

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+MI-WeA

Hard X-Ray Photoemission for Probing Buried Interfaces

Moderators: Zahid Hussain, ALS-LBNL, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm SA+AS+MI-WeA-1 Element-resolved Electronic Band Structure of Ga(Mn)As Measured by Standing-wave Hard X-ray Angle-resolved Photoemission, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory; M Gehlmann, C Kuo, University of California, Davis; T Lee, Diamond Light Source Diamond House, Harwell Science and Innovation Campus; L Plucinski, Forschungszentrum Juelich GmbH, Germany; J Minar, University of West Bohemia; C Schneider, Forschungszentrum Juelich GmbH, Germany; C Fadley, University of California, Davis

Electronic band structure of the dilute magnetic semiconductor $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ was obtained using hard X-ray angle-resolved photoemission. The element- and site-sensitivity of the measurements was achieved by forming a strong X-ray standing-wave generated by Bragg reflection from the (111) atomic planes of both undoped GaAs and Mn-doped thin films. Due to the uneven occupancy of (111) planes by either Ga(Mn) or As atoms, the element-specific band structure can be obtained with a help of the SW modulation in core levels. Measured momentum- and element-resolved bulk electronic structure was compared to element-projected Bloch spectral functions with excellent agreement between experiment and theory. Apart from the site specific decomposition of the electronic structure, the SW measurements also confirmed a substitutional presence of Mn atoms at the Ga sites. This novel technique should be applicable to a broad range of complex materials.

2:40pm SA+AS+MI-WeA-2 Probing Surface Band Bending of Polar GaN by Hard X-ray Photoemission Combined with X-ray Total Reflection, Shigenori Ueda, NIMS, Japan

GaN is known as a polar semiconductor due to an alternative stacking of Ga and N layers along the c-axis. Ohsawa *et al.* [1] showed the difference in valence band spectral shapes of the bulk Ga- and N-polar GaN single crystals by using polarization dependent hard X-ray photoemission spectroscopy (HAXPES). In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. The change of incidence angle within 1 degree around the critical angle of X-ray total reflection drastically changes the attenuation length of X-ray in solids.

We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline GaN for Ga and N polar faces in the case of inelastic mean free path of 2.17, 3.73, and 7.69 nm. Undoped n-type GaN crystal with fine polished surfaces was used. For the Ga-polar face, large band bending behavior was observed, while the band bending was small for the N-polar face. The Ga 3s and N 1s core-level spectra also showed the polarity dependent band bending behavior. We found that

GaN near the surface is degraded in both the polar faces. This result suggests that high quality single crystalline GaN with fine surface treatment is required for detecting the intrinsic electronic structure of GaN. Finally we note that HAXPES combined with X-ray total reflection is useful method for depth-resolved electronic structure measurements, since the data acquisition time in this method is 10 or more faster than that in TOA dependent measurement, and the matrix element effect is almost negligible in this method.

References

- [1] T. Ohsawa *et al.*, Appl. Phys. Lett. **107**(2015) 171604.
- [2] Y. Takata *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **547**(2005) 50.
- [3] M. Lozac'h *et al.*, Sci. Technol. Adv. Mater. **14**(2013) 015007.
- [4] S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Rel. Phenom. **21**(1981) 285.

3:00pm SA+AS+MI-WeA-3 Interfaces in Cycled Battery Electrodes: Insights from HAXPES Studies, Julia Maibach, Karlsruhe Institut of Technology (KIT), Germany

INVITED

Rechargeable ion batteries such as lithium and sodium ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. The contacts between the different materials are key to the electrochemical energy storage process and at the surfaces of the electrodes and at the interfaces to the electrolyte, reactions crucial to long-term, safe battery operation take place. Due to its surface and chemical sensitivity, photoelectron spectroscopy has therefore become a widely used tool to characterize and understand the processes and phenomena in these electrochemical energy storage systems.

Looking in more detail, a battery electrode itself is a complex system as it consists of many different components such as the active storage material, conductive additives as well as binders to keep the particles attached to a metal foil, which acts as a current collector. This complexity of mixed materials and morphologies further increases when the electrodes are cycled electrochemically due to the desired storage processes and due to reactions with the battery electrolyte leading to interface layer formation.

These highly complex systems of cycled battery electrodes bring new challenges when studied with photoelectron spectroscopy. In this presentation, observed peak shifts for cycled battery electrodes will be discussed in depth. Particular emphasis will be given to the buried interfaces. Here, hard x-ray photoelectron spectroscopy (HAXPES) is one of the few available techniques that can access the buried interface while maintaining the chemical information from the delicate battery interface layers. Based on HAXPES experiments, the role of the buried interfaces and their importance in both battery operation as well as in photoelectron spectroscopy characterization of cycled electrodes will be discussed.

Additionally, spectral changes due to electrode potentials as well as lithiation effects will be discussed. These strongly depend on the nature of the active material and therefore need to be considered carefully to achieve consistent data interpretation. Combining all presented effects, a strategy for photoelectron spectroscopy experiments on cycled battery electrodes will be proposed that takes buried interfaces into account.

4:20pm SA+AS+MI-WeA-7 Development of Ambient Pressure HAXPES and other HAXPES Measurements at SPring-8 for Buried Interface, Yasumasa Takagi, Japan Synchrotron Radiation Research Institute (JASRI), Japan

INVITED

A near ambient pressure photoelectron spectroscopy measurement that use with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline. The excitation light of 7.94 keV focused to a beam size of 20 μm x 20 μm on the sample surface was used. The standard aperture size at the top of the front cone in the spectrometer is a diameter of 300 μm . In this report, we replaced the front cone with our home-made one with an aperture diameter of 30 μm to increase the pressure limit in the AP-HAXPES measurement. Meanwhile, we have adapted the working distance of 60 μm in order not to perturb the gas environment at the sample surface.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. The intensity decay of the Au 4f spectra with an increasing gas pressure from 1 Pa to 100 kPa. Here we use "100 kPa" as the atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak at the atmospheric pressure, the peaks of $4f_{5/2}$ and $4f_{7/2}$ can be detected. The signal-to-noise ratio can be improved by a prolonged acquisition time. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found in the spectrum at the atmospheric pressure in an acquisition time of 30 min. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}:4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard value of the Au 4f peaks. Thus, a photoelectron spectroscopy under atmospheric pressure was successfully obtained using an aperture of 30 μm .

Wednesday Afternoon, October 24, 2018

5:00pm **SA+AS+MI-WeA-9 Operando HAXPES Investigations of La Manganite-based Resistive Memories**, *Eugénie Martinez*, CEA/LETI-University Grenoble Alpes, France; *B Meunier*, Univ. Grenoble Alpes, CEA, LETI & LMGP, CNRS, France; *D Pla*, Univ. Grenoble Alpes, LMGP, CNRS, France; *R Rodriguez-Lamas*, Univ. Grenoble Alpes, LMGP, CNRS France; *M Burriel*, *C Jimenez*, Univ. Grenoble Alpes, LMGP, CNRS, France; *J Rueff*, Synchrotron SOLEIL, France; *Y Yamashita*, *S Ueda*, NIMS, Japan; *O Renault*, CEA/LETI-University Grenoble Alpes, France

The use of perovskite oxides in resistive random access memories (RRAMs) is considered for the next generation of non-volatile memories (NVMs) [1]. Indeed, their highly tunable ionic and electronic transport properties open new possibilities for multilevel storage capacity. In particular, manganese oxides, such as LaMnO_{3+d} (LMO), are among the most promising candidates [2]. The switching mechanism is related to oxygen transport, yielding to the creation and annihilation of oxygen vacancies through the functional layer. However, two main mechanisms based on filaments or 2D interfacial effects must be discriminated to better understand and control the devices properties.

We investigate here the key role of oxygen in the switching mechanism of LMO-based RRAMs using hard X-ray photoelectron spectroscopy (HAXPES). This technique allows learning about electrochemical reactions involved in the structure with sufficient depth sensitivity. Operando HAXPES was performed at Soleil and SPring-8 to investigate in-situ resistive switching. Measurements were done while biasing the memory with opposite polarities, to reach successively low and high resistance states. In particular, a chemical analysis of the interface between the active electrode and the LMO was done after *Set* and *Reset* operations.

Results show modifications of the oxygen core level spectra. The peak assigned to interfacial LMO shifts as a function of bias voltage, contrary to the bulk LMO component. These results highlight variations in charges concentration at the electrode/LMO interface, as a result of creation/annihilation of interfacial defects, such as oxygen vacancies. Complementary trends regarding $\text{La}3d$ and $\text{Mn}3s/2p$ spectra will be discussed in terms of oxidation and reduction phenomena, related to variations of the oxygen content at the electrode/LMO interface.

[1] Jin YL, Jin KJ, Ge C, Lu HB, Yang GZ, Resistive switching phenomena in complex oxide heterostructures, *Modern Physics Letters B*, 2013;27(29)1330021.

[2] Pan F, Gao S, Chen C, Song C, Zeng F, Recent progress in resistive random access memories: Materials, switching mechanisms and performance, *Mater. Sci. Eng. R* 2014,83:1-59.

5:20pm **SA+AS+MI-WeA-10 Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids**, *Alexander Gray*, Temple University **INVITED**

Angle-resolved photoelectron spectroscopy, or ARPES, is a powerful and well-established experimental technique for probing the momentum-resolved electronic structure of matter. In this talk, I will discuss several promising new directions in this field, which stem from experimental and theoretical studies wherein angle-resolved photoemission is carried out at higher excitation energies, namely in the soft and hard x-ray regimes. I will focus specifically on the recent studies of novel engineered quantum materials and heterostructures, which aim at gaining a clear understanding of the depth-dependent nanoscale evolution of materials' electronic properties at the surface, in the bulk, and across the buried interfaces by using multiple modalities of hard and soft x-ray angle-resolved photoemission both separately and in tandem with each other.

6:00pm **SA+AS+MI-WeA-12 Surface/Interface Coupling in Buried Oxide Interfaces**, *Conan Weiland*, National Institute of Standards and Technology (NIST); *A Rumaiz*, Brookhaven National Laboratory; *G Sterbinsky*, Argonne National Laboratory; *J Woicik*, National Institute of Standards and Technology (NIST)

Oxide interfaces can host a variety of properties not found in the bulk materials. The interface between LaAlO_3 (LAO) and SrTiO_3 (STO) is a prototypical example; the interface of these two insulators can show conductivity, ferromagnetism, and even superconductivity. The source of these interface properties is still a matter of debate, with potential explanations including electronic reconstruction due to the polar discontinuity at the interface, chemical intermixing, and oxygen vacancies at either the interface or LAO surface. Hard x-ray photoelectron spectroscopy (HAXPES) is an excellent tool to probe these interfaces due to the enhanced and tunable probe depth afforded by a synchrotron source. We have used a combination of variable kinetic energy HAXPES and

ambient pressure soft x-ray photoelectron spectroscopy (AP-XPS) to investigate the interplay between LAO film and surface structure and the LAO/STO interface. We find Al surface enrichment for most LAO films, while AP-XPS shows significant band shifts in the presence of water vapor. The role of these LAO surface features on the LAO/STO interface conductivity will be discussed.

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