

Applied Surface Science

Room: Cochiti - Session AS-TuM

Electron Spectroscopies

Moderator: S.R. Bryan, Physical Electronics

8:00am **AS-TuM1 Recent Developments in Quantitative XPS and AES**, *C.J. Powell*, National Institute of Standards and Technology
INVITED

An overview will be given of some recent developments to improve quantitative XPS and AES [1]. First, guidance is now available for choosing integration limits in the measurement of XPS peak intensities [2]. A recent comparison of reported peak intensities in simulated XPS spectra with known intensities showed large deviations if the integration limits were chosen inappropriately. Second, Tanuma et al. have reported a new set of inelastic mean free paths (IMFPs) for 41 elemental solids that were calculated from experimental optical data for electron energies from 50 eV to 30 keV [3]. These IMFPs agree well with recent calculations and measurements. Third, examples will be given of the use of simple predictive formulae that are available for the effective attenuation length, mean escape depth, and information depth in AES and XPS [4]. Fourth, the effects of elastic scattering and analyzer-acceptance angle on the analysis of angle-resolved XPS data have recently been analyzed [5]. Calculations were made of photoelectron intensities at selected emission angles for films of $\text{SiO}_{1.6}\text{N}_{0.4}$ and $\text{HfO}_{1.9}\text{N}_{0.1}$ of various thicknesses on Si with the NIST SESSA Database [6]. Ratios of intensities for each line from the film for the least realistic model condition (elastic scattering “off”, small analyzer-acceptance angle) to those from the most realistic model condition (elastic scattering “on”, finite analyzer-acceptance angle) changed relatively slowly with emission angle but the corresponding intensity ratios for the Si(substrate) 2p line changed appreciably with emission angle; such changes can lead to erroneous results in the analysis of angle-resolved XPS data [5]. Fifth, examples will be given of a new NIST database to provide backscattering correction factors for AES using an advanced model that accounts for attenuation of the primary beam in the surface region of the sample and the instrumental configuration [7]. Finally, mention will be made of a set of reference energies for 59 Auger transitions in 42 elemental solids that should be useful for the determination of chemical shifts in AES and XPS [8].

[1] C. J. Powell and A. Jablonski, *J. Electron Spectrosc. Relat. Phenom.* 178-179, 331 (2010).

[2] C. J. Powell and J. M. Conny, *Surf. Interface Anal.* 41, 804 (2009).

[3] S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* (to be published).

[4] A. Jablonski and C. J. Powell, *J. Vac. Sci. Technol. A* 27, 253 (2009).

[5] C. J. Powell, W. S. M. Werner, and W. Smekal (to be published).

[6] <http://www.nist.gov/srd/nist100.htm>.

[7] A. Jablonski and C. J. Powell (to be published).

[8] C. J. Powell, *J. Electron Spectrosc. Relat. Phenom.* (to be published).

8:40am **AS-TuM3 Effect of Monochromator X-ray Bragg Reflection on Photoelectric Cross Section**, *A. Herrera-Gomez*, CINVESTAV, 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 in 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 the asymmetry factor $\beta \sim 1$. The differences are directly related to the β factor within the dipole approximation, which is the first order treatment of photoemission; i.e., they are not due to higher order quadruple terms.

9:00am **AS-TuM4 Photovoltage, Photoconductivity and Charging Probed by Dynamical XPS Measurements**, *S. Suzer*, Bilkent University, Turkey

We have developed a technique for recording the shifts in the positions of the XPS peaks in response to different forms of electrical stimuli for probing dynamics of charging/discharging processes of thin dielectric films, which we have named as Dynamic XPS. Modulation of the electrical signals in the forms of square, sinusoidal and triangular waves at different frequencies enables us to extract some dielectric properties of surface structures, such as effective resistance, and capacitance values in a chemically resolved fashion. We have also introduced photo-illumination as an additional form of the stimuli and have been using this technique for investigating the combined optical + electrical responses of semiconductive (Si and GaAs) as well as photoactive (CdS and TiO_2) materials towards better understanding of the different photo-processes, like photoconductivity and/or photovoltage development, etc. We use our dynamic measurements to help in distinguishing various fundamental processes, by using the frequency dependence as an additional tool. This makes XPS a more powerful technique for characterizing today's demanded nano or optoelectronic devices. The methodology will be introduced, and several examples will be presented.

9:20am **AS-TuM5 Order-Disorder Transition for Corrugated Au Layers**, *K. Fukutani*, University of Nebraska-Lincoln, *N. Lozova*, Louisiana State University, *S.M. Zuber*, University of Wrocław, Poland, *N. Wu*, *P.A. Dowben*, University of Nebraska - Lincoln, *P. Galiy*, Ivan Franko National University of Lviv, Ukraine, *Y.B. Losovyj*, Louisiana State University

Atomic-scale structure of the growth of a gold film on Mo (112) was investigated by means of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) up to several monolayers (ML) of gold coverage. Both LEED and STM results establish that Au grows on Mo(112) in a layer-by-layer mode, for at least the first two monolayers. A number of ordered structures are formed and both the first and second layers adopt the Mo(112) 1x1 surface structure upon completion. For some gold layers on Mo(112), notably the 1.66 monolayer 3x1 and 1.75 monolayer 4x1 gold overlayers, we find evidence of a phase transition associated with increasing disorder in gold layers with structural corrugation and anisotropic band structure. The signature of this phase transition, at temperatures in the range of 400–500 K, is a sharp decrease in the overlayer effective Debye temperature. Angle-resolved photoemission spectroscopy (ARPES) suggests coverage dependent changes in the electron-phonon coupling for gold adlayer.

9:40am **AS-TuM6 Surface Characterization of Gold Nanoparticles and Their Interaction with Protein G B1 Domain**, *S. Techane*, *L. Baugh*, *L.J. Gamble*, *P.S. Stayton*, University of Washington, *D.R. Baer*, Pacific Northwest National Laboratory, *D.G. Castner*, University of Washington

The purpose of this research is to study the interactions of biomolecules with nanoparticles using model systems. Model proteins and nanoparticle surfaces are used to simplify the complex biological/nanoparticle surface environment and develop a fundamental understanding of the interactions at this interface. Protein G B1 domain was used as a model protein. Wild type Protein G B1 (WT) has a uniform distribution of negatively charged residues on its surface. Using site-directed mutagenesis to neutralize six charged residues at one end of the protein, a mutant ($\Delta 6$) was created possessing a global charge dipole along its long axis. This variation in surface charge affected the biomolecular interaction with nanoparticle surfaces. Gold nanoparticles (AuNPs) with self-assembled monolayers of carboxylic alkanethiols (COOH-SAM) were used as the well-defined model surface.

We previously reported that AuNPs 14nm in diameter and functionalized with C16 COOH-SAM were more monodisperse in size and shape relative to those with larger diameter, and more stable in solution relative to those functionalized with shorter-chain COOH-SAMs. To accurately interpret XPS data and account for the curvature effect, and to quantitatively analyze overlayer thickness (T) and roughness (R), we used SESSA combined with geometric correction methods. The C16 COOH-SAM on flat Au was modeled with SESSA at photoelectron take-off angles from 5 to 85°. Corresponding ARXPS experiments were also performed. T and R were optimized to find the best agreement between the simulated and experimental results. It was necessary to add a hydrocarbon contamination layer (CL) at the surface of the COOH-SAMs in the simulations. For the C16 COOH-SAM on flat Au, the best conditions were $T=1.1\text{\AA}/\text{CH}_2$, $R=1.05$ and $CL=1.5\text{\AA}$. After applying a geometric correction, $T=0.9\text{\AA}/\text{CH}_2$

and $R=1.05$ was obtained for the SAM on AuNPs with similar CL. Studies to minimize CL are underway.

WT and $\Delta 6$ B1-protein G were adsorbed onto 14nm-AuNP-C16 COOH-SAM at various protein concentrations. Following adsorption and centrifugation, the final supernatant containing unbound protein and AuNPs with bound protein were analyzed by colorimetric assay and XPS, respectively. Both methods showed that $\Delta 6$ adsorbed more than WT. As $\Delta 6$ concentration increased, the N signal (unique to the protein) increased and the Au signal (unique to the surface) decreased, following similar trends as observed in the adsorption isotherm curve. Based on our preliminary study, a %N of 13.6 ± 0.3 corresponded to a monolayer of $\sim 0.95 \mu\text{g}/\text{cm}^2$. Further studies to accurately determine thermodynamic adsorption parameters and the AuNP concentration are underway.

11:00am AS-TuM10 Charging Compensation Method in XPS with Positive Voltage and Low Energy Electron Beam, M. Shima, K. Tsutsumi, T. Tazawa, JEOL Ltd., Japan

X-ray photoelectron spectroscopy (XPS) is widely used for qualitative, quantitative and chemical state analysis on various material surfaces, because XPS can obtain more stable spectra even in charged insulator surfaces than Auger electron spectroscopy. However in many cases, XPS spectra would be even distorted and shifted to high binding energy side by the positive surface charging caused by photoelectron emission. And we identify the chemical state of materials from peak position and peak shape. As a result, such a charging effect reduces the usefulness of XPS. The most widely used method for suppression of surface positive charging is to irradiate low energy electron to the sample surface. But operator should select electron flood gun conditions carefully such as accelerating voltage and the amount of the electron flux, because once the electron flux and accelerating voltage is set too high, peak shape will be distorted again and peak position turn to the lower binding energy side.

At this time, we propose a new charge compensation method that electrons irradiated from flood gun will be maintained efficiently on an insulator surface by applying positive voltage underside of insulator sample. The mechanism of this method is to accumulate excess electrons on the top of an insulator like a capacitor. Electrons maintained on insulator sample surface remove the differential positive charging, even when X-ray irradiation makes another differential charging. In addition, our experiment results shows that surface potential of insulator sample is determined simply by accelerating voltage of flood gun and it is independent of applied positive voltage for sample under the conditions that adequate electrons are supplied from flood gun. It is found that this charge compensation method has ideal mechanism; we can control not only peak shape in ideal shape but also its peak position.

In the presentation we will show some XPS experimental results with this method and discuss them.

11:20am AS-TuM11 Applications of Hard X-ray Photoelectron Spectroscopy for Characterization of a Hybrid Ti-Si Sol-Gel, J.L. Fenton, G. Mitchell, Y. Srivastava, Y.Q. Rao, B. Weaver, R. Auger, The Dow Chemical Company

Hard x-ray photoelectron spectroscopy (HAXPS), in particular variable kinetic energy photoelectron spectroscopy (VKE-XPS), is becoming increasingly useful to determine chemical and elemental information from the "bulk" of materials compared to traditional XPS. In addition, VKE-XPS allows for non-destructive depth profiling of materials that pose a greater challenge for Angle-Resolved XPS (ARXPS) such as materials with rough surfaces. This talk will present the application of VKE-XPS to hybrid Ti-Si based sol-gels to understand potential chemical or elemental changes as a function of excitation kinetic energy.

11:40am AS-TuM12 Inline Production Monitoring of Carbon Doped Polysilicon Using X-Ray Photoelectron Spectroscopy, B. Dickson, ReVera Incorporated, H. Lee, W. Namkoong, Samsung Electronics Co., M. Kwan, H. Pois, T.C. Larson, ReVera Incorporated

X-ray photoelectron spectroscopy [XPS] is a well respected compositional and thickness metrology technique. Historically, XPS has been used as an off-line characterization method limited to laboratories. The introduction of fully automated, small spot XPS systems in the fab now enables in-line metrology with results in minutes instead of days. This paper details the production control monitoring of carbon composition in carbon doped polysilicon films which are used in flash devices. Measuring carbon doped polysilicon for inline production has two main challenges: sensitivity and stability. Sensitivity to different carbon dosage processes as well as the process variation of day to day production has been demonstrated. In addition to compositional sensitivity, high resolution XPS can measure the different chemical bonding states of C. Because the carbon doped polysilicon surface is very unstable, with surface carbon accumulating on the wafers' surface over time in the form of amorphous carbon and an

atomic molecular contamination [AMC] layer, the main carbon dopant bonding state signal is separated from non-doped carbon bonding state signals. For stability, the ReVera Veraflex has developed an application to separate the naturally increasing AMC carbon from the stable doped carbon atomic composition, enabling a robust statistical process control [SPC] method.

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