

# Friday Morning, November 2, 2012

## Applied Surface Science

Room: 20 - Session AS+TF+VT-FrM

### Surface Analysis using Synchrotron Techniques

**Moderator:** A. Herrera-Gomez, UAM-Azcapotzalco and CINVESTAV-Queretaro, Mexico, J.C. Woicik, National Institute of Standards and Technology

8:20am **AS+TF+VT-FrM1 Surface and Interface Analyses by X-ray Absorption and Hard X-ray Photoemission Spectroscopies**, *Q. Xiao, X. Cui*, Canadian Light Source, Canada, *H. Piao*, General Electric Global Research Center, *Y.F. Hu*, Canadian Light Source, Canada, *T.K. Sham*, The University of Western Ontario, Canada

Synchrotron-based techniques, such as X-ray absorption spectroscopy (XAS) and variable energy X-ray photoemission spectroscopy (XPS) are increasingly applied to the characterization of surfaces and interfaces of advanced materials. This presentation will introduce the XAS and variable energy XPS capabilities in the study of thin films and nanomaterials at the Canadian Light Source—the third generation synchrotron in Canada. Advantages of these techniques over the conventional techniques (such as lab-based XPS) will be demonstrated using examples in studies of two types of materials: (1) Gate oxide development on SiC and (2) heterogeneous nanocatalysts. In particular, examples using the recently commissioned high energy XPS at the SXRMB beamline (up to 10 KeV) will be highlighted.

8:40am **AS+TF+VT-FrM2 Differences in the Electronic Structure Highly-Oriented Films of H<sub>2</sub>, Fe-, Co-, and Cu-Phthalocyanines Revealed by NEXAFS Spectroscopy**, *T.M. Willey, M. Bagge-Hansen, J.R.I. Lee, R. Call, L. Landt, T. van Buuren*, Lawrence Livermore National Laboratory, *C. Colesniuc, C.M. Monton, I. Schuller*, University of California, San Diego

Phthalocyanines are extensively studied as molecular semiconductor materials for chemical sensors, dye-sensitized solar cells, and other applications. Phthalocyanines offer high tunability through the choice of metal center atom; nearly all transition metals and many other heavier elements can reside at the relatively stable square planar center of the phthalocyanines. H<sub>2</sub>, Fe-, Co-, and Cu-phthalocyanine molecules in films deposited on gold substrates show prostrate orientation, as opposed sapphire substrates, where phthalocyanines stand in a more upright conformation under deposition conditions used. Angular dependence in NEXAFS, commonly attributable to  $\pi^*$  and  $\sigma^*$  resonances, in both carbon and nitrogen K-edges, quantify the orientational order. H<sub>2</sub>-phthalocyanine shows the cleanest angular dependence, with nearly no intensity in the  $\pi^*$  regime with normal beam incidence. Metal L-edges in prostrate films, on the other hand, have dramatic variation in angular dependence of resonances into empty states. Fe- and Co- resemble the K-edges; StoBe DFT shows that the lowest-energy allowed resonances are indeed molecular  $\pi^*$  states, with a high degree of mixing with the  $d_{xz}$  and  $d_{yz}$  orbitals of the metals. In contrast, the intense, in-plane resonance of the Cu-PC L-edge LUMO resembles a molecular  $\sigma^*$  state. Confirmed by StoBe, the  $d_{x^2-y^2}$  character at the Cu center is responsible for this intense in-plane resonance. NEXAFS thus directly probes the electronic structure, illuminating the uniqueness of Cu-compared to H<sub>2</sub>, Fe-, and Co- phthalocyanines.

9:00am **AS+TF+VT-FrM3 Hard X-ray Photoelectron Study of Graphene/ h-BN Layer Structures Grown on Polycrystalline Cu Substrates**, *L. Kövér*, MTA ATOMKI, Hungary, *L. Tapasztó*, Inst. Tech. Physics and Materials Sci. & Korea-Hungary Joint Lab for Nanosciences, Hungary, *C. Hwang*, KRISS & Korea-Hungary Joint Lab for Nanosciences, Republic of Korea, *L.P. Biró*, Inst. Tech. Physics and Materials Sci. & Korea-Hungary Joint Lab for Nanosciences, Hungary, *I. Cserny, J. Tóth, A. Csik*, MTA ATOMKI, Hungary, *W. Drube, S. Thiess*, Deutsches Elektronen-Synchrotron DESY, Germany

#### INVITED

Graphene-hexagonal BN layer structures are recently in the focus of interest having a great potential importance as promising candidates to be utilized in many electronic and spintronic ultrathin device applications. Hard X-ray photoelectron spectroscopy (HAXPES) based on application of synchrotron radiation for excitation is a useful tool for revealing multilayer structures nondestructively providing information on the chemical state of the components at the surface and (even in the case of deeply embedded) interface layers. The aim of the present study is to test the applicability of the HAXPES method for characterizing graphene-hexagonal BN layer systems. h-BN and single layer graphene/multilayer h-BN structures were grown on polycrystalline Cu substrates using the Chemical Vapor Deposition technique [1]. HAXPES measurements were performed at the

BW2 beamline of the DORIS III synchrotron at DESY using the Tunable High Energy XPS facility [2] and monochromatic photons of 3000 eV energy. The surface layer structure of the same samples were also studied with conventional XPS in ATOMKI using non-monochromated Al K $\alpha$  radiation [3]. For obtaining information on the order and relative depth of the particular layers the dependence of the XPS and HAXPES spectra on the angle of emission of photoelectrons was also studied. Our results demonstrate the advantage of the combination of XPS and HAXPES measurements, the use of the Auger parameter for identifying the chemical state of the components at the interface between the layer structure and the substrate, the removal of the overlap between the Auger spectra from the substrate and the photoelectron spectra of the overlayer structure in the HAXPES spectra. In addition, HAXPES, due to the high energy resolution and sensitivity applied, makes possible the separation and identification of the contributions from atoms in different chemical states to photoelectron peaks of the components of the layer structure, and the quantitative estimation of their relative intensity, even at near grazing photon beam incidence (high surface sensitivity).

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[2] W. Drube, T. M. Grehk, R. Treusch and G. Materlik, J. Electron Spectrosc. Relat. Phenom. **88-91**, 683 (1998).

[3] L. Kövér, D. Varga, I. Cserny, J. Tóth, K. Tökési, Surf. Interface Anal. **19**, 9 (1992).

9:40am **AS+TF+VT-FrM5 Beyond Hard X-ray Photoelectron Spectroscopy: Simultaneous Combination with X-ray Diffraction**, *G.R. Castro, J. Rubio-Zuazo*, SpLine at the European Synchrotron Radiation Facility, France

Nowadays, the great challenge in materials science is the incorporation of complex systems in the area of the nano-technologies. A fundamental aspect is the production of materials with specific and controlled properties. Many of these materials are aggregates of different components, frequently multilayer thin films where the interface and the surface play a key role. Therefore, it is very important to develop an experimental set-up capable to investigate different aspects under identical experimental conditions, in particular to differentiate between surface and bulk properties.

*Hard X-ray photoelectron spectroscopy (HAXPES)* is a powerful novel emerging technique for bulk compositional, chemical and electronic properties determination in a non-destructive way. It benefits from the exceptionally large escape depth of high kinetic energy photoelectrons enabling the study of bulk and buried interfaces up to several tens of nanometres depth. At SpLine, the Spanish CRG beamline at the European Synchrotron Radiation Facility (ESRF), we have developed a novel and exceptional set-up that combine HAXPES and X-ray diffraction ( X-ray Reflectivity, Surface X-ray Diffraction, Grazing Incidence X-ray Diffraction and reciprocal space maps ). Both techniques can be operated simultaneously on the same sample and using the same excitation source. The set-up includes a robust 2S+3D diffractometer with its main axis vertical hosting an UHV chamber equipped with a unique photoelectron spectrometer (few eV < E<sub>kin</sub> < 15keV), X-ray tube (Mg/Ti), 15 keV electron gun and auxiliary standard surface facilities: MBE, ion gun, LEED, sample heating/cooling system, leak valves, load-lock port, etc.. The photon energy ranges between 7 and 45 keV. The HAXPES analyzer is an electrostatic cylinder-sector (FOCUS HV CSA), with a compact geometry and high transmission due to second order focusing. The analyzer is capable to handle kinetic energies both up to 15 keV and down to a few eV with the same analyzer setup and power supply. The SpLine station offers a unique opportunity to obtain, on a same sample and under identical experimental conditions, simultaneous information about the electronic properties, chemical composition and geometric/crystalline structure of bulk, buried interfaces and surfaces. This *novel tool* for non-destructive characterization of bulk and buried interfaces is available to the *scientific community*.

In this contribution, we will present a general view of HAXPES-XRD station available at SpLine. Three aspects will be specially addressed: physical background, experimental set-up and selected examples.

10:00am **AS+TF+VT-FrM6 Spectroscopic Imaging using Vector Potential Photoelectron Microscopy, R. Browning, R. Browning Consultants**

A new class of electron microscope, vector potential photoelectron microscopy (VPPEM) has been developed. This microscope will enable the chemical microanalysis of a wide range of samples using photoelectron spectroscopy (PES). The microscope is a full field spectroscopic imaging technique with a very large equivalent depth of focus. The unique imaging properties of this method opens up many experimental opportunities including the chemical microanalysis of a wide range of real world samples. Highly structured, three dimensional samples, such as fiber mats and fracture surfaces can be imaged, as well as insulators, and magnetic materials. The new microscope uses the vector potential field from a solenoid magnet as a spatial reference for imaging. A prototype instrument has demonstrated imaging of Au grids, uncoated silk, magnetic steel wool, and micron sized single strand tungsten wires.

10:20am **AS+TF+VT-FrM7 Trends in Synchrotron-based Photoemission; High Energy and High Pressure, H.J. Bergersen, J. Åhlund, R. Moberg, VG Scienta, Sweden**

The fields of Hard X-ray Photoelectron Spectroscopy (HAXPES) and High Pressure Photoemission (HiPP) are growing fast. In this contribution we present instrument development and results within HAXPES and HiPP as well as the merged field of HiPP-HAXPES.

Photoelectron spectroscopy (PES) is an excellent tool in surface science due to the possibility to probe electronic and geometric structure. During the past decade Angle Resolved Photoelectron Spectroscopy (ARPES) has had a remarkable upswing, due to the development of parallel angular detector analyzers, and is today used routinely for band mapping, depth profiling and X-ray diffraction (XPD) in the Ultra Violet (UV) and soft X-ray regime. With higher energies (hard X-rays), in combination with improvements in PES detection techniques, this tool can be extended to the HAXPES regime, enabling studies of bulk materials. Here we demonstrate new development of analysers capable of measuring angular resolved spectra in the High Energy regime as well as results obtained using such analyzers.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. Here we present a HiPP instrument developed in collaboration with Advanced Light Source (ALS). This instrument allows standard PES measurements as well as spatial and angle resolved spectra at HiPP conditions. Some recent results include spatially resolved investigations of solid oxide electrochemical cells (SOC:s) and electrochemical properties of junctions.

Finally, we report on recent advances in constructing a new generation of instrumentation combining HiPP and HAXPES. A novel electron analyser, designed for optimal transmission in combination with very efficient differential pumping, will be presented together with preliminary results.

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