Applied Surface Science
Room: C2 - Session AS-WeM

Electron Spectroscopies
Moderator: R.L. Opila, University of Delaware

8:00am **AS-WeM1 Probing Photoinduced Charging in CdS and CdSe Films by Dynamical XPS Measurements**, *H. Sezen, **S. Suzer***, Bilkent University, Turkey

Photoconductive materials have gained renewed interest in recent years due to the advancements in controlling their electronic and optical properties, which exhibit strong size, shape and chemical composition dependence. Recently, 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 in thin dielectric films, which we have named as Dynamical XPS. In the present contribution, we introduce photoillumination as an additional form of stimuli and investigate the combined optical + electrical response of thin CdS and CdSe films deposited on silicon substrates containing ca. 5 nm thermal oxide layer. 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 the SiO_2 and CdS (or CdSe) surface structures both under and without photoillumination. Experimental results will be presented, discussed, and compared with those of simulations.

8:20am **AS-WeM2 Energy Filtered PhotoElectron Microscopy**, *K. Winkler, **M. Maier***, Omicron NanoTechnology GmbH, Germany, *M.E. Escher,* Focus GmbH, Germany, *B. Kroemker, D. Funnemann*, Omicron NanoTechnology GmbH, Germany

Photoelectron emission microscopy (PEEM) in combination with a high-resolution energy filter (ΔE in the 100meV regime)[1] is a non-destructive and versatile surface characterisation technique with the ability to solve upcoming scientific metrology issues [2].

Looking at the Roadmap for Semiconductors today, scaling down of devices faces growing complexity of the related issues. To overcome these issues often requires detailed analysis at a local scale where understanding of materials in the form of small objects or patterns is of great importance. Hence the need for new spatially-resolved, non-destructive and comprehensive analysis tools becomes clear.

To identify the chemical compounds in a local sample area, energy-filtered PEEM is a very valuable metrology tool combining high spatial resolution with high-resolution spectroscopy. Continuous improvements of PEEM instruments nowadays enable local nano-spectroscopy with the highest lateral resolution in convenient laboratory conditions [3]. Imaging XPS with unsurpassed lateral resolution and quantitative analysis of the local work function allow for a detailed understanding of the surface chemistry, including locally resolved doping effects [4] on small structures used for semiconductor devices and even smaller silicon nano-wires[5].

In addition, recent experiments have shown the feasibility for a new class of experiments for band structure analysis. Advanced spectroscopic PEEM instruments allow a new approach to analyse the electronic structures of samples. Thus band structure mapping with a large acceptance angle of ±90° without the need for eucentric sample rotation becomes possible [6]. Together with full control over the analysed local area, the technique is ideally suited to investigate the electronic properties of single grains or small devices. Hence, this method opens up the path to a new class of experiments allowing e.g. dedicated local band structure tailoring.

*1. M. Escher et al. J. Electron. Spectrosc. Relat. Phenom. **144** (47), pp. 1179-1182 (2005).*

*2. M. Senoner et al. Jurnal of Surface Analysis **12**, pp 78-82 (2005).*

*3. O. Renault et al., Surface Science. **601**, pp 4727 - 4732(2007).*

4. N. Barrett et al. submittet to J Phys Condens Matter (2008) .

*5. A. Bailly et al. Nano Lett., **8** (11), pp 3709–3714 (2008).*

*6. B. Krömker et al. Rev Sci Instrum. **79**, 053702 (2008).*

9:00am **AS-WeM4 Some Problems of Quantitative Applications of High (up to 15 keV) Energy X-ray Photoelectron Spectroscopy**, ***L. Kover***, Institute of Nuclear Research of the HAS, Hungary

X-ray photoelectron and Auger spectroscopy, using hard X-rays for excitation and high energy resolution (HAXPES), due to the availability of the 3rd generation synchrotrons and advanced electron spectrometers, has shown a spectacular development recently allowing to utilize its non-destructive capability for providing a deeper insight into the bulk electronic structure of solids and the chemical composition of buried layers and interfaces lying at depths of several tens of nm. Quantitative analytical applications of HAXPES e. g. for studies of materials with new, important functions and complex physical, electronic and chemical structure are highly desired, however, some conditions are significantly different compared to the case of the conventional XPS. Although surface excitations and elastic electron scattering are playing a smaller role at higher electron energy and the inelastic background becomes less important, the low photoionization cross sections request a careful design of the experiments, non-dipole effects influencing the angular distribution of photoelectrons are non-negligible and effects of atomic recoil should be taken into account in the case of low atomic number components when looking at chemical shifts or energy broadening of core photoelectron lines. In addition, the available data for parameters (e. g. parameters characterizing electron transport in solids in the 2-15 keV electron energy range) necessary for quantitative chemical analysis using HAXPES are rather sparse and our present knowledge is limited concerning the role of intrinsic (core hole induced) excitations. In this contribution the magnitude and the energy dependence of physical parameters (derived from experiment or estimated using model calculations) relevant for quantitative applications of HAXPES are discussed together with new experimental data and simple models proposed for describing high energy photoinduced electron spectra. Acknowledgements: The support of the HASYLAB/DESY and the European Community under Contract RII3-CT-2004-506008 (IA-SFS) as well as by the Hungarian project OTKA 67873 is gratefully acknowledged.

9:20am **AS-WeM5 Hydrogen Quantification at Surfaces by Electron Spectroscopy**, ***F. Yubero***, CSIC, Spain **INVITED**

The quantification of H at the surface is a subject of key importance. However, direct quantification of this element at the surface region (<2-3 nm) is not an easy task. Note for example that H does not show photoemission peaks in standard surface analysis by XPS. An indirect way to quantify it is by means of High Resolution Electron Energy Loss Spectroscopy, but only those H atoms participating in the vibrational absorption spectra would be observed. It is also possible H quantification with surface sensitivity by means of Nuclear Reaction Analysis, but this technique is not easily available.

Recently it has been proposed a method to quantify the H content at the surface of a-C:H samples based in the analysis of elastically backreflected electrons with primary energies about 1500 eV [1,2]. It is based on the fact that the recoil energy of the incident electrons depends on the atomic mass of the atoms located at the surface that act as scatter centres. Fairly consistent analysis were found for a-C:H materials and polymer surfaces. [1,2]. This new strategy of analysis has also been use to distinguish between H and deuterium (D) at the surface of ice water. The possibilities of this new technique, in combination with standard X-ray photoemission, for example for the study of polymer surfaces that have been labelled with either H or D, will be discussed.

[1] F. Yubero, V.J. Rico, J.P. Espinós, J. Cotrino, A.R. González-Elipe, Applied Physics Letters 87, 084101 (1-3) (2005)

[2] V.J. Rico, F. Yubero, J.P. Espinós, J. Cotrino, A.R. González-Elipe, D. Garg, S. Henry, Diamond and Related Materials 16, 107-111 (2007)

10:40am **AS-WeM9 Hot Electron Transport Properties of Thin Copper Films Using Ballistic Electron Emission Microscopy**, ***J.J. Garramone***, *J.R. Abel, I.L. Sitnitsky,* University at Albany, *L. Zhao, I. Appelbaum,* University of Maryland, *V.P. LaBella*, University at Albany

Copper is widely used material for electrical interconnects within integrated circuits. In addition it has been recently utilized as a base layer for hot electron spin injection and readout into silicon[1]. Integral to both their application is the knowledge of the electron scattering length. Surprisingly little work exists that directly measures the scattering length of electrons in copper. One method for studying hot electron transport on the nanometer length scale is ballistic electron emission microscopy (BEEM). BEEM is a three terminal scanning tunneling microscopy (STM) based technique, where electrons tunnel from a STM tip into the grounded metal base of a Schottky diode[2]. The electrons that transverse the metal overlayer and surmount the Schottky barrier are measured as the BEEM current by a backside contact to the semiconductor.

In this study we used BEEM to measure the hot electron attenuation length of copper on Si. The samples consists of Au/Cu/Si(001) Schottky diodes and the measurements were taken at 77K under UHV conditions. The Au capping layer is used to inhibit the growth of copper's native oxide. Analysis of BEEM current as a function of tip bias yield a Schottky barrier height of 0.64±0.02 eV. The barrier height is in good agreement with

previous current-voltage measurements[3-5]. This, along with Rutherford backscattering spectrometry, indicates that we are measuring the Cu/Si Schottky height and have the ability to measure the attenuation length of copper by measuring the BEEM current as a function of Cu thickness. The measured hot electron attenuation length of Cu is 41.64±1.2 nm at a tip bias of 0.9 eV. The attenuation length decreases monotonically with increasing tip bias and is in good agreement with electron-electron scattering as derived from Fermi liquid theory with the addition of an elastic scattering term that is independent of tip bias. This provides insight into sources of both elastic and inelastic scattering of electrons in Cu.

References:

[1] Biqin Huang, et al., Phys. Rev. Lett. 99 177209 (2007)

[2] L. D. Bell and W. J. Kaiser, Phys. Rev. Lett. 61 2368 (1988)

[3]R. W. Soshea, et al., Phys. Rev. 138 A1182 (1965)

[4] J. M. Seiller, et al., Solid State Commun. 15 973 (1974)

[5]C. R. Crowell, et al., Phys. Rev. 127 2006 (1962)

11:00am **AS-WeM10 XPS Imaging Techniques for the Chemical Characterization of Fuel Cell Membrane Electrode Assemblies***,* ***A.E. Wright****, T.S. Nunney, R.G. White,* Thermo Fisher Scientific, UK, *K.S. Reeves, K.L. More, H.M. Meyer III*, Oak Ridge National Laboratory

Fuel cell technology is reliant on the successful development of membrane electrode assemblies (MEA), which consist of a proton exchange membrane (PEM) sandwiched between catalyst-containing anode and cathode layers. X-ray photoelectron spectroscopy (XPS) with its high surface sensitivity and chemical state sensitivity is an ideal technique for characterizing fuel cell MEA chemical composition. Typically MEA membranes are in the range of 20-50µm thick, ruling out practical usage of conventional Ar ion or other profiling methods to obtain chemical composition profiles. To overcome these sample analysis constraints the MEA samples were prepared using an ultra low-angle microtomy (ULAM) technique. With the ULAM sectioning technique it is possible to extend a ~25 µm thick membrane to present an analysis area of over 400µm. Extending the analysis area of the MEA cross-section improves the opportunity to extract chemical state imaging information using a non-microscopy based technique such as XPS. Minimization of X-ray induced damage, preserving of chemical state information, is considered a significant experimental consideration for XPS polymer analysis. For this reason, rapid acquisition modes are preferred. This presentation will focus on the practicalities of rapid of XPS image acquisition methods and automated data review and processing techniques for the study of MEA structures

Research supported by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cell, and Infrastructure Technologies Program. Research at the ORNL SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Dept. of Energy.

11:20am **AS-WeM11 Formation of Hydroxyapatite Films on Thin Etridonate Films formed on Stainless Steel and Titanium Studied by Core and Valence Band XPS - A Potentially Biocompatible Surface for Implants***, F. Gao,* ***P. Sherwood***, Oklahoma State University

This work reports the preparation of hydroxyapatite films formed on metals which were coated with a thin oxide free film of metal etidronate. The metals studied were stainless steel and titanium. The key to adhesion of the hydroxyapatite films is the initial formation of a thin, oxide free, etidronate film on the metal. It was not found possible to prepare the hydroxyapatite films directly on the metal surfaces. Since hydroxyapatite is a key component of bone and teeth, it is likely that the coated metals will have desirable biocompatible properties, and that these treated metals may find applications in the production of medical implants. The surface chemistry of the films was examined by core and valence band X-ray photoelectron spectroscopy. The valence band spectra were interpreted by cluster and band structure calculations. The valence band spectra proved especially valuable in the identification of the surface chemistry of the films.

11:40am **AS-WeM12 Enhancing Information Extracted from XPS Spectra using a Near Real-Time Data Analysis Package***,* ***A.S. Lea****, K.R. Swanson, J.R. Haack, M.H. Engelhard, D.R. Sisk, D.R. Baer,* Pacific Northwest National Laboratory, *J.E. Castle,* University of Surrey, UK, *S. Tougaard*, University of Southern Denmark

The utilization of x-ray photoelectron spectroscopy (XPS) for the analysis of different types of materials is rapidly growing around the world due to the importance of surface and interfaces and the need for a more detailed analysis of many types of these materials. But, as the use of XPS expands, the knowledge of the technique by the typical user actually decreases and the knowledge and methods that have been developed over the years is not readily transferred to new users. To address this need, a method to automate some aspects of data analysis being developed in the Environmental Molecular Sciences Laboratory (EMSL) and is described here.

Real-time (or near real-time) analysis of the XPS data as it is collected has several potential advantages to scientists and instrument operators. It not only has the potential to improve the turn-around time for data analysis and the sophistication of data analysis reportable to the User, but also to reduce the labor involved in data analysis and reporting, resulting in significant time (and cost) savings. The rapid data analysis can also impact the amount of data that needs to be collected and alter the course of planned measurements. Our development of a near real time XPS analysis has goals to provide atomic composition, carbon contamination layer thickness and component segregation (layer) information as soon as adequate data is collected on a specimen. This real-time data analysis package follows many elements of the expert system approach proposed by Castle[1] and some analysis methods developed by Tougaard[2]. A set of rules and algorithms are used to address a well defined series of analysis objectives to characterize the surface in terms of atomic concentration, layer sequences, and enrichment/depletion of elements as a function of depth.

We will demonstrate the rapid identification of the presence of carbon contamination (using an expert system approach to contrast this with carbon incorporation in the sample), production of a corrected surface composition analysis when the carbon is contamination, and determination of surface enrichment (or depletion) capabilities of our data analysis package using several examples of samples we have analyzed in our laboratory.

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2. Tougaard, S., *J. Vac. Sci. Technol. A* 21(4) (2003) 1081-1086.

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