoM4 Corrections for Backscattering Effects in Quantitative Auger Analyses, *A. Jablonski,* Polish Academy of Sciences, Poland, *C.J. Powell*, National Institute of Standards and Technology

The backscattering factor (BF) has long been recognized as an important matrix-correction factor for quantitative AES. The BF definition ("fractional increase in the Auger current due to backscattered electrons" [1]) has been shown to be unsatisfactory since the "fractional increase" can be negative at low primary energies and more grazing-incidence of the primary electrons [2]. ISO/TC 201 is considering the definition of a new term, the backscattering correction factor (BCF), as a "factor equal to the ratio of the total Auger-electron current arising from ionizations in the sample caused by both the primary electrons and the backscattered electrons to the Auger-electron current arising directly from the primary electrons." NIST recently released a new BCF Database [3] for AES. This database provides BCFs from Monte Carlo simulations for two models, a simplified model based on the previous BF definition which is relatively rapid and an advanced model based on the proposed BCF definition which is more accurate but slower. BCFs can be determined for a solid of arbitrary composition, a user-specified instrumental configuration, and primary energies up to 30 keV.

Examples will be given of the dependence of the BCF for Pd $M_5N_{45}N_{45}$ Auger electrons on various instrumental conditions (primary energy, primary-beam angle of incidence (θ_0), and analyzer acceptance solid angle) [4]. BCFs calculated from the advanced model of electron transport in the surface region of the Pd sample varied weakly with analyzer half-cone angle for $\theta_0 = 0°$ but more strongly for $\theta_0 = 80°$ where there were BCF differences varying between 19% at a primary energy of 1 keV and 6% at a primary energy of 5 keV. These BCF differences are due partly to variations of the density of inner-shell ionizations within the information depth for the detected Auger electrons. The latter variations are responsible for differences larger than 10% between BCFs from the widely used simplified BCF model and those from the more accurate advanced model for primary energies less than about 5 keV for $\theta_0 = 80°$. These and other BCF differences indicate that the simplified model can provide only approximate BCF values. In addition, the simplified model does not provide any BCF dependence on Auger-electron emission angle or analyzer acceptance angle. Comparisons will also be made with measured BCFs for elemental solids.

[1] ASTM E 673-03, "Standard Terminology Relating to Surface Analysis," in Annual Book of ASTM Standards, Vol. 3.06, 2010, p. 655.

[2] A. Jablonski, Surf. Science 499, 219 (2002).

[3] http://www.nist.gov/srd/nist154.cfm .

[4] A. Jablonski and C. J. Powell, Surf. Science 604, 1928 (2010).

9:40am AS-MoM5 Effect of Monochromator X-ray Bragg Reflection on Photoelectric Cross Section, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The photoelectric differential cross section plays a fundamental role for assessing the relative concentration of the various elements present within the XPS probing depth. Accounting for the different issues affecting the cross section is paramount not only for quantitative chemical studies (including angle-resolved XPS) but also for a proper comparison between the results obtained with different XPS tools, or in the same tool but with different X-ray sources. In XPS experiments employing monochromatized light, the X-ray Bragg reflection undergone by the beam at the monochromator crystal causes a partial polarization of the X-rays. The photoelectric cross section is affected since it depends on the angle between the electric field vector and the direction of the escaping electrons. An expression for the photoelectric differential cross section is presented that accounts for the effect of the monochromator and of the geometrical configuration of the XPS tool. The correction is as large as 9% for s-orbitals and reduces to up to 5% for orbitals with $\beta \sim 1$. The differences are directly related to the beta factor within the dipole approximation, which is the first order treatment of photoemission; i.e., they are not due to higher order quadruple terms.

10:00am AS-MoM6 An XPS Investigation of CdS Based Photoresistor During Operation, *S. Suzer, H. Sezen*, Bilkent University, Turkey

We have recently developed a technique for recording the shifts in the positions of the XPS peaks in response to different waveforms of electrical and/or optical stimuli for probing the dynamics of the developed electrical potentials originating from intrinsic or extrinsic (like doping) properties of semiconductive materials such as charging/discharging, photoconductivity, surface photovoltage, band-bending/flatting/inversion, etc.[1-6] We have also shown that fast data acquisition (in the snapshot mode) and laterally spatial resolved XPS analysis (an area mapping mode) helps us to compare and

align extracted electrical behaviors and chemical information from the sample. For a better understanding of a realistic performance (or failure) of a device during operation, we have extended our measurements to a CdS based photoresistor, where we have mapped the position of the Cd3d peak over an area of 5 mm x 5mm while the device is under operation without and under photoillumination. This method allows us to detect defects and malfunctioning sites/domains. We will present our methodology with experimental results and an electrical circuit model.

(1) Sezen H., Suzer, S. *Surface Science*, **2010**, *604*, L59.

(2) Suzer, S., Sezen, H., Ertas, G., Dâna, A. *Journal of Electron Spectroscopy and Related Phenomena* **2010**, 176, 52.

(3) Sezen, H., Ertas, G., Suzer, S. *Journal of Electron Spectroscopy and Related Phenomena*, **2010**, 178-9, 373.

(4) Sezen H., Suzer, S. *Journal of Vacuum Science and Technology A*, **2010**, *28*, 639.

(5) Sezen, H., Ozbay, E., Aktas, O., Suzer, S. *Applied Physics Letters* **2011**, 9*8*, 111901.

(6) Sezen, H., Suzer, S. *Journal of Spectroscopy and Dynamics* (in press).

10:40am   AS-MoM8   Coronene Ion Bombardment Effects in the Quantitative Analysis of Polymeric Materials by XPS, *G.E. Hammer*, *L.J. Gamble, D.G. Castner*, University of Washington

XPS has long been a primary technique for the analysis of material surfaces, providing quantitative analysis of elemental atomic concentrations and chemical bonding states. When combined with ion sputter etching, it has provided a similar level of detail in depth profiling of metals, semiconductors, and inorganic compounds; however, the damage produced by ion bombardment precluded the depth profiling of organic and polymeric specimens. More recently it has been shown that sputter etching by carbon cluster ions significantly reduces the apparent damage to such materials, presumably the result of a combination of a reduced damage layer thickness and efficient removal of the damaged material. In this work we have used a coronene $(C_{24}H_{12}{}^+)$ ion source to sputter etch a series of organic compounds and polymers, including trehalose, poly(amide), poly(glycolic acid), poly(lactic acid), poly(ethylene glycol), poly(methyl methacrylate), poly(acrylonitrile), poly(ethylene terephalate), poly(vinyl chloride), and poly(tetrafluoroethylene). Specimens were sputtered to a steady-state condition and analyzed by XPS. Elemental composition and chemical bonding were compared to the original surface and the theoretical values. These data will be used to refine our understanding of cluster ion bombardment effects in polymers, and to interpret data from the analysis of future materials and devices.

11:00am   AS-MoM9   Using A C60 Ion Source For Routine Surface Chemical Analyses, *W. Stickle*, *M.D. Johnson, D.K. Bilich*, HP ADL Corvallis, *C. Knutson, W. Wang, W. Cowell*, Oregon State University

$C60^+$ ion sources are becoming one of the routinely used tools in the surface chemical analysis laboratory. While finding early acceptance and utility in the TOF SIMS community because of its direct applicability to organic systems, the C60 ion source is now a standard option for photoelectron spectroscopy tools. Routine use of this ion source requires characterization and understanding of the surface that is being created during the ion milling process. Such characterizations include the shape and roughness of the resulting surface, changes in chemistry of the surface created by the ion milling process and changes in the mechanical characteristics of the surface that might influence the interpretation of the surface analytical results. Full characterization requires the preparation of standards and also validation of the measurements. The characterization of the application of the C60 ion source for a variety of common polymers such as PMMA, SU8 and polycarbonate are discussed. Further, anticipating the examination of mixed mode systems, the application of the $C60^+$ source for the characterization of inorganic materials such as titania, hafnia and alumina multilayered structures as well as metal-metal oxide layered structures is presented where sputter induced chemistry from the $C60^+$ source is observed.

11:20am   AS-MoM10   Large Area Quantitative XPS Imaging for Small Feature Compositional Screening, *S.J. Coultas*, *C.J. Blomfield, S.J. Hutton, A.J. Roberts,* Kratos Analytical Ltd, UK, *D.J. Surman*, Kratos Analytical Inc.

Many technologically important devices require nanometre level chemical characterisation over areas of several square mm, or even cm, for applications such as coating continuity and integrity or contamination monitoring.

The traditional approach when employing XPS for this application has been to acquire a number of small area spectra at different points. The advent of quantitative parallel XPS imaging introduced the possibility of faster acquisition times and higher spatial resolution than the traditional small XPS probe approach.

Here we present an alternative approach whereby multiple features are simultaneously analysed over a large area using XPS imaging. Acquisition conditions and post acquisition data treatment to optimise this approach on a range of samples will be discussed

This approach provides both a faster and more easily interpreted graphical method for multiple feature analysis.

We present examples of this approach on a variety of samples.

11:40am   AS-MoM11   A New Type of Detector for Dynamic XPS Measurements, *K. Winkler*, *P. Baumann, B. Kroemker, G. Pruemper, A. Feltz*, Omicron NanoTechnology, Taunusstein, Germany

Real time observation of fast processes occurring in a time window of a few milliseconds to a few minutes have been always difficult to observe by x-ray excited photoemission (XPS) studies under laboratory conditions. However the demand to understand the chemistry of surface processes e.g. during heating processes, electro migration and diffusion is of high relevance in various research fields.

In this contribution we will report on first results of a new multi-anode detector concept with 128 individual anodes, preamplifiers and counters. It has the capability to allow for quantitative XPS studies on fast time scales with good signal to noise ratio excited with a monochromated Al Ka laboratory source. The detector can be operated in snapshot XPS mode. This mode allows recording an energy window in the spectrum versus time with high repetition-rates and good energy resolution, e.g. a 15 eV detectable energy window with an approximate energy resolution of 0.5 eV.

As an early application we report on results of removing an in-situ grown SiO2layer on a Si substrate. The measurement was made during a sample temperature ramp from 600 to 900 degree Celsius within a time frame of one hour. The target of the experiment was to analyze the time window in which the oxide was removed.

Snapshot spectra have been recorded with an acquisition time of 0.5 seconds per spectrum to follow the evolution of the subcomponents Si4+ to Si0during the heating process of the Silicon. The snapshot series with >5000 spectra shows the evolution of the peak versus time. The complete removal of the oxide occurred at a very small temperature window around 850°C. A closer look into the data revealed that the removal of the oxide from the silicon took place in about 2.5 minutes. Within this transition time 300 spectra have been recorded.

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