

## Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

### Room 9 - Session SA+AS+HC+SS-WeA

#### In Situ and Operando Characterization of Interfacial Reactions in Energy & Electronic Devices

**Moderators:** Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory, Elke Arenholz, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-WeA-1 Probing Solid-Gas and Solid-Liquid Interface Using APXPS**, *Zhi Liu*, ShanghaiTech University, PR China, China; *J Cai, Q Liu*, ShanghaiTech University, PR China; *Y Han*, Chinese Academy of Sciences, PR China; *J Liu*, ShanghaiTech University, PR China; *M Mao, H Zhang*, Chinese Academy of Sciences, PR China; *Y Li*, ShanghaiTech University, PR China

#### INVITED

Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Most of the research has been focused on the solid-gas interfaces. [1] Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. [2] In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell. I will also give a brief introduction on the APXPS development in Shanghai.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study interface phenomena at Solid-Gas and Solid-Liquid Interfaces.

#### References

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2. S. Axnanda et. al, Scientific Reports, 5,9788 (2015).

3:00pm **SA+AS+HC+SS-WeA-3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces**, *Hongxuan Guo, E Strelcov, A Yulaev*, NIST, Center for Nanoscale Science and Technology; *S Nemšák, D Mueller, C Schneider*, Peter Grünberg Institute and Institute for Advanced Simulation, Germany; *A Kolmakov*, NIST, Center for Nanoscale Science and Technology

The liquid-solid electrochemical interfaces are a central topic of modern energy-related electrochemistry and catalysis research. For the last two decades, this research line benefited greatly from the development of differentially pumped electron optics and refreshable sample delivery systems which became an experimental core of the modern ambient pressure electron spectroscopy. An alternative experimental approach to atmospheric pressure electron microscopy (SEM<sup>1</sup>, SPEM<sup>2</sup>, PEEM<sup>3</sup>) and spectroscopy (XPS<sup>4,5</sup>, XAS<sup>3,6</sup>) has been recently tested. In this approach, high electron transparency and molecular impermeability of the graphene membrane was employed to separate the liquid or gaseous sample from ultra-high vacuum environment of electron spectrometer.

In this presentation, we will show our recent work on design and performance of the static and fluidic microfabricated arrays (MCA) capped with bilayer graphene. With such a liquid cell, we characterized water and aqueous solution employing synchrotron-based and standard laboratory XPS, SEM, EDX, and Auger spectroscopy setups<sup>7</sup>. In particular, Cu electroplating and copper sulfate electrolyte polarization at the graphene working electrode have been studied spectroscopically in real time and nanoscopic spatial resolution.

#### Acknowledgement

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2. A. Kolmakov, D. A. Dikin, L. J. Cote, J. Huang, M. K. Abyaneh, M. Amati, L. Gregoratti, S. Günther and M. Kiskinova, Nature nanotechnology 6 (10), 651-657 (2011).

3. H. Guo, E. Strelcov, A. Yulaev, J. Wang, N. Appathurai, S. Urquhart, J. Vinson, S. Sahu, M. Zwolak and A. Kolmakov, Nano letters (2017).

4. J. Kraus, R. Reichelt, S. Günther, L. Gregoratti, M. Amati, M. Kiskinova, A. Yulaev, I. Vlasiouk and A. Kolmakov, Nanoscale 6 (23), 14394-14403 (2014).

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7. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlasiouk and A. Kolmakov, ACS Applied Materials & Interfaces (accepted) (2017).

3:20pm **SA+AS+HC+SS-WeA-4 A 3D Printed Liquid Cell for Soft X-ray Absorption Spectroscopy**, *Tom Regier, T Boyko, J Dynes*, Canadian Light Source, Inc., Canada; *Z Arthur*, Canadian Light Source, Inc.; *M Banis*, University of Western Ontario, Canada

Research methods that enable operando studies on energy materials are an important tool for the rational design of materials for renewable energy and carbon neutral technologies. Of particular value is the ability to observe the change in configuration of the 3d orbitals in transition metal based catalysts. Using the excitation of 2p electrons into vacant 3d orbitals, synchrotron based L-edge measurements allow for clear observation of chemical state and co-ordination geometry information from the first row transition elements. Challenges related to the operating in-situ flow cells in soft x-ray beamline endstations have been overcome and operando measurements are now possible at several facilities.

We report on the design of a 3D printed liquid flow cell with built-in electrodes for operando measurements of the transition metal L-edges. The disposable cells can be quickly customized for specific experiments and can be pre-ordered for lab-based characterization before attempting synchrotron measurements. Beamline instrumentation allows for highly sensitive fluorescence yield measurements with 10 micron spatial resolution or 1 minute time resolution.

4:20pm **SA+AS+HC+SS-WeA-7 In Operando Quantification of Valence Changes in Memristive Devices**, *R Dittmann, Christoph Baeumer*, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany; *D Cooper*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France; *C Schmitz, S Menzel, C Schneider, R Waser*, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany

#### INVITED

Memristive devices based on resistive switching in transition metal oxides are attractive candidates for next-generation non-volatile memory applications. It is suspected that voltage-driven oxygen-ion migration and the resulting nanoscale redox processes drive the resistance change in these materials<sup>1,2</sup>. Direct observation and quantification of the switching mechanism itself, however, remain challenging because the net changes of structure, stoichiometry, and valence state during switching are very small and occur primarily at electrode interfaces or within nanoscale filaments.

Here we will present local changes in the chemical and electronic structure of SrTiO<sub>3</sub>-based memristive devices utilizing *in operando* characterization tools like transmission electron microscopy (TEM) and photoemission electron microscopy (PEEM). SrTiO<sub>3</sub> is chosen as a single crystalline model material, which offers a well-understood platform and well-characterized spectroscopic signatures.

To overcome the surface sensitivity typically limiting PEEM investigations of memristive devices, photoelectron-transparent graphene top electrodes are used to attain spectroscopic information from the buried SrTiO<sub>3</sub> layer<sup>3</sup>. During *in situ* switching, reversible changes of the O K-edge absorption spectra within spatially confined regions provide a quantitative map of the oxygen vacancy concentration, confirming that the resistance change is caused by localized oxygen evolution and reincorporation reactions rather than purely internal movement of oxygen vacancies<sup>4</sup>.

A remarkable agreement between experimental quantification of the redox state and device simulation reveals that changes in oxygen vacancy concentration by a factor of 2 at electrode-oxide interfaces cause a modulation of the effective Schottky barrier and lead to >2 orders of magnitude change in device resistance. These findings allow realistic device simulations, opening a route to less empirical and more predictive design of future memory cells.

<sup>1</sup> R. Waser and M. Aono, Nat. Mater. 6, 833 (2007).

<sup>2</sup> R. Waser, R. Dittmann, G. Staikov, and K. Szot, Adv. Mater. 21, 2632 (2009).

# Wednesday Afternoon, November 1, 2017

<sup>3</sup> C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser, and R. Dittmann, *Nat. Commun.* **7**, 12398 (2016).

<sup>4</sup> C. Baeumer, C. Schmitz, A. H. H. Ramadan, H. Du, K. Skaja, V. Feyer, P. Muller, B. Arndt, C. Jia, J. Mayer, R. A. De Souza, C. Michael Schneider, R. Waser, and R. Dittmann, *Nat. Commun.* **6**, 9610 (2015).

5:00pm **SA+AS+HC+SS-WeA-9 Magnetic Skyrmions in Ultrathin Magnetic Films and Nanostructures**, *Jan Vogel*, Institut Néel, CNRS/UGA, Grenoble, France; *O Boulle, R Juge*, SPINTEC, CNRS/CEA/UGA, Grenoble, France; *D Chaves, S Pizzini*, Institut Néel, CNRS/UGA, Grenoble, France; *S Je, G Gaudin*, SPINTEC, CNRS/CEA/UGA, Grenoble, France; *T Mentès, A Locatelli*, Elettra-Sincrotrone Trieste, Italy; *M Foerster, L Aballe*, ALBA Synchrotron Light Facility, Spain

**INVITED**

Magnetic skyrmions are chiral spin structures with a whirling spin configuration. Their topological properties, small size and sensitivity to small current pulses have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion were first experimentally observed in bulk materials [1] and in epitaxial ultrathin films [2], under a strong external magnetic field or at low temperature. More recently, it was predicted that they can also be created in thin magnetic films in stacks with structural inversion asymmetry [3]. We have used high lateral resolution PhotoEmission Electron Microscopy combined with X-ray Magnetic Circular Dichroism (XMCD-PEEM) to show that skyrmions with a size around 150 nm can indeed be stabilized at room temperature and without external magnetic field, in nanostructures of Pt/Co/MgO with a Co thickness of 1 nm [4]. The high sensitivity of the technique allows measuring very thin Co layers buried under protecting cover layers. The vectorial information obtained by rotating the sample with respect to the incoming x-ray direction allowed us obtaining information on the 3-dimensional spin structure of the skyrmions, directly showing the chiral spin configuration with left-handed chirality.

We investigated the dependence of the skyrmion size on an applied magnetic field, revealing that already a moderate field of 4 mT can reduce the skyrmion diameter to a size of 70 nm. We also studied the motion of skyrmions in micron-wide strips of Pt/Co/MgO induced by current pulses. The results show that skyrmions can be moved with moderate current pulses with current densities of some  $10^{11}$  A/m<sup>2</sup>, leading to velocities of several tens of m/s.

Our measurements show that synchrotron-based magnetic imaging using PEEM is very powerful for studying the static and dynamic properties of skyrmions in ultrathin magnetic films.

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5:40pm **SA+AS+HC+SS-WeA-11 O<sub>2</sub> Pressure Dependence of SiO<sub>2</sub>/Si Interfacial Oxidation Rate Studied by Real-time Photoelectron Spectroscopy**, *Shuichi Ogawa*, Tohoku University, Japan; *A Yoshigoe*, JAEA, Japan; *S Ishidzuka*, National Institute for of Technology, Akita College, Japan; *Y Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si surfaces under the non-equilibrium conditions were used to form a high-quality Si oxide films and/or enlarge the oxidation rate. For example, rapid thermal oxidation (RTO) is performed under the raising the temperature, and then thick oxide can be formed without preventing the dopant diffusions[1]. In addition, the oxidation rate of RTO process is faster than that of constant temperature oxidation (CTO) though the highest temperature of RTO is as same as that of CTO[2]. Based on these knowledges, it is predicted that the oxidation rate at the SiO<sub>2</sub>/Si interface can be quickened even by increase of the O<sub>2</sub> pressure. In this study, the increased O<sub>2</sub> pressure dependence of the interface oxidation rate which proceeds contentiously after Si(001) surface oxidation was investigated using real-time photoelectron spectroscopy.

The oxidation experiment was performed using the surface reaction analysis apparatus placed at the BL23SU of SPring-8, Japan. A clean Boron doped p-type Si(001)2x1 surfaces were oxidized at 400°C under the O<sub>2</sub> pressure of 3.2x10<sup>-5</sup> Pa. When clean surfaces were completely covered by the Si oxide, the O<sub>2</sub> pressure was elevated to P<sub>O<sub>2</sub>(int)</sub> in order to enhance the interfacial oxidation. The P<sub>O<sub>2</sub>(int)</sub> was changed between 6.4x10<sup>-5</sup> Pa to 3.2x10<sup>-3</sup> Pa. O 1s and Si 2p spectra were measured repeatedly during the oxidation. The time evolution of O 1s photoelectron intensity (I<sub>O1s</sub>) was used for investigation of the oxidation rate.

From the I<sub>O1s</sub>, we can estimate the completion of surface oxidation as 3200 s. An O<sub>2</sub> pressure was increased up to 1.5x10<sup>-3</sup> Pa at this time, and then the

interface oxidation was enhanced. The enhanced interfacial oxidation rates were obtained from the differential of I<sub>O1s</sub>. The P<sub>O<sub>2</sub>(int)</sub> dependence of the interfacial oxidation rate shows that the O<sub>2</sub> pressure increase makes the interfacial oxidation rate fast, and the interface oxidation rate is proportional to the square root of P<sub>O<sub>2</sub>(int)</sub>.

This result cannot be explained using traditional oxidation models, because the proportional relationship between the interface oxidation rate and square root of P<sub>O<sub>2</sub>(int)</sub> indicates that the interface oxidation rate is limited by an O<sub>2</sub> diffusion through the oxide. However, the thickness oxide is much thinner than 1 nm, so that it cannot be thought that the rate-limiting reaction of interfacial oxidation is O<sub>2</sub> diffusion. To explain the kinetics, we propose the new interface oxidation model named "Unified Si oxidation model mediated by point defects"[3].

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[2] S. Ogawa et al., *J. Chem. Phys.*, **145**, 114701 (2016).

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6:00pm **SA+AS+HC+SS-WeA-12 Highly Time-resolved Insights into the Sputter Deposition of Metal Electrodes on Polymer Thin Films for Organic Electronics**, *Franziska Löhner, V Körstgens*, Technische Universität München, Germany; *M Schwartzkopf*, Deutsches Elektronensynchrotron DESY, Germany; *A Hinz, O Polonskyi, T Strunskus, F Faupel*, Christian-Albrechts-Universität zu Kiel, Germany; *S Roth*, Deutsches Elektronensynchrotron DESY, Germany; *P Müller-Buschbaum*, Technische Universität München, Germany

With their easy processability, high flexibility and tuneable optical properties, organic electronics (OE) offer a wide range of potential applications. Especially photoactive polymers have received attention in recent years as candidates for organic photovoltaics (OPV) and light emitting diodes (OLEDs). Although based on organic materials, their electrodes are typically made from metals due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OE devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes happening at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ grazing incidence small and wide angle x-ray scattering (GISAXS/GIWAXS) [1]. These techniques allow insights into the structural evolution of the metal on the organic film, which depends on various parameters such as the deposition rate or the film morphology. Making use of the brilliant synchrotron light source Petra III at DESY [2], we can study the deposition behavior of the metal on the polymer film with outstandingly high spatial and temporal resolution. The acquired large data sequences are tracked in real-time and further analyzed using the fast data reduction software DPDAK [3]. The final film morphology is characterized via scanning electron microscopy and X-ray reflectometry. UV/Vis absorption and reflection measurements complete our work. The metal layer formation can be described by applying an appropriate growth model based on our earlier work. [4] The model is refined in an iterative process of GISAXS simulations and data fitting. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

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