Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 9 - Session SA+AS+HC+SS-TuA

Frontiers of Photoelectron Spectroscopy: Surface & Interface Processes with Variable Depth Probe, High Spatial or Temporal Resolution

Moderators: Geoff Thornton, University College London, Carla Bittencourt, University of Mons, Belgium

2:20pm **SA+AS+HC+SS-TuA-1 AVS 2017 Medard W. Welch Award Lecture: Ionic Liquid Surface Science***, **Hans-Peter Steinrück**[1],* University Erlangen-Nuernberg, Germany **INVITED**

Ionic liquids (ILs) are molten salts with a melting point below 100◦C. They represent a new class of liquid materials with unique property profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van der Waals interactions of their ions. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as 'task-specific ionic liquids'. Applications range from catalysis and organic synthesis to tribology, protective coatings and gate dielectrics. In catalysis, two important concepts are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. The interface of the IL with the gas phase/vacuum or with the solid support plays an important role. Therefore, knowledge about surface and interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. In contrast to most other liquids, ionic liquids have a very low vapor pressure, and thus can be studied with the methods of ultrahigh vacuum-based surface science. One particularly powerful method is angle-resolved X-ray photoelectron spectroscopy. Thereby, detailed information on their surface composition, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes, on the growth of ultrathin IL-layers, and even on reactions in the liquid phase, can be obtained. Several examples will be discussed illustrating the power of surface science to study this new materials class. Many of the derived conclusions are considered representative for liquid surfaces in general.

F. Maier, I. Niedermaier, and H.-P. Steinrück, *"Perspective: Chemical Reactions in Ionic Liquids Monitored through the Gas (Vacuum)/Liquid Interface",* J.Chem. Phys. **2017** (in press)

H.-P. Steinrück and P. Wasserscheid, "*Ionic Liquids in Catalysis*", Catal. Lett. **2015**, *145*, 380.

H.-P. Steinrück, "*Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions*", Phys. Chem. Chem. Phys. **2012**, *14*, 2510.

H.-P. Steinrück, "*Surface Science goes liquid !*", Surf. Sci. **2010**, *604*, 481.

3:00pm **SA+AS+HC+SS-TuA-3 *In Situ* Characterization of Semiconductor Nanowire Devices by Nano-Focus X-ray Photoemission Microscopy and Spectroscopy***, S McKibbin, **Andrea Troian**, S Yngman,* Lund University, Sweden*; H Sezen, M Amati, L Gregoratti,* Elettra-Sincrotrone Trieste, Italy*; A Mikkelsen, R Timm,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. X-ray photoemission spectroscopy (XPS) has been proven highly suitable for studying surface composition and electronic properties of homogeneous NWs [3]. However, in order to better understand NW device performance, it is essential to also investigate NW heterostructures, with nm-scale lateral resolution and during device operation.

Here, we will present nano-focus XPS results from material and doping heterostructures in InP and GaInP NWs intended for photovoltaic application [2]. We used scanning photoemission microscopy (SPEM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (Ga)InP *pn*-junctions and InP/GaP tunnel junctions, obtained from In 3d, In 4d, and P 2p XP spectra acquired along the heterostructure NW. Electrical contacts were provided to both ends of the investigated NW, allowing to vary the source-drain bias along the NW during SPEM characterization. We will present detailed results on the influence of built-in potential and external forward and backward bias on the surface potential distribution across NW interfaces.

In another approach, we aim at revealing *in-situ* the interplay of surface chemical composition and local electronic properties. As a model system, we chose InAs NWs consisting of several segments of wurtzite and zincblende crystal structure [4]. At the interface between such segments, we confirmed a staggered type-II electronic band alignment, obtained from nano-focus XP spectra along externally biased NWs. After removing the native oxide from the NW surface by atomic hydrogen annealing [4] in the XPS UHV chamber, the same NW instead showed flat-band conditions, which is preferential for electronic application [1]. We will discuss future plans of using the dynamic high pressure option of the ESCAMicroscopy beamline for changing the surface chemistry of NWs while simultaneously investigating them with SPEM and nm-scale spectroscopy.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

[3] R. Timm *et al.,* Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.,* Nano Lett. **15**, 4865 (2015).

[4] M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

3:20pm **SA+AS+HC+SS-TuA-4 Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells***, **Daniela Schoen**,* Helmholtz-Zentrum Berlin, Germany

Photons and electrons are two common relaxation products upon X-ray absorption, enabling fluorescence yield and electron yield detections for X-ray absorption spectroscopy (XAS). The ions that are created during the electron yield process are relaxation products too, which are exploited in this study to produce ion yield for XA detection. The ionic currents measured in a liquid cell filled with water or iron(III) nitrate aqueous solutions exhibit characteristic O K-edge and Fe L-edge absorption profiles as a function of excitation energy. Application of two electrodes installed in the cell is crucial for obtaining the XA spectra of the liquids behind the membrane. Using a single electrode can only probe the species adsorbed on the membrane surface. The ionic-current detection, termed as total ion yield (TIY) in this study, also produces an undistorted Fe L-edge XA spectrum, indicating its promising role as a novel detection method for XAS in liquid cell.

5:00pm **SA+AS+HC+SS-TuA-9 Non-destructive Depth Profiling of $LaAlO_3$/$SrTiO_3$ Interfaces***, **Conan Weiland**,* NIST*; A Rumaiz,* National Synchrotron Light Source II, Brookhaven National Laboratory*; G Sterbinsky,* Advanced Photon Source, Argonne National Laboratory*; J Woicik,* NIST

The interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) is known to be conductive, even though both LAO and STO are insulators. The interface may also host a variety of interesting phenomena such as a two-dimensional electron gas, ferromagnetism, and superconductivity. Various mechanisms have been proposed to explain the formation of the conductive interface, including the 'polar catastrophe', wherein the polar discontinuity at the interface leads to a diverging potential allowing electronic reconstruction, oxygen vacancies at the interface or at the LAO surface, and chemical intermixing, amongst others.

Synchrotron-based variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) is a unique and powerful tool to non-destructively probe the chemical and electronic structure of buried interfaces such as that between LAO and STO. Using VKE-XPS, we have analyzed a series of LAO films on STO and have observed compositional variations in the LAO films as a function of depth: Al-enrichment occurs at the LAO surface. Additionally, an electric field was observed in some samples. In this presentation we will discuss the relevance of these results on the formation of conductive LAO/STO interfaces.

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[1] **Medard W. Welch Award Winner**

5:20pm **SA+AS+HC+SS-TuA-10 Hard X-ray Photoelectron Spectroscopy Study of the Resistive Switching in Te-based Conductive Bridging Random Access Memories*, Munique Kazar Mendes,*** *E Martinez, O Renault, R Gassilloud, M Bernard, M Veillerot,* CEA/LETI-University Grenoble Alpes, France*; J Ablett,* Synchrotron SOLEIL, France*; N Barrett,* SPEC, CEA Saclay - University Paris-Saclay, France

Conductive bridging random access memories (CBRAM) are emerging devices for the next generation of non-volatile memories (NVM) (1). The CBRAM mechanism is related to ionic transport and electrochemical reactions, which give rise to the formation and dissolution of a conductive filament through the insulating dielectric layer (2). Data storage relies on switching the resistivity between two high (HRS) and low (LRS) resistance states by applying voltage or current pulses. We investigate the electrochemical reactions involved in the switching mechanism of Al_2O_3-based CBRAMs with different active electrodes (TiTe and ZrTe) (3). We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The HAXPES experiments were performed at the Galaxies beamline (Soleil) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between these different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. For the TaN/TiTe/Al_2O_3/Ta stack, results highlight, the reduction of Ti together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the O^{2-} form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte (Al_2O_3). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode. These results reveal the important role of oxygen migration in the filament formation/dissolution. ToF-SIMS measurements are also performed to get complementary in-depth chemical information. We will finally compare the two active electrodes to investigate the influence of the composition on the switching mechanism.

References

1. Kozicki MN, Barnaby HJ. Conductive bridging random access memory—materials, devices and applications. Semicond Sci Technol. 2016;31(11):113001.

2. Waser R, Dittmann R, Staikov G, Szot K. Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges. Adv Mater. 2009 Jul 13;21(25-26):2632–63.

3. Jameson JR, Kamalanathan D. Subquantum conductive-bridge memory. Appl Phys Lett. 2016 Feb 1;108(5):053505.

5:40pm **SA+AS+HC+SS-TuA-11 Correlation of the Magnetic and Magnetotransport Properties, Electronic and Atomic Structure of Strongly Correlated Complex-oxide Thin Films with the Oxygen Vacancies and Films Thickness*, German Rafael Castro,*** Spanish CRG BM25 Beamline at the ESRF, France*; J Rubio Zuazo,* SpLine Spanish CRG BM25 Beamline at the ESRF, France

Herewith, we present structural, electronic, morphological and magnetotransport properties of thin films of perovskite-manganese oxides (maganites) grown on SrTiO3(001) by oxygen assisted pulsed laser deposition (PLD) methods, using Hard X-ray Photoelectron Spectroscopy (HAXPES), and Grazing Incidence X-ray diffraction (GIXRD).

Perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. La_{1-x}CaxMnO_3–type perovskite-manganese oxides are strongly correlated electron systems and exhibit, in the Ca doping range between 0.15 and 0.5, a ferromagnetic–paramagnetic (FM) phase transition accompanied by a metal–insulator (MI) transition that results in a colossal magneto-resistance behaviour. In bulk $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), the transition temperature TFM, TMI rises for 33% Ca doping level reaching values close to room temperature. The results shown here are focused on the study of the influence of buried interfaces and the oxygen vacancies on the electric and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films grown on $SrTiO_3$(001)

The growth of these materials in thin film form opens possibilities for magneto-electronic devices applications. The atomic and electronic structures, as well as the oxygen content, are followed simultaneously by GIXRD and HAXPES. Combining GIXRD, HAXPES and transport techniques, we have established a correlation between the electronic, atomic structure and magnetic and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films as a function of the oxygen vacancies and films thickness.

6:00pm **SA+AS+HC+SS-TuA-12 Synchrotron–Based X-ray Spectroscopy Studies of Inorganic-Organic Hybrid Halide Perovskite Materials Surfaces and Properties*, Deidra Hodges,*** *S Shahriar, A Mishra, V Castaneda, V Vidal, M Martinez, N Garcia, J Munoz, J Lopez,* University of Texas at El Paso

Recently, the methylammonium lead iodide $CH_3NH_3PbI_3$ perovskites have attracted a lot of attention as a possible absorber material for thin film solar cells due to their bandgap energy, high optical absorption coefficients and low-cost solution-processing deposition approaches. Methylammonium lead iodide $CH_3NH_3PbI_3$ perovskite solar cells have evolved with transformative potential with laboratory efficiencies greater than 20%. Perovskite absorber materials are very inexpensive to synthesize and simple to manufacture, making them an extremely commercially viable option. Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to a Newport certified 20.1% in 2015, making this the fastest-advancing solar cell technology to date. These devices are known for their high photon absorptivity, tunable large direct band gaps with superior carrier charge transports, and low-cost methods of fabrication. Methylammonium lead tri-iodide $CH_3NH_3PbI_3$ perovskites thin films and single crystals were prepared for synchrotron-based X-ray spectroscopy studies of the perovskite materials surfaces and properties. The perovskite thin films and single crystals were characterized at the National Synchrotron Light Source (II) (NSLS-II) at Brookhaven National Laboratory (BNL). Synchrotron-radiation-based chemical analysis using X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES) spectroscopy were performed on samples for detailed analysis into chemical composition, stoichiometry, and material surface properties.

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